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①⁵⁴ **Light-sensitive elements for radiographic use and process for the formation of an X-ray image.**

①⁵⁷ A light-sensitive silver halide element for radiographic use with X-ray intensifying screens comprising coated on at least one side of a transparent support base at least a spectrally sensitized silver halide emulsion layer and, between the base and a silver halide emulsion layer, a hydrophilic colloid layer containing substantially light-insensitive silver halide grains on which a spectral sensitizing dye is adsorbed, said dye adsorbed on said grains having the absorption in a region of the electromagnetic spectrum corresponding substantially to the spectral sensitivity of the silver halide emulsion, is characterized by the fact that said silver halide grains are low iodide silver bromiodide grains having an average grain size in the range of from 0.01 to 0.1 μm adsorbed with said spectral sensitizing dye to form a J-band.

The invention allows the use of low coverage weights of silver halide light-sensitive elements and provides X-ray images with a favorable image quality and sensitivity ratio.

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Light-Sensitive Elements For Radiographic Use And Process For The Formation Of An X-Ray Image

FIELD OF THE INVENTION

5 The present invention refers to light-sensitive silver halide elements to be used in radiography and, more in particular, to light-sensitive silver halide elements to be used with intensifying screens to obtain improved X-ray images.

10 BACKGROUND OF THE INVENTION

In radiography, and particularly in medical radiography, light-sensitive elements having silver halide emulsion layers coated on one side of a transparent base are used. It is known to be more preferable to
15 use silver halide emulsions on both sides to obtain better developability as compared to single-side coated elements. Light-sensitive elements having silver halide emulsion layers coated on one side and, more preferably, on both sides of the base are generally used in association with intensifying screens in order to reduce the X-ray exposure necessary to obtain the required image. Generally, one intensifying screen is used on each side of the light-sensitive element. The silver halides used in the light-sensitive elements are
20 sensitive or sensitized to a region of the electromagnetic spectrum corresponding to the wavelength of the light emitted by the luminescent materials used in the intensifying screens, thus obtaining significant amplification factors.

The quality of image obtained upon exposure and development of said radiographic elements is negatively affected by light scattering and crossover exposure.

25 Light scattering occurs both in single and double emulsion layer coated radiographic materials when light emitted by one screen is diffused (scattered) by silver halide grains causing a reduction in image sharpness.

Crossover exposure, which also causes a reduction in image sharpness, occurs in double emulsion layer coated radiographic materials when light emitted by one screen passes through the adjacent emulsion
30 layer and the support and, the light having been spread by the support, image-wise exposes the emulsion layer on the opposite side of the support.

The crossover exposure causes poor definition even if light-sensitive elements are used which employ reduced silver halide coverages to lower the costs or increase the processing speed of the element. In fact, the decrease of the emulsion turbidity increases the amount of light available for crossover and therefore
35 worsens the image.

To reduce the crossover phenomenon, dyes or pigments can be used within the photographic element. The absorption of said dyes or pigments is in a region of the electromagnetic spectrum corresponding to the wavelength of the light emitted by the intensifying screens. The dyes or pigments absorb some of the light emitted by the intensifying screen so that imaging of the rear emulsion by the forward screen is
40 reduced by absorbance of the light from the forward screen by the anticrossover layer. These dyes or pigments are eliminated during the photographic developing, fixing and washing process of the exposed material; they can be for instance washed away or, more preferably, bleached while processing the radiographic element.

The dyes can be incorporated in any layer of the light-sensitive element: in the emulsion layer, in an
45 intermediate layer between the emulsion and the base, or in the subbing layer of the support base. It is preferred to incorporate the dyes in a layer different from that containing the emulsion to avoid possible desensitization phenomena. Since 1978, Minnesota Mining and Manufacturing Company has sold a radiographic element under the name of 3M Trimax™ Type XUD X-Ray Film to be used in combination with 3M Trimax™ Intensifying Screens. Such radiographic element comprises a transparent polyester base,
50 each surface of which has a silver halide emulsion layer sensitized to the light emitted by the screens. Between the emulsion and the base is a gelatin layer containing water-soluble acid dyes, which dyes can be decolorized during processing and have an absorption in a region of the electromagnetic spectrum corresponding to the wavelength of the light emitted by the screens and of the spectral sensitivity of the emulsion. The dyes are anchored in the layer by means of a basic mordant consisting of polyvinylpyridine.

