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(54) Radiographic intensifying screen-film combination

(57) A radiographic screen/film combination has been described comprising a duplitized film 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 comprises luminescent phosphor particles emitting at least 50 % of their emitted radiation in the wavelength range between 540 and 555 nm,
ii) said film comprises, in a light-sensitive silver halide emulsion layer, cubic, {100} or {111} tabular silver halide grains rich in silver chloride, spectrally sensitized to irradiation in the said wavelength range between 540 and 555 nm by a combination of green sensitizing dyes, being

-a benzimidacarbocyanine dye according to the formula (I), given in the description and in the claims and a benzoxacarbocyanine dye corresponding to the general formula (II) given in the description and in the claims. Said radiographic screen/film combination has luminescent phosphor particles, preferably gadolinium oxisulphide phosphor particles, emitting at least 80 % of their emitted radiation in the wavelength range between 540 and 555 nm.

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Description

1. Field of the invention.

[0001] This invention relates to a screen-film combination of a radiographic intensifying phosphor screen and a light-sensitive silver halide photographic material comprising emulsion grains rich in silver chloride.

2. Background of the invention.

[0002] Combinations of intensifying screens provided with luminescent phosphors and light-sensitive silver halide photographic materials are conventionally used for medical diagnosis. By X-ray radiation the luminescent phosphors in the screen panel or panels are converting X-rays into visible radiation, thereby exposing the film material in contact with the said panel (for single-side coated materials as e.g. in mammography) or panels (for duplitized materials as e.g. in chest imaging).

[0003] It is clear that in order to get a black-and-white image to be examined on the film that after said exposure the film material is processed in a wet processing cycle, requiring appropriate chemistry. A normal processing cycle, whether or not performed in an automatic processing machine, is following the steps of developing, fixing, rinsing an drying. The more film material is passing in the corresponding processing solutions of developer and fixer, the more both of them become exhausted. In order to overcome that problem replenishing is rehired.

[0004] As nowadays ecology becomes more and more important it is recommended to reduce amounts of processing chemicals (developer, fixer and corresponding replenishers) to a considerable extent in order to reduce chemical waste.

[0005] Reduction of waste amounts of chemicals from the developer, the fixer and especially the corresponding replenishers is advantageously attainable when in the light-sensitive silver halide photographic material use is made of emulsion crystals rich in silver chloride having a much higher solubility (and processability) than e.g. crystals rich in silver bromide (a factor of about 100). Moreover combination with the more "ecologically acceptable" ascorbic acid or derivatives thereof seems to offer an acceptable alternative.

[0006] Especially when the light-sensitive silver halide emulsion crystals have been made sensitive to visible light as e.g. to blue or green light emitted from blue light or green light emitting intensifying phosphor screens respectively, the corresponding spectral sensitizers make arise the problem of insufficient removal from the film material, thereby causing residual colour, also called "dye stain", increase minimum density and deviate image tone from the desired outlook of the processed image.

[0007] In order to provide, after processing of the (preferably forehardened) photographic material, a black-and-white image having a suitable gradation and especially high covering power and low crossover (leading to a high sharpness) it is recommended as e.g. in US-A's 4,414,304; 4,425,425 and 4,425,426 to make use of emulsion crystals or grains having a tabular habit and a high aspect ratio. Tabular grain emulsions having a high aspect ratio are indeed known to provide several advantages over more conventional spherical grains as, e.g., a high covering power, a high sensitivity and a lower coating weight, which saves costs in manufacturing. Said lower coating weight is especially preferred if rapid processing applications are required, which is nowadays an ever more returning demand. As {111} tabular grains rich in silver chloride are thermodynamically unstable during preparation crystal habit modifiers are required in order to stabilize their crystal habit during precipitation as has e.g. been disclosed in US-A's 5,061,617; 5,176,992; 5,178,998; 5,183,732; 5,185,239; 5,221,602; 5,252,452; 5,286,621; 5,298,388; 5,399,478; 5,411,852 and 5,601,969.

[0008] Optimization of sensitometric characteristics attainable with such {111} tabular grains rich in silver chloride further requires partial desorption of the stabilizing crystal habit modifier in order to admit adsorption of one or more spectral sensitizers onto specific sites of the surface of the tabular grains. Added before or during chemical ripening crystal habit modifiers and spectral sensitizers act as site directors for sensitivity specks in order to provide the required sensitometry, especially with respect to sensitivity or speed. Attaining the required sensitometry, even in rapid processing applications making use of minimum amounts of replenisher solutions of developer and fixer, and further getting an image having the desired contrast, high definition (low cross-over), covering power and image tone without showing disturbing residual colouration remains an ever lasting demand.

[0009] For {100} tabular grains rich in silver chloride coated in light-sensitive radiographic materials the same properties are desired after processing, taking into account that such grains are offering an advantage over {111} tabular grains with respect to crystal habit stability: opposite to {111} tabular crystals rich in silver chloride a crystal habit stabilizer is not required as becomes clear from the related patents as e.g. US-A's 5,264,337; 5,292,632; 5,314,798; 5,320,938; 5,395,746; 5,413,904; 5,457,021 and 5,498,511; WO's 93/6521 and 94/22051; EP-A's 0 617 320, 0 638 840, 0 645 670, 0 731 382 and 0 770 909 and EP-Application No. 96203207, filed November 15, 1996.

[0010] Moreover for cubic grains rich in silver chloride coated in light-sensitive materials for diagnostic imaging the same requirements are desired again: as has e.g. been shown in EP-A 0 709 730 even for those cubic crystals a sensitivity and covering power as high as for tabular grains is attainable, depending on the processing conditions, especially

related with the developer composition wherein the presence of thiocyanate ions is of utmost importance.

3. Objects of the present invention.

[0011] Therefore it is an object of the present invention to provide a screen-film image-forming combination or system wherein a light-sensitive silver halide photographic material is combined with an intensifying screen in order to obtain an image suitable for medical diagnosis, having a very good image quality, i.e., low fog level, high overall-contrast with an enhanced sharpness (low cross-over) after rapid processing of the said material, wherein little or no residual colour or dye stain is observed in the processed material even when minimum amounts of developer, fixer and their corresponding replenishers are used in the said processing.

4. Summary of the invention.

[0012] In order to reach the objects of the present invention a radiographic screen/film combination, also called screen/film system, has been provided comprising a duplitized film 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 comprises luminescent phosphor particles emitting at least 50 % of their emitted radiation in the wavelength range between 540 and 555 nm, as e.g. terbium doped gadolinium oxysulphide phosphor particles;
ii) said film comprises, in a light-sensitive emulsion layer, cubic, {100} or {111} tabular silver halide grains rich in silver chloride, spectrally sensitized to irradiation in the said wavelength range between 540 and 555 nm by a combination of green sensitizing dyes, being

-a benzimidacarbocyanine.dye according to the formula (I), given in the description and in the claims hereinafter and a
benzoxacarbocyanine dye corresponding to the general formula (II) as given in the description and in the claims hereinafter.

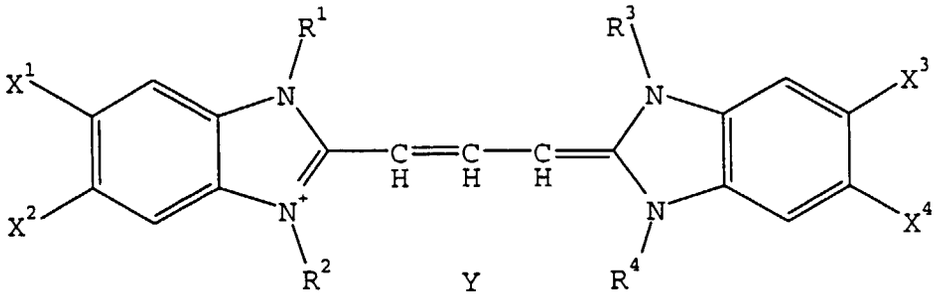
[0013] Said radiographic screen/film combination wherein said pair of supported or self-supporting X-ray intensifying screens comprise luminescent phosphor particles, preferably gadolinium oxisulphide phosphor particles, more preferably emits at least 80 % of the emitted radiation in the wavelength range between 540 and 555 nm.

5. Detailed description of the invention.

[0014] In order to prevent residual colour or dye stain after rapid processing in low replenishing conditions it is most favourable when even no antihalation dyes are used, although dye stain may also be present after processing due to the presence, in high amounts, of spectral sensitizing dyes, especially when tabular grain emulsions, having a large surface to volume ratio, are coated in the light-sensitive emulsion layers; to a lesser extent however when emulsions having cubic crystals are coated. It has now unexpectedly been observed that in the presence of a specific combination of benzimidazolo- and benzoxazolo carbocyanine dyes, used as green sensitizing dyes for the spectral sensitization of {111} and {100} tabular emulsion grains and of cubic emulsion grains in the wavelength range between 540 and 555 nm, wherein said emulsions are coated in the light-sensitive emulsion layer(s) of a silver halide photographic material used in the screen/film combination of the present invention, the objects of the present invention, particularly with respect to cross-over and dye stain after processing are effectively realized.