In the practical solution of reducing the crossover exposure by using a mordanted dye layer (as

described for instance in the European Patent Application 101,295), some problems are created which up to now have not yet been solved properly. In fact, the improvement of image definition involves not only a natural decrease of the light-sensitive element sensitivity caused by the absorption of the transmitted and diffused light which otherwise would take part in the formation of a part of the image, but also the possibility of desensitization phenomena due to the migration of dye not firmly mordanted in the silver halide emulsion layer. There is also a problem with residual stain even after processing, the retention of significant quantities of thiosulfate from the fixing bath which causes image yellowing upon longtime storage on shelf, and lengthening of the drying times after processing because of element thickening.

Other approaches have been suggested to reduce crossover, as reported hereinbelow.

US Patent 3,923,515 discloses a relatively lower speed silver halide emulsion between the support and a higher speed silver halide emulsion layer to reduce crossover.

US Patent 4,639,411 discloses a photographic element, to be used with blue emitting intensifying screens, having reduced crossover, said element comprising coated on both sides of a transparent support a blue sensitive silver halide emulsion layer and, interposed between the support and the emulsion layer, a blue absorbing layer comprising bright yellow silver iodide grains of a specific crystal structure.

Japanese Patent Application 62-52546 discloses a radiographic element of improved image quality comprising coated on both sides of a transparent support a light sensitive silver halide emulsion layer and, interposed between the support and the emulsion layer, a layer containing water insoluble metal salt particles having adsorbed on their surface a dye. Said dye has a maximum absorption within the range of ± 20 nm of the maximum absorption of said silver halide and corresponds to the light emitted by intensifying screens. Silver halides are disclosed as preferred metal salt particles.

Japanese Patent Application 62-99748 discloses a radiographic element of improved image quality comprising coated on both sides of a transparent support a light-sensitive silver halide emulsion layer and, interposed between the support and the emulsion layer, a silver halide emulsion layer having substantially no light-sensitivity.

The approaches of using light-insensitive silver halide layers as anticrossover layers interposed between the support and the light-sensitive silver halide emulsion layers, although preferred to using dyes or pigments, encounter some problems such as the increase of silver coverage and bad bleaching characteristics in photographic processing (residual stain).

SUMMARY OF THE INVENTION

In one aspect this invention is directed to substantially light-insensitive very fine grain low iodide silver bromoiodide grains, having adsorbed on their surface spectral sensitizing dyes to form a sharp absorption band (J-band).

In another aspect this invention is directed to a silver halide X-ray element to be used with X-ray intensifying screens comprising a transparent support base having coated on at least one of its sides a spectrally sensitized silver halide emulsion layer and, between the support base and the silver halide emulsion layer, a hydrophilic colloid layer containing substantially light-insensitive silver halide grains on which a spectral sensitizing dye is adsorbed, said dye adsorbed on said grains having absorption in a region of the electromagnetic spectrum corresponding substantially to the spectral sensitivity of the silver halide emulsion, wherein said substantially light-insensitive silver halide grains are low iodide silver bromoiodide grains having an average grain size in the range of from 0.01 to 0.1 μm adsorbed with said spectral sensitizing dye to form a J-band.

Said X-ray element offers advantages in crossover reduction without causing negative effects, such as significant loss of sensitivity, residual stain, image instability upon storage and excessive element thickening.

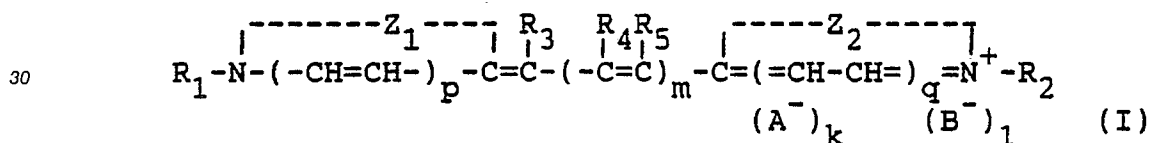
DETAILED DESCRIPTION OF THE INVENTION

Accordingly, in one aspect, the present invention relates to a substantially light-insensitive silver halide emulsion comprising silver halide grains on which a spectral sensitizing dye is adsorbed, characterized by the fact that said silver halide grains are low iodide silver bromoiodide grains having an average grain size of from 0.01 to 0.1 μm adsorbed with said spectral sensitizing dye to form a J-band.

The term "low iodide grains" in the present invention means a total percentage of halide in the grains of more than 0.2 mole percent and less than 10 mole percent iodide. Preferably the silver iodide provided by the silver bromiodide grains is limited to less than 5 mole percent of the total silver halide present in the grains, and more preferably less than 3 mole percent. Silver iodide grains of at least 1 mole percent are preferred to produce the desired J-band.

Said silver bromiodide grains are substantially light-insensitive, that is they do not form any image upon conventional exposure (e.g. for a 10^{-2} sec time) to radiations of a wavelength in the range from 420 to 700 nanometers and development in standard black and white and color developers. Such sensitivity can be generally described as being of less than 1 ASA. In the case of the emulsions of the present invention, they preferably are of a sensitivity lower than 10^{-1} ASA. The grain size of said light-insensitive silver bromiodide grains is particularly restricted. The grains are 0.1 μm or less in mean diameter. The minimum mean diameters of the grains are limited only by synthetic convenience. Typically, grains of at least 0.01 μm in mean diameter are employed. The light-insensitive silver bromiodide grains of the present invention have adsorbed on their surface spectral sensitizing dyes that exhibit absorption maxima in the blue and/or green and/or red portions of the visible spectrum. Spectral sensitizing dyes according to this invention produce J aggregates if adsorbed on the surface of the silver halide grains and a sharp absorption band (J-band) with a bathochromic shifting with respect to the absorption maximum of the free dye in aqueous solution. Spectral sensitizing dyes producing J aggregates are well known in the art, as illustrated by F. M. Hamer, *Cyanine Dyes and Related Compounds*, John Wiley and Sons, 1964, Chapter XVII and by T. H. James, *The Theory of the Photographic Process*, 4th edition, Macmillan, 1977, Chapter 8.

In a preferred form, J-band exhibiting dyes are cyanine dyes. Such dyes comprise two basic heterocyclic nuclei joined by a linkage of methine groups. The heterocyclic nuclei preferably include fused benzene rings to enhance J aggregation. The heterocyclic nuclei are preferably quinolinium, benzoxazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthoxazolium, naphthothiazolium and naphthoselenazolium quaternary salts. J-band type dyes preferably used in the present invention have the following general formula (I):



wherein Z_1 and Z_2 may be the same or different and each represents the elements necessary to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds such as oxazoline, oxazole, benzoxazole, the naphthoxazoles (e.g., naphth{2,1-d}oxazole, naphth{2,3-d}oxazole, and naphth{1,2-d}oxazole), thiazoline, thiazole, benzothiazole, the naphthothiazoles (e.g., naphtho{2,1-d}thiazole), the thiazoloquinolines (e.g., thiazolo{4,5-b}quinoline), selenazoline, selenazole, benzoselenazole, the naphthoselenazoles (e.g., naphtho{1,2-d}selenazole, 3H-indole (e.g., 3,3-dimethyl-3H-indole), the benzindoles (e.g., 1,1-dimethylbenzindole), imidazoline, imidazole, benzimidazole, the naphthimidazoles (e.g., naphth{2,3-d}imidazole), pyridine, and quinoline, which nuclei may be substituted on the ring by one or more of a wide variety of substituents such as hydroxy, the halogens (e.g., fluoro, bromo, chloro, and iodo), alkyl groups or substituted alkyl groups (e.g., methyl, ethyl, propyl, isopropyl, butyl, octyl, dodecyl, 2-hydroxyethyl, 3-sulfopropyl, carboxymethyl, 2-cyanoethyl, and trifluoromethyl), aryl groups or substituted aryl groups (e.g., phenyl, 1-naphthyl, 2-naphthyl, 4-sulfophenyl, 3-carboxyphenyl, and 4-biphenyl), aralkyl groups (e.g., benzyl and phenethyl), alkoxy groups (e.g., methoxy, ethoxy, and isopropoxy), aryloxy groups (e.g., phenoxy and 1-naphthoxy), alkylthio groups (e.g., ethylthio and methylthio), arylthio groups (e.g., phenylthio, p-tolythio, and 2-naphthylthio), methylenedioxy, cyano, 2-thienyl, styryl, amino or substituted amino groups (e.g., anilino, dimethylanilino, diethylanilino, and morpholino), acyl groups (e.g., acetyl and benzoyl), and sulfo groups,