[0015] In the context of the present invention said specific combination of green sensitizing dyes consists of

-a benzimidacarbocyanine.dye according to the formula (I)

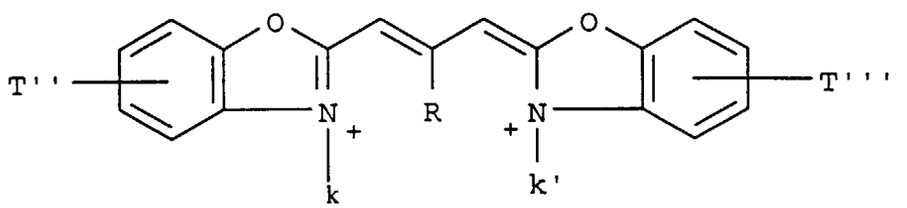


(I)

wherein

R^1 and R^3 are methyl or ethyl, but are differing from each other;
R^2 and R^4 are substituted or unsubstituted C_2 to C_6 alkyl, more preferred that both are differing from each other and that one of R^2 and R^4 represents a fluoro substituted alkyl;
X^1, X^2, X^3 and X^4 are each independently hydrogen, methyl or fluoro-substituted methyl, provided that at least one of X^1 and X^2 and at least one of X^3 and X^4 are not hydrogen;
Y represents an ion in order to balance the charge of the molecule;

and a benzoxacarbocyanine dye corresponding to the general formula (II)



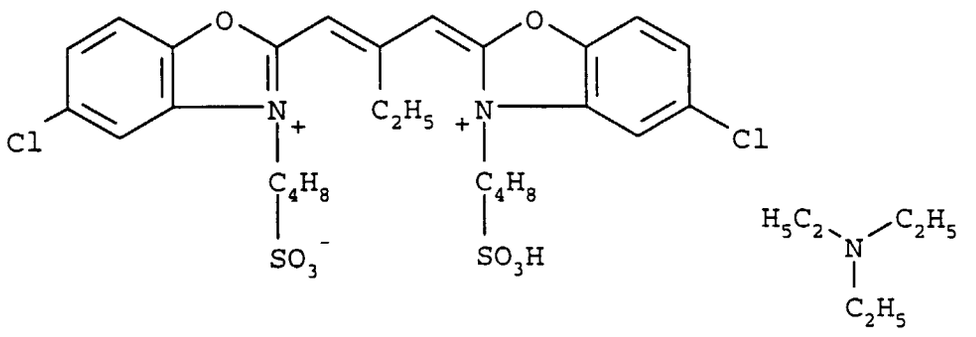
(II)

wherein

R represents H, CH_3 or CH_2CH_3;
T'' and T''' each independently represents one of the following substituents in the 4-, 5- or 6-position:
H, Cl, phenyl, CH_3, OCH_3, provided that at least one of T'' and T''' represents a (substituted or unsubstituted) phenyl-group;
k'=$(CH_2)_nSO_3M$ or $(CH_2)_nOSO_3M$
k =$(CH_2)_mSO_3^-$ or $(CH_2)_mOSO_3^-$
M= H, Na or K
n= 2, 3 or 4
m= 2, 3 or 4

[0016] In a preferred embodiment R^2 is trifluoroethyl and R^4 is sulfoethyl, sulfopropyl, 3-sulfobutyl or 4-sulfobutyl, whereas X^1 and X^3 are hydrogen and X^2 and X^4 are each trifluoromethyl.

[0017] As a benzoxazole dye according to the formula (II), the dye according to the formula (II.1) given hereinafter is preferred:

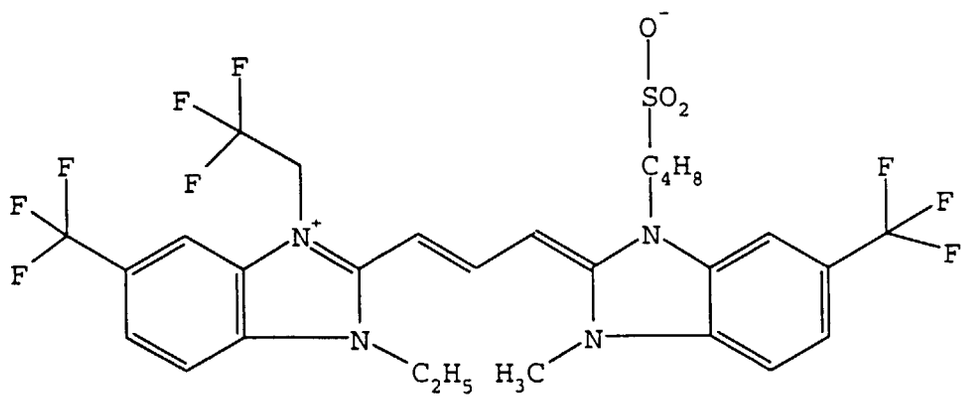


(II.1)

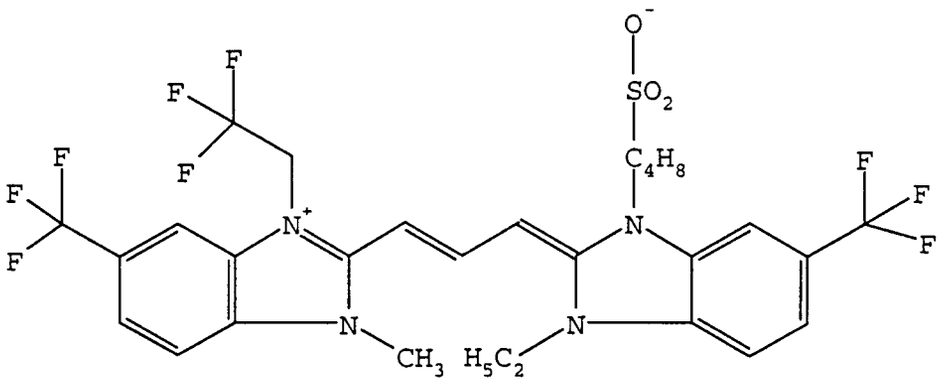
[0018] The benzimidazolocarbocyanine and benzoxazolocarbocyanine spectral sensitizers according to the formulae (I) and (II) respectively are added consecutively in a preferred molar ratio amount between 2:100 and 50:100 to the emulsions coated in the film material used in the radiographic screen/film combination of the present invention.

[0019] The synthesis of benzimidacarbocyanine dyes according to the formula (I) and use thereof as spectral sensitizing dyes for silver halide emulsions has been described in EP-A's 0 506 077 and 0 506 584. More in general trifluorosubstituted benzimidazolocarbocyanines have been described in GB-A's 01,020,295 and 01,111,903.

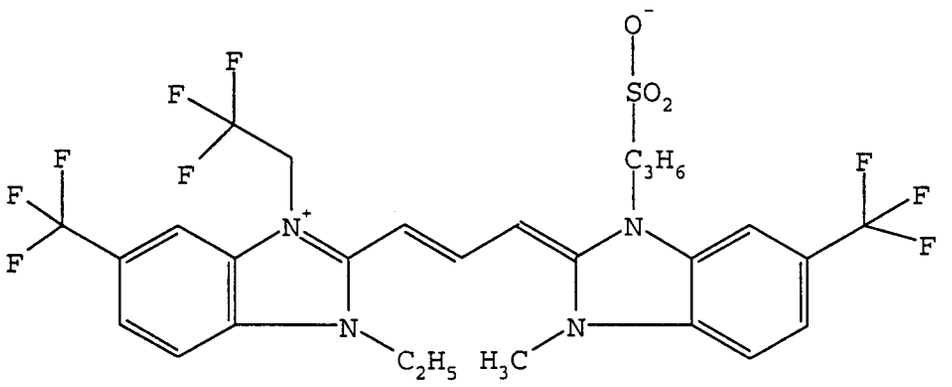
[0020] Typical examples of said trifluorosubstituted benzimidazolocarbocyanines for use in the present invention are given hereinafter in the formulae (I.1) to (I.5):



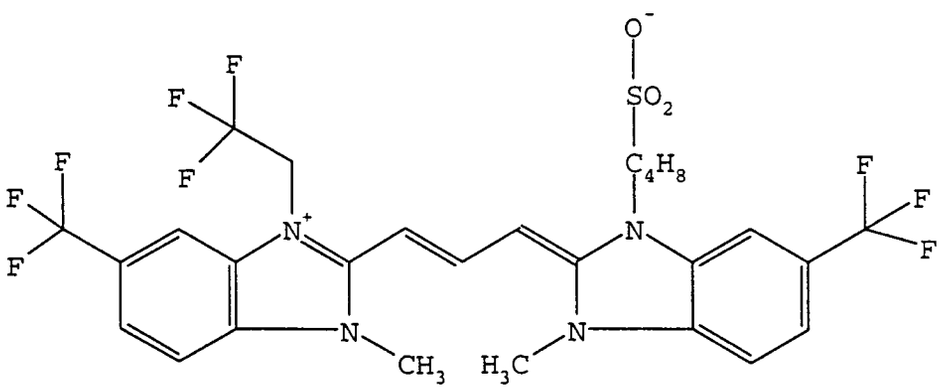
(I.1)



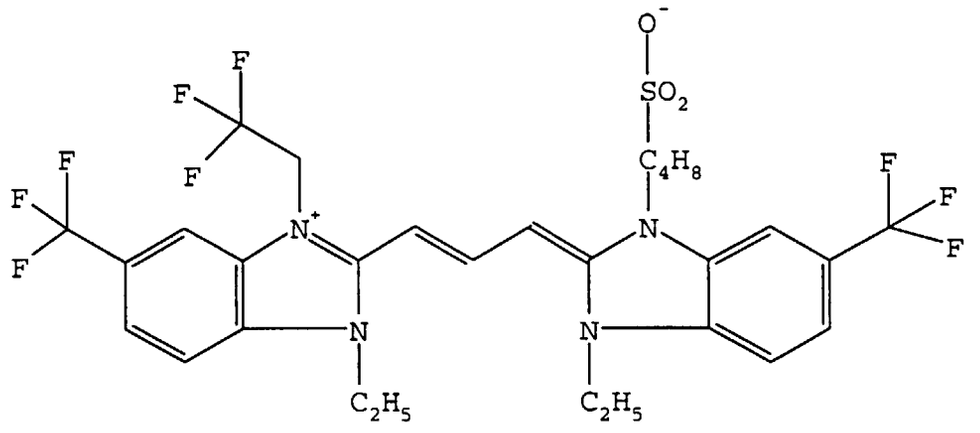
(I.2)



(I.3)



(I.4)



(I.5)

[0021] As has already been set forth in the background of the present invention it is an object to provide a suitable radiographic screen-film combination wherein in the film {111} or {100} tabular emulsion grains or cubic emulsion grains are coated.

More particularly according to the present invention the film of the radiographic film-screen combination comprises {111} tabular silver halide grains rich in silver chloride having an average aspect ratio of 5 or more, an average grain thickness of at most 0.2 μm, and account for at least 50 % of the total projective area of all grains. In a more preferred embodiment in the radiographic screen-film combination according to the present invention said film comprises {111} tabular silver halide grains rich in silver chloride having an average aspect ratio of from 8 to 20, an average grain thickness of from 0.06 μm to 0.20 μm, and account for at least 70 % of the total projective area of all grains.

Preparation methods of such {111} tabular emulsion grains rich in silver chloride have been described in e.g. US-A's 5,494,788; 5,567,580 and 5,601,969; in EP-A's 0 678 772 and 0 770 909 and in Research Disclosure No. 38846, published August 1, 1996.

[0022] In another embodiment said radiographic screen-film combination according to the present invention comprises {100} tabular silver halide grains rich in silver chloride in the film; wherein said grains have an average aspect ratio of 2 or more, an average grain thickness of at most 0.3 μm, and account for at least 40 % of the total projective area of all grains.

In a more preferred embodiment said film comprises {100} tabular silver halide grains rich in silver chloride having an average aspect ratio of 5 or more, an average thickness of at most 0.25 μm, and account for at least 50 % of the total projected area of all grains. Preparation methods of such {100} tabular grains have been described in US-A's 5,498,518; 5,593,820 and 5,607,828, wherein an oxidized cationic starch has been described as a peptizer, in EP-A's 0 724 190, 0 762 192 (wherein a polyalkylene block copolymer has been used as a surfactant), 0 770 909, and 0 767 400 (wherein colloidal silica has been used as a protective colloid) and in EP-Application No. 97203311, filed October 24, 1997.

[0023] In still another embodiment the radiographic screen-film combination according to the present invention comprises cubic silver halide grains rich in silver chloride having an average sphere equivalent diameter of from 0.2 up to 1.0 μm, more preferably from 0.4 up to 1.0 μm and most preferably from 0.6 up to 1.0 μm. Preparation methods of such grains have e.g. been given in EP-A 0 709 730 and in US-A's 5,397,687 and 5,543,284, wherein, in the last reference, colloidal silica has been used as a protective colloid in the said preparation method.

[0024] A combination of silver halide emulsion grains of the same or different types coated in one or in two adjacent layers at one and/or at both sides of the support of the film material is also enclosed in the present invention, provided that at least one, and preferably all of said emulsion grains are spectrally sensitized with the specific combination of both green spectral sensitizers according to the general formulae (I) and (II), representing a benzimazolocarbocyanine and benzoxazolocarbocyanine respectively.

[0025] In the radiographic screen-film combination according to the present invention, the total amount of coated silver halide in said film, expressed as an equivalent amount of silver nitrate, is less than 8.0 g/m^2.

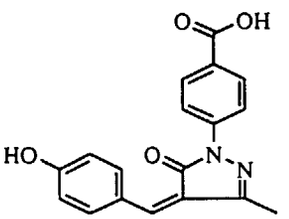
[0026] A conventional radiographic layer arrangement can be provided according to the one described in EP-A 0 770 909. Therein a multilayer light-sensitive silver halide photographic negative image type material has been described

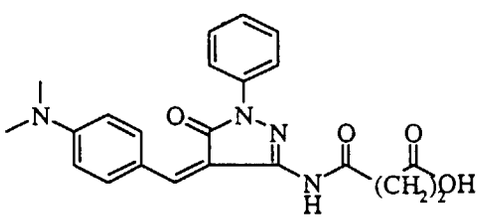
comprising on at least one side of a support a multilayer composition of at least two layers of negative image type silver halide emulsions adjacent to each other, wherein the emulsion layer closest to the said support comprises tabular emulsion crystals selected from the group consisting of silver chloride, silver chlorobromide, silver chloroiodide, silver chlorobromoiodide, silver bromide and silver bromoiodide having a {111} crystal habit and silver chloride, silver chlorobromide, silver chloroiodide and silver chlorobromoiodide having a {100} crystal habit and wherein the adjacent layer(s) farther from the said support comprise(s) essentially cubic emulsion crystals selected from the group consisting of silver chloride, silver chlorobromide and silver bromide and wherein the halide composition of the said cubic emulsion crystals or of the said tabular emulsion crystals or both includes chloride.

[0027] In another embodiment as described in EP-A 0 752 617 a method has been provided in order to get a radiographic silver halide material by coating on at least one side of a support, covered with a hydrophobic subbing layer comprising as a latex copolymer vinylidene chloride, methylacrylate and itaconic acid, following hydrophilic layers: at least one gelatinous dye containing layer comprising one or more dyes, at least one silver halide emulsion layer, at least one protective antistress layer, and optionally an afterlayer, characterised in that said hydrophilic layers have a swelling ratio of not more than 200 % and in that said hydrophilic layers are coated simultaneously by the slide-hopper coating or by the slide-hopper curtain coating technique, opposite to the time consuming technique described in US-A 5,077,184.

[0028] In a preferred embodiment according to the present invention a layer arrangement as claimed in the said EP-A 0 752 617 has been provided, wherein one or more merostyryl dye is present as antihalation dye(s) in the gelatinous dye containing layer situated between the subbing layer, being in direct contact with the support in order to provide good adhesion of coatings, and the light-sensitive emulsion layer more close to the said subbing layer. Preferred amounts of dyes are chosen in order to get a ratio by weight of dye to gelatinous hydrophilic binder between 0.4 and 1.3. Preferred merostyryl dyes have e.g. been described in US-A 4,311,787. Said merostyryl dyes are further characterized by a solubility at an alkaline pH of at least 8 (as e.g. in processing conditions) and insolubility at pH values less than 6.0. In order to get a good discoloration said merostyryl dye is present in form of a microprecipitated dispersion and is preferably prepared according to the methods described in EP-A 0 724 191.

A preferred merostyryl dye for use as a so-called antihalation dye, contributing to the lowering of cross-over of the material according to the material in the screen/film combination according to the present invention are the merostyryl dyes having a pyrazolon nucleus the formulae of which are given hereinafter:





[0029] A radiographic screen-film combination is thus provided wherein said film further comprises, in order, a support, a subbing layer, a gelatinous dye containing layer, the light-sensitive emulsion layer and a protective antistress layer, wherein in the said dye containing layer said dye(s) is (are) merostyryl dyes having a pyrazolon nucleus, in favour of cross-over percentage.

[0030] In the practice of the present invention the light emitted imagewise by said X-ray intensifying screen irradiates a contacting photographic silver halide emulsion layer film which after exposure is developed to form therein a silver image in conformity with the X-ray image. For use in common medical radiography (projection radiography) the X-ray film comprises a transparent film support, coated on both sides with a silver halide emulsion layer. During the X-ray irradiation said film is arranged in a cassette between two X-ray intensifying screens each of them making contact with its

corresponding silver halide emulsion layer.

[0031] Phosphors suitable for use in the conventional radiographic diagnostic image forming system 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).

[0032] Specific intensifying screens emitting green radiation have further been disclosed in GB-A 1,489,398; and in US-A's 4,431,922 and 4,710,637. A typical green emitting phosphor used therein is a gadolinium oxisulphide phosphor, just as the preferred phosphor used in the screen of the film/screen combination according to the present invention.

[0033] In the film/screen combination according to the present invention the 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 between 540 and 555 nm, wherein said luminescent particles have a composition according to the formula (III)

$$Gd_2O_2S:Tb \qquad (III).$$

[0034] X-ray intensifying screens according the present invention are thus self-supporting or supported X-ray intensifying screens and 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 in order to protect said layer. A primer layer is sometimes provided between the phosphor containing layer and the substrate in order to closely bond said layer thereto.

[0035] Examples of support materials include cardboard, plastic films such as films of cellulose acetate, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile, polystyrene, polyester, polyethylene terephthalate, polyamide, polyimide, cellulose triacetate and polycarbonate; metal sheets such as aluminum foil and aluminum alloy foil; ordinary papers; baryta paper; resin-coated papers; pigment papers containing titanium dioxide or the like; and papers sized with polyvinyl alcohol or the like. A plastic film is preferably employed as the support material.

[0036] 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. Such supports can be highly light reflecting as e.g. polyethyleneterephthalate comprising a white pigment, e.g. $BaSO_4$, TiO_2, 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 according to the present invention.

[0037] In most applications the phosphor layers contain sufficient binder to give structural coherence to the layer. In view of a possible phosphor recovery from worn-out screens the binder of the phosphor containing layer is preferably soluble and remains soluble after coating.

[0038] Useful binders, a non-limitative survey of which is given herein, include proteinaceous binders, e.g. gelatin, polysaccharides such as dextran, gum arabic, and synthetic polymers such as polyvinyl butyral, polyvinyl acetate, nitrocellulose, ethylcellulose, vinylidene chloride-vinyl chloride copolymer, polyalkyl (meth)acrylate, vinyl chloride-vinyl acetate copolymer, polyurethane, cellulose acetate, cellulose acetate butyrate, polyvinyl alcohol, polystyrene, polyester, etc. These and other useful binders are disclosed e.g. in US-A's 2,502,529; 2,887,379; 3,617,285; 3,300,310; 3,300,311 and 3,743,833.