R_1 and R_2 can be the same or different and represent alkyl groups, aryl groups, alkenyl groups, or aralkyl groups, with or without substituents, (e.g., carboxymethyl, 2-hydroxyethyl, 3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, 2-methoxyethyl, 2-sulfatoethyl, 3-thiosulfatoethyl, 2-phosphonoethyl, chlorophenyl, and bromophenyl),

R_3 represents a hydrogen atom,

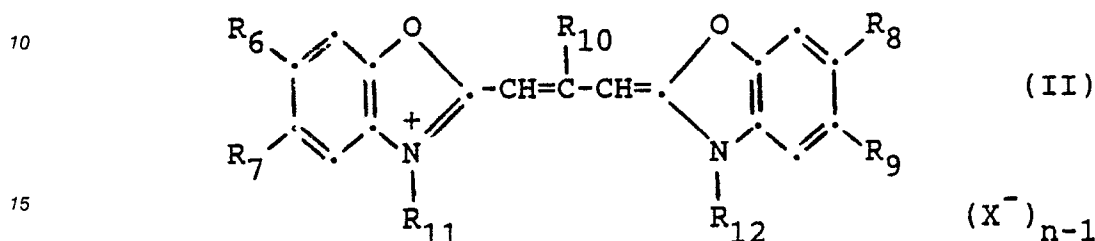
R_4 and R_5 can be the same or different and represent a hydrogen atom or a lower alkyl group of from 1 to 4 carbon atoms,

p and q are 0 or 1, except that both p and q preferably are not 1,

m is 0 or 1 except that when m is 1 both p and q are 0 and at least one of Z₁ and Z₂ represents imidazoline, oxazoline, thiazoline, or selenazoline,

A is an anionic group, B is a cationic group, and k and l may be 0 or 1, depending on whether ionic substituents are present. Variants are, of course, possible in which R₁ and R₃, R₂ and R₅, or R₁ and R₂ together represent the atoms necessary to complete an alkylene bridge.

More preferably said dye adsorbed on said substantially light-insensitive silver bromoiodide grains is represented by the following general formula (II):



wherein

R₁₀ represents a hydrogen atom or a lower alkyl group of from 1 to 4 carbon atoms (e.g. methyl, and ethyl),

R₆, R₇, R₈ and R₉ each represents a hydrogen atom, a halogen atom (e.g. chloro, bromo, iodo, and fluoro), a hydroxy group, an alkoxy group (e.g. methoxy and ethoxy), an amino group (e.g. amino, methylamino, and dimethylamino), an acylamino group (e.g. acetamido and propionamido), an acyloxy group (e.g. acetoxy group), an alkoxycarbonyl group (e.g. methoxycarbonyl, ethoxycarbonyl, and butoxycarbonyl), an alkyl group (e.g. methyl, ethyl, and isopropyl), an alkoxycarbonylamino group (e.g. ethoxycarbonylamino) or an aryl group (e.g. phenyl and tolyl), or, together, R₆ and R₇ and, respectively, R₈ and R₉ can be the atoms necessary to complete a benzene ring (so that the heterocyclic nucleus results to be, for example, an α -naphthoxazole nucleus, a β -naphthoxazole or a β,β' -naphthoxazole),