[0039] A mixture of two or more of these binders may be used, e.g., a mixture of polyethyl acrylate and cellulose acetobutyrate.

[0040] 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.

[0041] The screen 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 0 648 254 and EP-A 0 647 258 or thermoplastic elastomers as described in US-A 5,641,968. 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 anti-oxidation compounds like IRGANOX 1010 and IRGASTAB T36 (trademarked products of CIBA-GEIGY, Basel, Switzerland), ANTIOXIDANT 330 (trademarked product of ETHYL CORP., Richmond, USA), VANOX 2246 (trademarked product of VANDERBILT ENERGY CORP., Denver, Canada) etc, this list being non-limitative. The binder used in screens according to the present invention, with high phosphor to binder ratio, can beneficially be a polymer P having a Tg $\leq$ 0 °C, an average molecular weight (M_{avg}) between 5000 and 10^7, being soluble in ethylacetate for at least 5 % by weight (% wt/wt). A self-supporting layer of 82 % by volume of phosphor particles in said polymer P, having a thickness so has to comprise 100 mg of phosphor particles per cm^2, has an elongation to break of at least 1 %. Such polymers have been disclosed in US-A 5,663,005.

[0042] The phosphor layer can be applied to the support by employing a method such as vapour deposition, sputtering and spraying but is usually applied by the following procedure.

[0043] Phosphor particles and a binder are added to an appropriate solvent as described hereinafter, and are then mixed in order to prepare a coating dispersion comprising the phosphor particles homogeneously dispersed in the binder solution. Said coating dispersion may further comprise a dispersing agent and plasticizer and filler material as described hereinafter.

[0044] The coating dispersion containing the phosphor particles and the binder is applied uniformly onto the surface of the support to form a layer of the coating dispersion. The coating procedure may proceed according to any conventional method such as doctor blade coating, dip-coating or roll coating.

[0045] For the preparation of highly abrasion resistant and chemically resistant phosphor-binder layers the binder is cured. Curing of the binder may proceed photochemically by means of UV radiation or with electron beam (EB) as described e.g. in Research Disclosure December 1977, item 16435, or proceeds purely chemically as described e.g. in US-A 4,508,636. It may also be cured by moisture as described in EP-A 0 541 146. Curing may also be performed by heating.

[0046] In the preparation of the phosphor screen having a primer layer between the substrate and the fluorescent layer, the primer layer is provided on the substrate beforehand, and then the phosphor dispersion is applied to the primer layer and dried to form the fluorescent layer.

[0047] After applying the coating dispersion onto the support, the coating dispersion is then heated slowly to dryness so as to complete the formation of a phosphor layer.

[0048] In order to remove as much as possible entrapped air in the phosphor coating composition it can be subjected to an ultra-sonic treatment before coating. The phosphor-binder layer (as described e.g. in US-A 4,059,768) can be calendered to improve the phosphor packing density in the dried layer.

[0049] Useful solvents for the binder of the phosphor containing layer, employable in the preparation of the phosphor coating dispersion include lower alcohols such as methanol, ethanol, n-propanol and n-butanol; chlorinated hydrocarbons such as methylene chloride and ethylene chloride; ketones such as acetone, butanone, methyl ethyl ketone and methyl isobutyl ketone; esters of lower alcohols with lower aliphatic acids such as methyl acetate, ethyl acetate and butyl acetate; ethers such as dioxane, ethylene glycol monoethylether; methyl glycol; and mixtures of the above-mentioned solvents.

[0050] Useful dispersing agents for the phosphor particles in the coating dispersion to improve the dispersibility of the phosphor particles therein, may contain a variety of additives such as a plasticizer for increasing the bonding between the binder and the phosphor particles in the phosphor layer. Examples of the dispersing agent include ionic and non-ionic well-known dispersing agents or combinations thereof, e.g., DISPERSE AYD (trade name of Daniel Products Company, New Jersey, USA) GAFAC RM 610 (a tradename a polyoxyethylene (20) sorbitan monopalmitate and monolaurate marketed by General Aniline and Film Company (GAF) New York, USA, polymeric surfactants such as the acrylic graft copolymer, PHOSPHOLIPON 90 (trade name) marketed by Nattermann-Phospholipid GmbH, Köln, W. Germany, silane dispersing agents and surfactants e.g. DOW CORNING 190 (trade name) and SILANE Z6040 (trade name) marketed by Dow Corning Corporation, Midland, Michigan, USA or glymo 3-glycidyloxypropylmethoxysilane or organosulfate polysilanes, unsaturated p-aminamide salts and high molecular acid esters such as ANTI TERRA U 80 (trade name) marketed by BYK-Chemie GmbH, Wesel, W. Germany, high molecular unsaturated polyesters, etc.. Dispersing agents are added in an amount of 0.05 to 10 % by weight based on the phosphor.

[0051] Useful plasticizers include phosphates such as triphenyl phosphate, tricresyl phosphate and diphenyl phosphate; phthalates such as diethyl phthalate and dimethoxyethyl phthalate; glycolates such as ethylphthalyl ethyl glycolate and butylphthalyl butyl glycolate; polymeric plastizers, e.g. and polyesters of polyethylene glycols with aliphatic dicarboxylic acids such as polyester of triethylene glycol with adipic acid and polyester of diethylene glycol with succinic acid.

[0052] After the formation of the fluorescent layer, a protective layer is generally provided on top of the fluorescent layer. In a preferred embodiment the protective coating has a layer thickness d comprised between 1 and 50 μm and an embossed surface roughness is applied for high ease of manipulation, thereby avoiding sticking, friction and electrostatic attraction with maintenance of an excellent image resolution. The embossed protective layer can be provided on the phosphor layer in order to protect it against mechanical and chemical damage by the steps of (1) coating onto said phosphor containing layer a liquid radiation-curable composition having at the coating temperature a viscosity of at least 450 mPa.s, measured with a Hoeppler viscometer,that does not penetrate for a substantial degree into the phosphor containing layer,

(2) providing an embossed structure to the coating, and
(3) curing said coating by radiation.

[0053] More details concerning preferred protective coatings with embossed surface are given in EP-A's 0 510 753

and 0 510 754.

[0054] Assemblies providing means for reducing cross-over to less than 10 % for radiation longer than 300 nm in wavelength have been described e.g. in US-A 5,259,016.

[0055] For processing, 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 without hardening agent;
-fixing said material in a fixer, optionally without hardening agent;
-rinsing and drying said material.

[0056] A normally used configuration in the processing apparatus shows the following consecutive tank units corresponding with, as consecutive solutions: developer-fixer-rinse water.

[0057] 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 fixing and one at the end before drying may also be present.

[0058] 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.

[0059] 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.

[0060] 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, l-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 and which are therefore incorporated herein by reference.

[0061] In order to reduce "sludge formation" which is favoured 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.

[0062] 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 odourless.

[0063] If however aluminum ions are present in the fixer composition for whatever a reason, the presence of a-keto-carboxylic acid compounds is recommended as has been described in EP-A's 0 620 483, 0 726 491 and in RD 16768, published March 1978. In the particular embodiment wherein rinsing between developing and fixing is excluded a method of processing an exposed black-and-white silver halide light-sensitive photographic material has been disclosed in EP-Application No. 97203096, filed October 6, 1997, said method comprising the steps of developing in a developer solution, followed by fixing in a fixer solution, comprising a hardening agent, preferably a compound providing aluminum ions, and wherein, in running equilibrium conditions, said fixer solution has a pH of at least 4.3, further followed by rinsing and drying,; characterized in that said developing step is performed in a developer comprising, in an amount of from 5 g up to 100 gram per litre, (iso)ascorbic acid, l-ascorbic acid or tetramethyl reductic acid as a developing agent, a precursor and/or a metal salt thereof. In a preferred embodiment a compound having an α-ketocarboxylic acid structure in an amount of not more than 3 g per litre is present in the said fixer solution while starting processing or in the said fixer replenisher.

[0064] It is further possible to use sodium thiosulphate as a fixing agent, at least partially as described in US-A 5,275,923, in order to maintain rapid fixing ability, thus avoiding an excess of the ecologically undesired but normally used ammonium ions. 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 from very low amounts of emulsion crystals rich in silver chloride. Preferred minimum regeneration or replenishment amounts are from 20 to 200 ml/m^2 , more preferred from 20 to 100 ml/m^2 and still more preferred from 20 to 50 ml/m^2 of developed material. Materials coated from higher amounts of silver will require the higher amounts of replenisher but in most practical cases replenishment amounts of less than 200 ml/m^2 are attainable.

[0065] Replenishment of a developer comprising ascorbic acid or derivatives thereof and a 3-pyrazolidone derivative has been described in EP-A 0 573 700, wherein a method is disclosed for processing, with constant activity, of an image-wise exposed silver halide photographic material comprising the steps of developing photographic material in a continuous automatic way by means of a developing solution containing an ascorbic acid analogue or derivative and a 3-pyrazolidone derivative as developing agents and replenishing said developing solution by means of at least one replenishing solution having a higher pH than the developing solution. In an alternative method the replenisher is added as a powder. Other references related therewith are EP-A 0 552 511; US-A 5,503,965 and further in EP-A 0 660 175, wherein a method of replenishment control is described. For the fixer preferred minimum regeneration or replenishment amounts are also from about 20 to 200 ml/m^2 , more preferred from 20 to 100 ml/m^2 and still more preferred from 20 to 50 ml/m^2 of developed material. When aluminum ions are present in the fixer solution in order to effect hardening, it is necessary to adjust the pH of the fixer in the range from 4.2 to 4.6 in order to get the highest hardening reactivity and to suppress swelling with washing water in the washing or rinsing step. For hardened materials having a swelling degree of the hydrophilic layers of less than 250 % and more preferably of less than 200 % it is not required for the fixer pH to held constant in the pH range from 4.2 to 4.6 as mentioned hereinbefore: in order to reduce irritating smell from sulphite ions in aqueous acidic medium which lead to sulphur dioxide vapour it is recommended to enhance pH to a value of 4.65 up to 5.00. A process whereby the quality of the fixer remains at an optimum level has been described in EP-Application No. 97201117, filed April 15, 1997.

[0066] Although it is possible to use whatever a processing unit adapted to the requirements described hereinbefore to reach the objectives concerning a perfect link between rapid processing and ecology, the objects of the present invention concerning processing have e.g. been realized in the processing unit CURIX HT 530, trade name product marketed by Agfa-Gevaert.

[0067] New developments however become available with respect to processing apparatus. In a conventional processing apparatus the sheet material is transported along a generally horizontal feed path, the sheet material passing from one vessel to another usually via a circuitous feed path passing under the surface of each treatment liquid and over dividing walls between the vessels. However, processing machines having a substantially vertical orientation have also been proposed, in which a plurality of vessels are mounted one above the other, each vessel having an opening at the top acting as a sheet material inlet and an opening at the bottom acting as a sheet material outlet or vice versa. In the present context, the term "substantially vertical" is intended to mean that the sheet material moves along a path from the inlet to the outlet which is either exactly vertical, or which has a vertical component greater than any horizontal component. The use of a vertical orientation for the apparatus leads to a number of advantages. In particular the apparatus occupies only a fraction of the floor space which is occupied by a conventional horizontal arrangement. Furthermore, the sheet transport path in a vertically oriented apparatus may be substantially straight, in contrast to the circuitous feed path which is usual in a horizontally oriented apparatus. The straight path is independent of the stiffness of the sheet material and reduces the risk of scratching compared with a horizontally oriented apparatus. In a vertically oriented apparatus, it is important to avoid, or at least minimize leakage of treatment liquid from one vessel to another and carry-over as the sheet material passes through the apparatus. Furthermore it is desirable that the treatment liquid in one vessel is not contaminated by contents of the adjacent vessels, that is neither by the treatment liquid of the next higher vessel nor by vapours escaping from the next lower vessel. In order to reduce consumption of treatment liquids, it is furthermore desirable to reduce the evaporation, oxidation and carbonization thereof. A solution therefore has been proposed in EP-A 0 744 656, wherein it has been disclosed that contamination and evaporation, oxidation and carbonization can both be reduced in a simple manner by a particular construction of the apparatus for the processing of photographic sheet material comprising a plurality of cells mounted one above the other in a stack to define a substantially vertical sheet material path through the apparatus, each cell comprising a housing within which is mounted a rotatable roller biased towards a reaction surface to define a roller nip there-between through which the sheet material path extends and associated sealing means serving to provide a gas-and liquid-tight seal between the roller and reaction surface on the one hand and a wall of the housing on the other. According to a first aspect, invention is characterised by means for connecting each cell to adjacent cells in the stack in a closed manner and according to a second aspect, the invention is characterized in that the roller is a drive roller.

[0068] Particularly the objectives set forth above may be achieved when the developing cell of the apparatus is a closed cell and the developing liquid contains an ascorbic acid developing agent as has been described in EP-Application No. 96201753, filed June 24, 1996. According to that invention, there is provided a method of processing photographic sheet material by making use of an apparatus comprising a plurality of processing cells arranged in order to define a sheet material path through the apparatus, at least one of the cells constituting a developing cell containing a developing liquid, characterized in that the developing cell is a closed cell and the developing liquid contains an ascorbic acid developing agent.

[0069] With respect to further characteristics of the processing apparatus we refer to EP-Application No. 96202032, filed July 17, 1996, wherein it was an object to provide an apparatus in which operating components can easily be replaced without the need for substantial re-programming of the CPU. This could be achieved when information con-

cerning characteristics of each operating component is stored in separate memory means.

[0070] A multi-component apparatus was thus provided comprising a plurality of operating components selected from output operating components, input operating components and combinations thereof, and a central processing unit operatively linked to said operating components, said central processing unit containing information concerning at least one desired operating sequence for said apparatus, characterized in that information concerning characteristics of each said operating component is stored in separate memory means. The programme which is typically carried in the CPU, is now seen as comprising two separable elements. Information concerning the desired function of the apparatus, i.e. logical data, such as the speed of sheet material through the apparatus, or the volume of liquid being pumped to vessels of the apparatus per unit time, continues to be stored in the CPU. Information concerning the characteristics of the operating components and their location, is separately stored for each operating component. The separate memory means is removable: when the service engineer removes a given operating component, he also removes the store of characteristics information pertaining to that operating component. As he replaces the removed operating component with a new one, he also provides a new information store, containing the characteristics information pertaining to the new operating component. The need for re-programming of the CPU is therefore avoided. The new information store is created off-site, for example as the new operating component is manufactured. In an alternative embodiment, the separate memory means is not removable, but is arranged to be by-passed or even re-programmed by the service engineer. Re-programming of the separate memory means is simpler than re-programming of the CPU. Improvements of that invention lie not only in the improved servicing characteristics but also in the quality assurance of replacement components.

[0071] As a rule, a processing apparatus for photographic sheet material comprises several treatment cells, most or all of which are in the form of vessels containing a treatment liquid, such as a developer, a fixer or a rinse liquid. As used herein, the term "sheet material" includes not only photographic material in the form of cut sheets, but also in the form of a web unwound from a roll. The sheet material to be processed is transported along a sheet material path through these vessels in turn, by transport means such as one or more pairs of path-defining drive rollers, and thereafter optionally to a drying unit. The time spent by the sheet material in each vessel is determined by the transport speed and the dimensions of the vessel in the sheet feed path direction.

[0072] From time to time it is necessary to clean the processing apparatus, in order to remove debris which may derive from the sheet material itself and deposits derived from the treatment liquids. The usual process for cleaning a processing apparatus, whether of the vertical or horizontal configuration, is to drain the treatment liquids and to flush the apparatus through with cleaning liquid. Water, optionally containing various additives and optionally at an elevated temperature, is the usual cleaning liquid. Therefore it has ever been an object to provide an apparatus in which the path-defining rollers can be separated from each other in the open position, in a simple and convenient manner. The way in which this can be achieved has been described in EP-Application No. 96202164, filed August 31, 1996, wherein the path-defining rollers are supported by bearings carried by eccentric sleeves which are stationary in the closed position, and where means are provided for partly rotating the sleeves thereby to withdraw the path-defining rollers from each other into the open position. A sheet material processing apparatus has thus been provided, comprising at least one treatment cell, a pair of rotatable path-defining rollers defining a sheet material path through the cell, the path-defining rollers having a closed position in which the path-defining rollers are biased into contact with each other to form a nip through which the sheet material path extends and an open position in which the path-defining rollers are spaced from each other, characterized in that the path-defining rol-lers are supported by bearings carried by eccentric sleeves which are stationary in the closed position, and means are provided for partly rotating the sleeves thereby to withdraw the path-defining rollers from each other into the open position.

[0073] It is clear that within the scope of this disclosure any screen/film combination may be used, wherein said screen comprises at least luminescent phosphors emitting green light as those according to the formula (III) in the wavelength range between 540 and 555 nm and wherein said film comprises {111} or {100} tabular silver halide crystals or cubic crystals rich in silver chloride spectrally sensitized with a combination of at least one benzimidacarbocyanine dye according to the formula (I) and at least one benzoxacarbocyanine dye according to the formula (II) in combination with a processing unit, provided that with minimum amounts of silver coated (total amount, expressed as an equivalent amount of silver nitrate of less than 4 g per m^2 and per side) a sufficient covering power is attained in the film material in rapid ecological processing (with e.g. ascorbic acid and/or derivatives thereof as developing agent(s) in a hardener-free developer and an odour-free fixer, optionally free from aluminum ions, thereby reducing sludge; and replenishing amounts for developer and fixer as low as possible, i.e. from about 20 ml/m^2 up to at most 200 ml/m^2) and provided that an optimal relationship is attained between sensitometry and image quality, especially sharpness, thanks to low cross-over exposure, without residual colour (dye stain), thus providing a good image tone.

[0074] Having described in detail preferred embodiments of the present invention it is understood by a person skilled in the art that, within the scope of the present invention, it is not limited thereto. The same applies to the Examples, given hereinafter, represented in order to illustrate the present invention.

5. EXAMPLES

Exposure

[0075] Pairs of screens were arranged in the same type of cassette and between the screens and in contact therewith a duplitized (double-side silver halide emulsion coated) film was inserted. The X-ray exposure proceeded according to ISO/DP9236 with 77 median kVp X-rays.

[0076] As a pair of screens, screens having Gd_2O_2S:Tb luminescent phosphors were used ("Ortho Regular" screen, tradename product from Agfa-Gevaert).

Films

A. Film materials comprising cubic grains rich in chloride were the following.

1.Preparation of cubic silver chloroiodide grain emulsion:

[0077] A silver chloride emulsion was prepared by a double jet technique. The silver halide composition was 100 mole % of chloride and the average grain size was 0.57 µm. Therefore following solutions were prepared.

Solution 1	
Water*	880 ml
Gelatin	46 g
Solution 2	
Water*	1000 ml
Silver nitrate	500 g
Solution 3	
Water*	1000 ml
Sodium chloride	173 g

* demineralized water

[0078] The UAg value of solution 1 (potential value expressed in mV versus a saturated silver/silver chloride reference electrode) was adjusted at a constant value of + 138 mV ± 2 mV before starting nucleation by dropwise addition of about 7 ml of a solution having 234 grams of sodium chloride after addition of 0.44 ml of a silver nitrate solution having a concentration of 50 g per liter of demineralized water.