R₁₁ and R₁₂ each represents an alkyl group (e.g. methyl, propyl, and butyl), a hydroxyalkyl group (e.g. 2-hydroxyethyl, 3-hydroxypropyl, and 4-hydroxybutyl), an acetoxyalkyl group (e.g. 2-acetoxyethyl and 4-acetoxybutyl), an alkoxyalkyl group (e.g. 2-methoxyethyl and 3-methoxypropyl), a carboxyl group containing alkyl group (e.g. carboxymethyl, 2-carboxyethyl, 4-carboxybutyl, and 2-(2-carboxyethoxy)-ethyl), a sulfo group containing alkyl group (e.g. 2-sulfoethyl, 3-sulfopropyl, 4-sulfobutyl, 2-hydroxy-3-sulfopropyl, 2-(3-sulfopropoxy)-propyl, p-sulfobenzyl, and p-sulfophenethyl), a benzyl group, a phenethyl group, a vinyl-methyl group, and the like,

X⁻ represents an acid anion (e.g. a chloride, bromide, iodide, thiocyanate, methylsulfate, ethylsulfate, perchlorate, and p-toluensulfonate ion), and

n represents 1 or 2.

The alkyl groups included in said substituents R₆, R₇, R₈, R₉, R₁₀, and R₁₁ and, more particularly, the alkyl portions of said alkoxy, alkoxycarbonyl, alkoxycarbonylamino, hydroxyalkyl, acetoxyalkyl groups and of the alkyl groups associated with a carboxy or sulfo group each preferably contain from 1 to 12, more preferably from 1 to 4 carbon atoms, the total number of carbon atoms included in said groups preferably being no more than 20.

The aryl groups included in said substituents R₆, R₇, R₈ and R₉ each preferably contain from 6 to 18, more preferably from 6 to 10 carbon atoms, the total number of carbon atoms included in said groups arriving up to 20 carbon atoms.

The following are specific examples of J-band sensitizing dyes belonging to those represented by the general formula (II) above:

Dye	R ₁₀	R ₆	R ₇	R ₈	R ₉	R ₁₁	R ₁₂	X	n
A *	C ₂ H ₅	H	5-Cl	H	5'-Cl	(CH ₂) ₃ SO ₃ ⁻	(CH ₂) ₃ SO ₃ H	-	1
B **	C ₂ H ₅	H	5-Cl	H	5'-C ₆ H ₅	(CH ₂) ₃ SO ₃ ⁻	(CH ₂) ₂ CHSO ₃ H	-	1
C	CH ₃	H	5-OCH ₃	H	5'-OCH ₃	C ₂ H ₅	(CH ₂) ₃ SO ₃ ⁻	-	1
D	C ₂ H ₅	6-CH ₃	5-Cl	H	5'-Cl	(CH ₂) ₄ SO ₃	(CH ₂) ₃ SO ₃ H	-	1
E	C ₂ H ₅	H	5-Cl	H	5'-Cl	C ₂ H ₅	C ₂ H ₅	J	2

* Triethylamine salt

** Sodium salt

According to the present invention, it has been found that the intensity of the sharp absorption band (J-band) shown by the spectral sensitizing dye adsorbed on the surface of the light-insensitive silver halide grains will vary with the quantity of the specific dye chosen as well as the size and chemical composition of the grains. The maximum intensity of J-band has been obtained with silver halide grains having the hereinbefore described sizes and the chemical compositions adsorbed with J-band spectral sensitizing dyes in a concentration of from 25 to 100 percent or more of monolayer coverage of the total available surface area of said silver halide grains. Optimum dye concentration levels can be chosen in the range of 0.5 to 20 millimoles per mole of silver bromiodide, preferably in the range of 2 to 10 millimoles.

The J-band spectral sensitizing dyes are preferably added to the fine grain low iodide silver bromiodide emulsions in the presence of a water soluble iodide or bromide salt. The J-band exhibited by said dyes adsorbed on said grains has been found to be increased by the presence of said salts. Said salts are more advantageously added to the silver halide emulsion before dye digestion, that is the pause following dye addition; said pause is preferably made at a temperature of 40 to 60 °C for a time of about 50 to 150 minutes. Typical water soluble salts include alkali metal, alkali earth metal and ammonium iodide and bromide such as ammonium, potassium, lithium, sodium, cadmium and strontium iodides and bromides. The amount of said water soluble iodide and bromide salts is advantageously in a range of from 50 to 5,000 mg per mole of silver, and preferably from 100 to 1,000 mg per mole of silver.

The fine grain low iodide silver bromiodide substantially light-insensitive emulsions of the present invention can be prepared by any of well-known procedures. Very fine grain emulsions known in the art as "Lippmann" emulsions are useful herein. According to a preferred procedure these emulsions can be formed by a double jet precipitation process wherein water soluble bromide and iodide salt are added concurrently with water soluble silver salt to a reaction vessel containing a dispersing medium.

The dispersing medium for said silver bromiodide grains can be chosen among those conventionally employed in the silver halide emulsions. Preferred dispersion media include hydrophilic colloids, such as proteins, protein derivatives, cellulose derivatives (e.g. cellulose esters), gelatin (e.g. acid or alkali treated gelatin), gelatin derivatives (e.g. acetylated gelatin, phthalated gelatin and the like), polysaccharides (e.g. dextran), gum arabic, casein and the like. It is also common to employ said hydrophilic colloids in combination with synthetic polymeric binders and peptizers such as acrylamide and methacrylamide polymers, polymers of alkyl and sulfoalkyl acrylates and methacrylates, polyvinyl alcohol and its derivatives, polyvinyl lactams, polyamides, polyamines, polyvinyl acetates, and the like. At the end of grain precipitation, water soluble salts are removed from the emulsion with procedures known in the art, such as ultra-filtration. Such substantially light-insensitive silver bromiodide grains are not chemically sensitized nor substantially physically ripened.

According to another aspect, the present invention refers to a silver halide light-sensitive element to be associated with X-ray intensifying screens and used in radiography.

Said light-sensitive silver halide element for use in radiography with X-ray intensifying screens according to the present invention comprises a transparent support base having coated on at least one of its sides, preferably on both of its sides, a spectrally sensitized silver halide emulsion layer and, between the support base and the silver halide emulsion layer, a hydrophilic colloid layer containing substantially light-insensitive silver halide grains on which a spectral sensitizing dye is adsorbed, said dye adsorbed on

said grains having the absorption in a region of the electromagnetic spectrum corresponding substantially to the spectral sensitivity of the silver halide emulsion, wherein said substantially light-insensitive silver halide grains are low iodide silver bromiodide grains having an average grain size in the range of from 0.01 to 0.1 μm adsorbed with said spectral sensitizing dye to form a J-band as hereinbefore described.

5 The light-sensitive element comprises a polymeric base of the type commonly used in radiography, for instance a polyester base, in particular a polyethylene terephthalate base.

On at least one surface, preferably on both surfaces of the base there is coated a silver halide emulsion layer in a hydrophilic colloid. The emulsions coated on the two surfaces may also be different and comprise emulsions commonly used in photographic elements, such as silver chloride, silver iodide, silver chloro-
10 bromide, silver chloro-bromo-iodide, silver bromide and silver bromo-iodide emulsions, the silver bromo-iodide emulsions being particularly useful for the X-ray elements. The silver halide crystals may have different shapes, for instance cubic, octahedral, spherical, tabular shapes, and may have epitaxial growth; they generally have mean sizes ranging from 0.2 to 3 micron, more preferably from 0.4 to 1.5 micron. The emulsions are coated on the base at a total silver coverage comprised in the range from about 3 to 6 grams
15 per square meter. The silver halide binding material used is a water-permeable hydrophilic colloid, which is preferably gelatin, but other hydrophilic colloids, such as gelatin derivatives, albumin, polyvinyl alcohol, alginates, cellulose hydrolized esters, hydrophilic polyvinyl polymers, dextrans, polyacrylamides, acrylamide hydrophilic copolymers and alkylacrylates can also be used alone or in combination with gelatin.