[0079] During the said nucleation step which was performed at a constant temperature of 60°C, there was simultaneously added to solution 1, while stirring at a stirring rate of 500 rpm, a part of solution 2 and of solution 3 over a period of 5 minutes at a flow rate of 3 ml/min.

[0080] After this nucleation step, UAg was readjusted at the same value of + 138 mV while solution 2 was added at an increasing flow rate varying from 3 ml per minute to 30 ml per minute simultaneously with solution 3, the flow rate of which was varied in order to maintain the same constant UAg-value over a period of 59 minutes and 42 seconds, meanwhile maintaining UAg at the same constant UAg value of + 138 mV.

[0081] The emulsion was washed with a solution of demineralized water containing 0.46 g of sodium chloride per litre after flocculation by addition of polystyrene sulphonic acid to the acidified emulsion. To the washed flocculate gelatin was added, followed by redispersion. So after addition of said gelatin a ratio of gelatin to silver nitrate in the emulsion of about 0.35 was obtained.

[0082] The pH-value of the said emulsion was adjusted at 5.20; the pAg-value at + 170 mV. To the dispersion obtained as described hereinbefore 3.8 mg of para-toluene thiosulphonate, 1 g of potassium iodide, 12.5 mg of chloro auric acid, 25 mg of ammonium thiocyanate and 25 mg of tetramethylthio-dithiocarboxylic acid diamide were added at 40°C. Addi-

tion of iodide before chemically ripening thus introduces iodide in the silver chloride emulsion to a concentration of 0.2 mol % vs. silver. Chemical sensitization was carried out at 52°C during 150 minutes.

2. Coating compositions.

[0083] A photographic material was prepared having on a subbed polyester base the gelatinous silver halide emulsions rich in silver chloride the preparation of which has been described above.

[0084] Before coating said emulsion was spectrally sensitized with a combination of two green sensitizers, corresponding with the formulae set forth in the Table hereinafter respectively, in amounts in order to get an optimized fog-speed relationship.

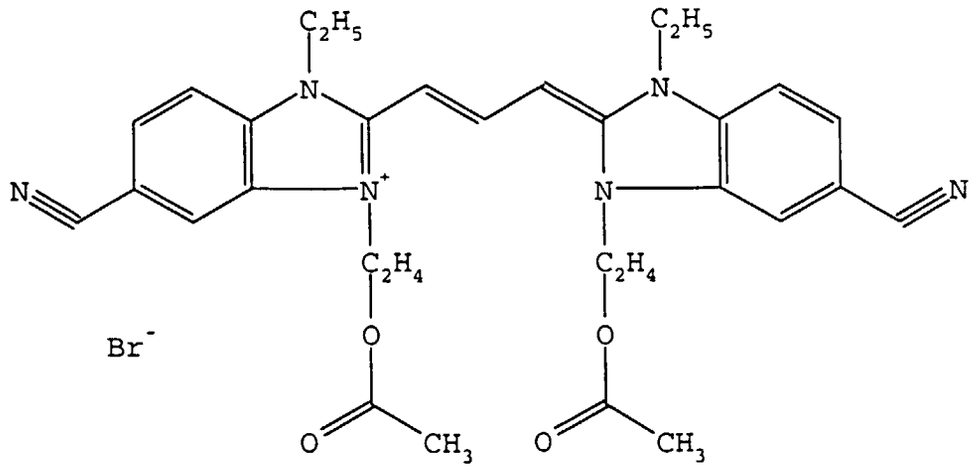
[0085] Further each emulsion was further stabilized with 1-p-carboxyphenyl-5-mercaptotetrazole and after addition of the normal coating additives the solutions were coated simultaneously together with a protective layer containing 1.3 g gelatine per m^2 per side on both sides of a polyethylene terephthalate film support having a thickness of 175 µm.

[0086] The resulting photographic material contained per side an amount of silver halide corresponding to 3.8 grams of $AgNO_3$ per m^2 and an amount of gelatin corresponding to 3.2 g/m^2.

[0087] In the comparative film No. 2 (TC1) spectral sensitization of the said cubic emulsion crystals rich in silver chloride was performed with oxacarbocyanine sensitizer anhydro-5,5'-dichloro-3,3'-bis-(n.sulfopropyl)-9-ethyloxacarbo-cyanine hydroxide, corresponding with the formula (II.1) given in the detailed description hereinbefore in an amount of 0.9 mmole per mole of silver coated, as sole green sensitizer. The total amount of silver coated per square meter was 7.56 g, expressed as an equivalent amount of silver nitrate.

-in the comparative film No.2 (TC2) spectral sensitizer according to the formula (I.5) was added in an amount of 0.2 mmole per mole of silver coated. The total amount of silver coated per square meter was 7.61 g, expressed as an equivalent amount of silver nitrate.

-in the comparative film No.3 (TC3) spectral sensitizer according to the formula hereinafter was coated in an amount of 0.03 mmole per mole of silver, together with the spectral sensitizer according to the formula (II.1) as in TC1 in the same amount of 0.9 mmole per mole of silver coated.



The total amount of silver coated per square meter was 7.43 g, expressed as an equivalent amount of silver nitrate.

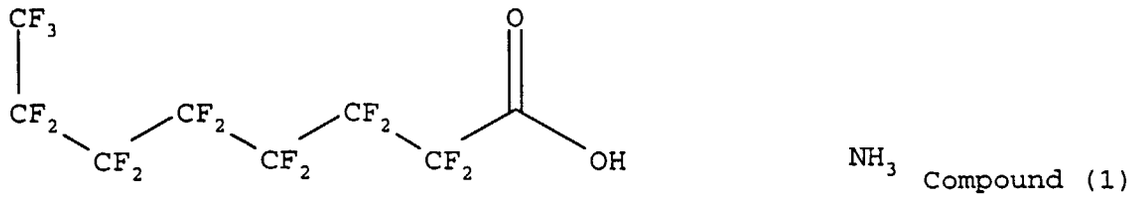
-in the film TI1 (inventive example) spectral sensitization of the said tabular emulsion crystals rich in silver chloride was performed with oxacarbocyanine sensitizer anhydro-5,5'-dichloro-3,3'-bis-(n.sulfopropyl)-9-ethyloxacarbo-cyanine hydroxide, corresponding with the formula (II.1) given in the detailed description in an amount of 0.9 mmole per mole of silver coated, in combination with green sensitizing dye according to the formula (I.4) in an amount of 0.06 mmole per mole of silver coated. The total amount of silver coated per square meter in film material TI1 was 7.46 g, expressed as an equivalent amount of silver nitrate.

-in the filmS TI2 and TI3 (both inventive examples) spectral sensitization of the said tabular emulsion crystals rich in silver chloride was performed with oxacarbocyanine sensitizer anhydro-5,5'-dichloro-3,3'-bis-(n.sulfopropyl)-9-ethyloxacarbo-cyanine hydroxide, corresponding with the formula (II.1) given in the detailed description in an

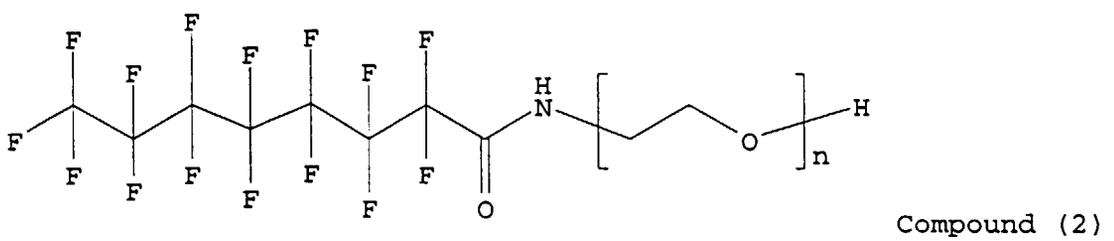
amount of 0.9 mmole per mole of silver coated, in combination with green sensitising dye according to the formula (I.5) in an amount of 0.03 and 0.06 mmole respectively per mole of silver coated. The total amount of silver coated per square meter in film materials TI2 and TI3 was 7.52 g and 7.56 g respectively, expressed as an equivalent amount of silver nitrate.

[0088] The emulsion layer in the different materials was overcoated with a gelatin covering layer (protective anti-stress layer) of 1.30 g of gelatin per m^2, having following composition at a coating pH value of 6.1:

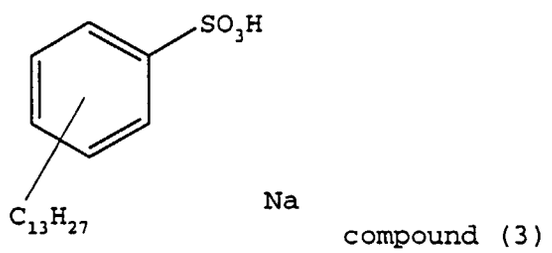
Protective layer	
Gelatin	1.1 g/m^2
Polyethyl acrylate latex	500 mg/m^2
Kieselsol	15 mg/m^2
Chromium acetic acid	5.5 mg/m^2
Compound (1)	7.5 mg/m^2
Compound (2)	19 mg/m^2
Mobilcer Q	25 ml/m^2
Compound (3)	8 mg/m^2



Compound (1)



Compound (2)



compound (3)

[0089] The processing was run in the developing liquid EXPDEV, followed by fixing in fixing liquid EXPFIX and rinsing

at the indicated temperature of 35°C for a total processing time of 45 seconds.

[0090] Processing of all film materials occurred in a developer, the composition of which has been given hereinafter.

Developer EXPDEV:	
demineralized water	700 ml
sodium erythorbate laq.	61.5 g
4,4'-hydroxymethyl-methyl-phenidone	2 g
potassium bromide	1 g
potassium thiocyanate	1 g
5-methyl-benzotriazole	0.03 g
potassium metabisulfite	23 g
aqueous potassium carbonate (765 g/l)	125 ml
aqueous potassium hydroxyde (755 g/l)	10 ml
1-hydroxy ethyl diphosphonic acid di-Na salt	1 g
Polyethylene glycol (M.W.: 400)	20 ml
pH (adjusted with acetic acid)	9.65
Water to make 1 l.	

[0091] The developed samples were fixed in fixer EXPFIX, followed by rinsing with water. The composition of the said fixer was as follows:

Fixer EXPFIX	
-Ammonium thiosulphate (60 % solution, wherein 1 ml comprises 0.778 g)	710 ml
-Sodium metabisulphite	80 g
-Sodium acetate	130 g
-Acetic acid	31 ml
pH ready-for-use (after dilution 1+3)	4.90

[0092] Sensitometric data are expressed for

-"fog" levels F, determined as the sum of support density and density due to real emulsion fog,
-speed values S, determined at a density of 1.0 above fog level, wherein said values are multiplied by a factor of 100.

[0093] The determination of the photographic speed S of said screens proceeded according to the International standard method ISO/DP9236 (42N2063) Revised edition of Nov. 1986 and are given in the Table as 1000/mGy for a density of 1.00 above fog as set forth hereinbefore.

[0094] In Table 1 results are summarized for the different film materials after exposure and processing as set forth above. Coated amounts of spectral sensitizer, expressed in mmole per mole of silver coated are given further, as well as cross-over %, determined in the following way: samples of the materials were placed between a single green light emitting screen and a white paper, replacing the second screen. This film-screen element, directed with its light emitting screen to the X-ray tube, was then exposed with varying X-ray doses, expressed as log E. After processing these samples in the above described processing cycle, the minimal dose (log E) needed to obtain a density of 0.5 above fog was determined for the front layer (log E front) and the back layer (log E back) separately. The cross-over (% C.O.) was then

calculated according to the following equation :

$$\% CO = 100/\text{antilog}(\log E \text{ back} - \log E \text{ front})$$

Table 1

Film	F	S	Dmax	Screen Speed	Crossover (%)	Abs.abs. (545 nm)
TC1	0.040	2.11	3.49	27	54	1.11
TC2	0.218	1.91	3.50	49	60	0.93
TC3	0.041	1.89	3.57	38	49	1.13
TI1	0.056	1.83	3.65	50	46	1.17
TI2	0.028	1.82	3.74	53	51	1.13
TI3	0.028	1.76	3.78	56	50	1.15

[0095] As becomes clear from the data given in Table 1 it is possible to get at least the required, and even a higher speed with an even better cross-over when use is made of a film/screen combination wherein the film material is coated from a emulsions rich in chloride wherein as in materials TI1-TI3 the said grains have been spectrally sensitized with a combination of green sensitizing dyes as claimed.:

-limitation of spectral sensitization by a benzoxazole sensitizer only (TC1) offers too low a sensitivity, although fog is excellent;
-limitation of spectral sensitization by a benzimidazole sensitizer (TC2) only offers a high sensitivity, but fog and cross-over percentage are both too high to be applicable;
-mixture of a benzoxazole and a benzimidazole sensitizer, differing from the benzimidazole sensitizers as claimed (TC3) results in a good fog level and an improved cross-over but in too low a speed level;
-mixture of a benzoxazole and a benzimidazole sensitizer, according to the present invention as claimed, wherein the benzimidazole spectral sensitizing dye offers good adsorbing J-aggregates at the crystal surface, absorbing light at the desired wavelength of 545 nm, results in an optimal relation between a high speed, a low fog and a low cross-over (TI1-TI3).

B. Film materials comprising tabular {111} grains rich in chloride were the following.

Preparation of silver chloroiodide {111} tabular grain emulsion:

[0096] The following solutions were prepared:

- 6 l of a dispersion medium (C) containing 480 mmoles of sodium chloride, 150 g of inert gelatin and 360 mg of adenine; temperature was established at 45 °C, pH was adjusted to 6.0;
- a 2.94 molar silver nitrate solution (A);
- a solution containing 2.813 moles of sodium chloride, 14 mmoles of potassium iodide and 398.1 mg of adenin (B1).

[0097] A nucleation step was performed by introducing solution A and solution B1 simultaneously in dispersion medium C both at a flow rate of 120 ml/min during 30 seconds. After a physical ripening time of 20 min during which the temperature was raised to 70 °C, the first growth step was performed by introducing by a double jet during 28 minutes and 50 seconds solution A starting at a flow rate of 10 ml/min and linearly increasing the flow rate to an end value of 27.4 ml/min, and solution B1 at an increasing flow rate in order to maintain a constant mV-value, measured by a silver electrode versus a saturated calomel electrode (S.C.E.), of +115 mV. At the end of the first growth step the flow rate of solution A was immediately decreased to 10 ml/min and the mV-value adjusted to + 135 mV and increased again to a flow rate of 19.8 ml/min during the following 16 minutes and 8 seconds, during which time the mV-value was further held constant at + 135 mV by a controlled increasing flow of B1. After a physical ripening time of 4 minutes a solution of 40 ml having 15 mmoles of potassium iodide was added at a constant flow rate of 2 minutes. The total iodide content of the tabular silver chloroiodide crystals was thereby enhanced to a value of up to 1.0 mole %.

[0098] After cooling to about 40°C the addition of 56 ml of polystyrene sulphonic acid in 2 minutes was started, the

pH value of the said dispersing medium was adjusted to a value of 3.5 with sulphuric acid and after cooling to 20°C the obtained flocculate was decanted and washed three times with an amount of 4 l of demineralized water (11°C) in order to remove the soluble salts present. After decanting to a volume of 2 l the washing procedure was repeated twice and after the last washing step, followed by sedimentation decantation was performed in order to have an emulsion volume as low as possible. An emulsion having {111} silver chloroiodide tabular grains with a variable iodide profile as in EP-A 0 678 772 was thus obtained.

[0099] The thus obtained silver chloride tabular emulsion showed the following grain characteristics:

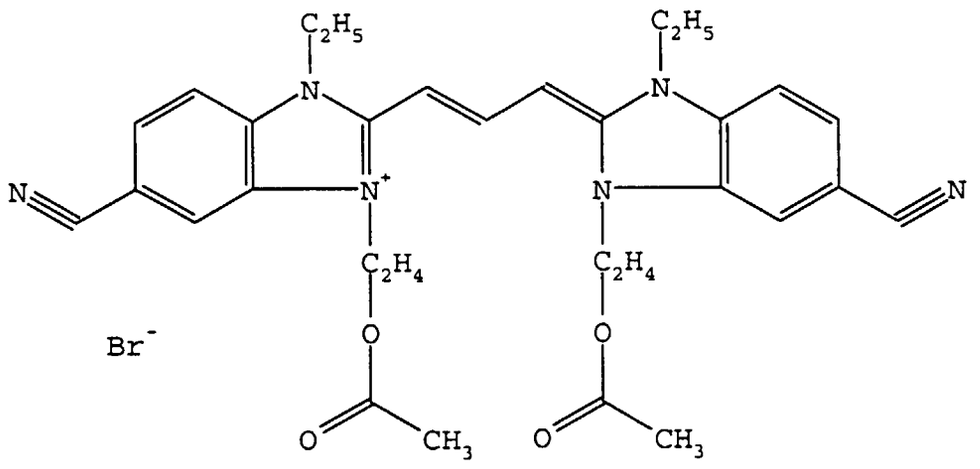
-an average equivalent circular diameter E.C.D. of 1.40 μm;
-an average thickness t of 0.14 μm;
-an average aspect ratio AR of 10.0.

[0100] These data were obtained from electron microscopic photographs: the diameter of the grain was defined as the diameter of the circle having an area equal to the projected area of the grain as viewed in the said photographs.

[0101] Before the start of the chemical ripening the mV-value of the emulsion was adjusted at +158 mV (against a silver/silver chloride reference electrode) with sodium chloride and the pH-value at 5.5 with sodium hydroxide. Chemical ripening agents were adapted to the crystal size of the emulsions.

[0102] Chemical ripening agents were gold thiocyanate, sodium thiosulphate as a source of sulphur and toluene thiosulphonic acid was used as predigestion agent. The amounts of each chemical ripening agent were optimized in order to obtain an optimal fog-sensitivity relationship after 2 hours at 70°C, without the presence of bromide ions, opposite to the required use thereof at a temperature of greater than 80°C as in US-A 5,494,788.

-in the comparative film No.3 (TC3') the spectral sensitizer according to the formula hereinafter was coated in an amount of 0.03 mmole per mole of silver, together with the spectral sensitizer according to the formula (II.1) as in TC1 (cubic grain emulsion) in the same amount of 0.9 mmole per mole of silver coated. This combination of spectral sensitizers corresponds with those added to the tabular silver chloroiodide grains in EP-A 0 678 772.



The total amount of silver coated per square meter was 6.86 g, expressed as an equivalent amount of silver nitrate.

-in the film TI' (inventive example) spectral sensitization of the said tabular emulsion crystals rich in silver chloride was performed with oxacarbocyanine sensitizer anhydro-5,5'-dichloro-3,3'-bis-(n.sulfopropyl)-9-ethyloxacarbo-cyanine hydroxide, corresponding with the formula (II.1) given in the detailed description in an amount of 0.9 mmole per mole of silver coated, in combination with green sensitizing dye according to the formula (I.4) in an amount of 0.06 mmole per mole of silver coated. The total amount of silver coated per square meter in film material TI' was 6.85 g, expressed as an equivalent amount of silver nitrate.

[0103] Coatings were further performed as described hereinbefore for materials having cubic crystal rich in silver chloride. Same exposure of the materials and processing conditions were applied, as well as the same sensitometric evaluation, the results of which have been illustrated hereinafter in the Table 2.

Table 2

Film	F	S	Dmax	Screen Speed	Crossover (%)	Abs.abs. (545 nm)
TC3'	0.057	1.52	3.45	81	52	0.91
TI'	0.042	1.54	3.60	81	51	0.95

[0104] As becomes clear from the data given in Table 2 it is possible to get at least the required speed, with an at least equal or even lower cross-over when use is made of a film/screen combination wherein the film material is coated from tabular grain emulsions rich in chloride wherein as in material TI hereinbefore the said grains have been spectrally sensitized with a combination of green sensitizing dyes as claimed.: a mixture of a benzoxazole and a benzimidazole sensitizer as claimed, differing from the benzimidazole sensitizers as in TC3' results in a comparable speed but with a lower fog level for the inventive coating.

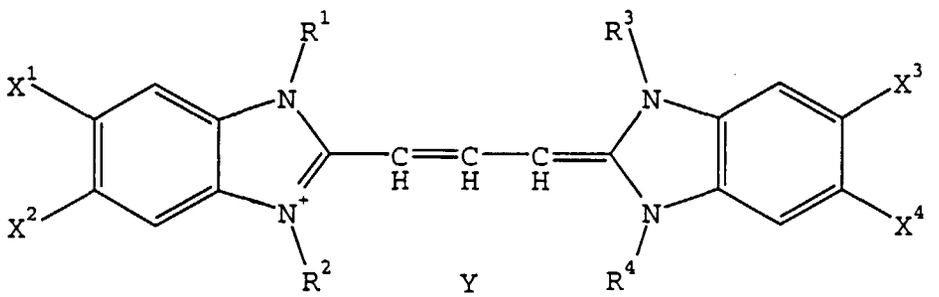
[0105] Use of a spectral sensitizing combination of a benzoxazole and a benzimidazole sensitizer, according to the present invention as claimed, for the emulsion grains rich in silver chloride, wherein the benzimidazole spectral sensitizing dye offers good adsorbing J-aggregates at the crystal surface, absorbing light at the desired wavelength of 545 nm thus results in an optimal relation between a high speed and a low fog as desired.

Claims

1. Radiographic screen/film combination comprising a duplitized film 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 comprising luminescent phosphor particles emitting at least 50 % of their emitted radiation in the wavelength range between 540 and 555 nm,
ii) said film comprises, in a light-sensitive silver halide emulsion layer, silver halide grains rich in silver chloride, spectrally sensitized to irradiation in the said wavelength range between 540 and 555 nm by a combination of green sensitizing dyes, being

-a benzimidacarbocyanine dye according to formula (I)

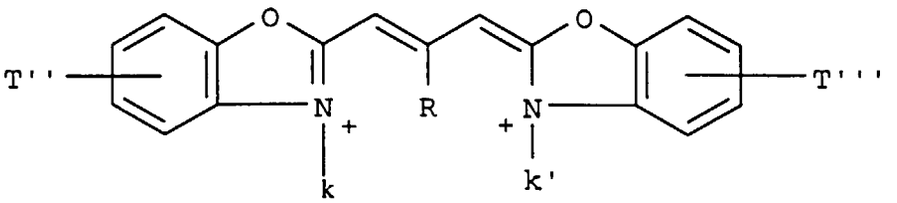


(I)

wherein

R^1 and R^3 are methyl or ethyl, but are differing from each other;
R^2 and R^4 are substituted or unsubstituted C_2 to C_6 alkyl,
X^1, X^2, X^3 and X^4 are each independently hydrogen, methyl or fluoro-substituted methyl, provided that at least one of X^1 and X^2 and at least one of X^3 and X^4 are not hydrogen;
Y represents an ion in order to balance the charge of the molecule; and

a benzoxacarbocyanine dye corresponding to the general formula (II)



(II)

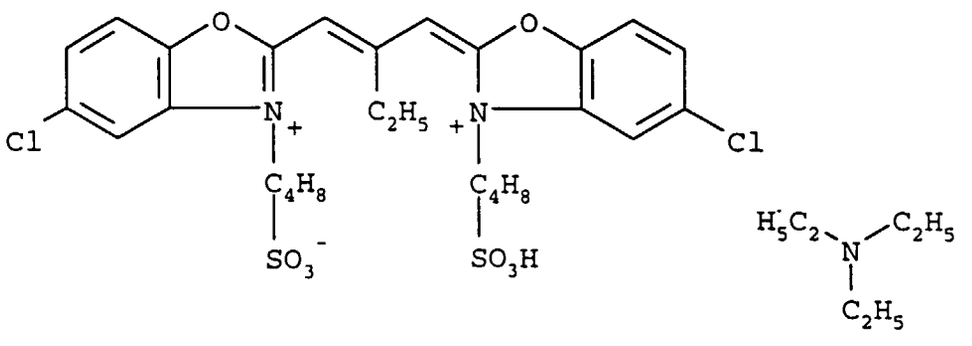
wherein

R represents H, CH_3 or CH_2CH_3;
T'' and T''' each independently represents one of the following substituents in the 4-, 5- or 6-position: H, Cl, phenyl, CH_3, OCH_3, provided that at least one of T'' and T''' represents a (substituted or unsubstituted) phenyl-group;
$k'=(CH_2)_nSO_3M$ or $(CH_2)_nOSO_3M$;
$k=(CH_2)_mSO_3^-$ or $(CH_2)_mOSO_3^-$;
M= H, Na or K;
n= 2, 3 or 4;
m= 2, 3 or 4.

2. Radiographic screen/film combination according to claim 1, wherein in formula (I) R^2 and R^4 are differing from each other and wherein one of R^2 and R^4 represents a fluoro substituted alkyl group.

3. Radiographic screen/film combination according to claim 1 or 2, wherein in formula (I) R^2 is trifluoroethyl and R^4 is sulfoethyl, sulfopropyl, 3-sulfobutyl or 4-sulfobutyl, whereas X^1 and X^3 are hydrogen and X^2 and X^4 are each trifluoromethyl.

4. Radiographic screen/film combination according to any of claims 1 to 3, wherein said benzoxacarbocyanine dye corresponds to formula (I.1):



(I.1)

5. Radiographic screen/film combination according to any of claims 1 to 4, wherein said luminescent phosphor particles emit at least 80 % of their emitted radiation in the wavelength range between 540 and 555 nm.

6. Radiographic screen/film combination according to any of claims 1 to 5, wherein said luminescent phosphor particles emitting radiation in the wavelength range between 540 and 555 nm are gadolinium oxisulphide phosphor particles having a composition according to formula (III)

$$Gd_2O_2S:Tb \qquad \text{(III)}.$$

7. Radiographic screen/film combination according to any of claims 1 to 6, wherein a molar ratio of benzimidacarbocyanine to benzoxacarbocyanine dyes is between 2:100 and 50:100.

8. Radiographic screen-film combination according to any of claims 1 to 7, wherein said film comprises {111} tabular silver halide grains rich in silver chloride having an average aspect ratio of 5 or more, an average grain thickness of at most 0.2 μm, and account for at least 50 % of the total projective area of all grains or {100} tabular silver halide grains rich in silver chloride having an average aspect ratio of 2 or more, an average grain thickness of at most 0.3 μm, and account for at least 40 % of the total projective area of all grains or cubic silver halide grains rich in silver chloride having an average sphere equivalent diameter of from 0.2 up to 1.0 μm.

9. Radiographic screen-film combination according to any of claims 1 to 8, wherein the total amount of coated silver halide in said film, expressed as an equivalent amount of silver nitrate, is less than 8.0 g/m^2.

10. Radiographic screen-film combination according to any of claims 1 to 9, wherein said film comprises, in order, a support, a subbing layer, a gelatinous layer containing one or more merostyryl dyes having a pyrazolon nucleus, a light-sensitive emulsion layer and a protective antistress layer.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 0061

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)
X	DATABASE WPI Section Ch, Week 9743 Derwent Publications Ltd., London, GB; Class E23, AN 97-461706 XP002065763 & JP 09 211756 A (KONICA CORP) * abstract * * column 10, line 32 - column 16, line 2 * * column 69, line 26 * * table 4, sample 3 * ---	1-10	G03C1/29 G03C1/18 G03C1/005 G03C5/17
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 009, 30 September 1997 & JP 09 133981 A (KONICA CORP), 20 May 1997 * abstract * * column 11, line 3 - column 26, line 46 * * column 29, line 1 - column 33, line 40 * * column 65, line 50 * * table 3, samples 6,7 * ---	1-10	
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 003, 31 March 1997 & JP 08 314048 A (KONICA CORP), 29 November 1996 * abstract * * column 9, line 1 - column 10, line 26 * * column 11, line 1 - column 14, line 36 * * column 47, line 41 * * table 1, samples 2-4 * * table 2, samples 10-12 * --- -/--	1-10	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
MUNICH	25 May 1998	Binder, R

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X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 98 20 0061

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)
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 002, 28 February 1997 & JP 08 262604 A (KONICA CORP), 11 October 1996 * abstract * * column 7, line 1 - column 8, line 34 * * column 9, line 5 - column 12, line 36 * * column 57, line 37 * * table 3, samples 12,13,18,19 * ---	1-10	
D,A	EP 0 506 584 A (EASTMAN KODAK COMPANY) 30 September 1992 * page 2, line 36 - line 56 * * page 3, line 29 - line 36 * * page 4, line 23 - line 25 * * table 1 * * claims 1,7-11 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

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MUNICH	25 May 1998	Binder, R

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25-05-1998

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