The light-sensitive element according to the present invention is associated with the intensifying
20 screens so as to be exposed to the radiations emitted by said screens. The screens are made of relatively thick phosphor layers which transform the x-rays into light radiation (e. g., visible light). The screens absorb a portion of x-rays much larger than the light-sensitive element and are used to reduce the radiation doses necessary to obtain a useful image. According to their chemical composition, the phosphors can emit radiations in the blue, green or red region of the visible spectrum and the silver halide emulsions are
25 sensitized to the wavelength region of the light emitted by the screens. Sensitization is performed by using spectral sensitizers as well-known in the art. The x-ray intensifying screens used in the practice of the present invention are phosphor screens well-known in the art. Particularly useful phosphor are the rare earth oxysulfides doped to control the wavelength of the emitted light and their own efficiency. Preferably are lanthanum, gadolinium and lutetium oxysulfides doped with trivalent terbium as described in US patent
30 3,725,704. Among these phosphors, the preferred ones are gadolinium oxysulfides wherein from about 0.005% to about 8% by weight of the gadolinium ions are substituted with trivalent terbium ions, which upon excitation by UV radiations, x-rays, cathodic rays emit in the blue-green region of the spectrum with a main emission line around 544 nm. The silver halide emulsions are spectrally sensitized to the spectral region of the light emitted by the screens, preferably to a spectral region of an interval comprised within 25
35 nm from the wavelength of maximum emission of the screen, more preferably within 15 nm, and most preferably within 10 nm. Many types and combinations of spectral sensitizers can be used. In a preferred form of the present invention particularly useful spectral sensitizing dyes are those which exhibit an absorption peak (J-band) in their aggregated state. In a preferred form of the present invention, particularly useful spectral sensitizing dyes are those represented by the general formula (I) above. In the most
40 preferred form of the present invention, wherein the phosphors of the screens are the gadolinium oxysulfides doped with trivalent terbium ions which emit light radiation comprised in the blue-green region of the visible spectrum, particularly useful dyes are those represented by formula (II) above and specific examples of dyes which absorb in the spectral region of emission of the gadolinium oxysulfides doped with trivalent terbium ions are those reported hereinabove. Preferably, the spectral sensitizing dye adsorbed on
45 the light-sensitive silver halide grains has the same formula of the spectral sensitizing dye adsorbed on the substantially light-insensitive very fine grain low iodide silver bromiodide grains as hereinbefore described.

The hydrophilic colloid layer containing the substantially light-insensitive very fine grain low iodide silver bromiodide emulsions is a layer coated between the base and the silver halide emulsion layer. It is apparent that in a radiographic element having both surfaces of the support coated with light-sensitive
50 emulsion layers either of the light-insensitive layers according to the present invention employed alone can effectively reduce crossover from both screens. Thus, only one light-insensitive layer is required, although for manufacture convenience double coated radiographic elements most commonly employ identical light-insensitive layers on opposite surfaces of the support. The hydrophilic colloid may be any colloid of the type generally used in the photographic elements as said above for the emulsion layer, the preferred colloid
55 being gelatin. The layer may be either an intermediate auxiliary layer coated between the subbing layer of the base and the emulsion layer or the same subbing layer of the base. As known, in fact, the photographic base is per se hydrophobic and needs a hydrophilic layer, viz. the subbing layer, to assure sufficient adhesion of the light-sensitive hydrophilic layers. The use of the subbing layer, which normally consists of

gelatin, to contain the substantially light-insensitive very fine grain low iodide silver bromoiodide emulsions according to the subject invention has the advantage of eliminating one layer, thus allowing a lower thickness of the photographic material and shorter drying times during the photographic processing. The thickness of the layer containing the substantially light-insensitive very fine grain low iodide silver bromoiodide emulsions according to the present invention is the normal thickness of layers used in the photographic elements as non light-sensitive layers (such as intermediate auxiliary layers or sublayers). Generally, said thickness ranges from 0.05 to 2 micron. Within such a range, as known in the art, a lower thickness, e.g. between 0.05 to 0.5 micron, is used when the layer works as a sublayer and a higher thickness, e.g. between 1 and 2 micron, is used when the layer works as an intermediate auxiliary layer. Besides, as known to the skilled in the art, the coating techniques used to coat the sublayer, i.e. the air knife coating technique, allow thinner layers than the coating techniques used to coat the auxiliary layers, e.g. the extrusion coating technique.

The sharp absorption band (J-band) shown by the spectral sensitizing dye adsorbed on the light-insensitive silver bromoiodide grains of the layer coated between the base and the light-sensitive silver halide emulsion layer according to the present invention has the aim of absorbing the light emitted by the intensifying screens and therefore of avoiding or reducing the cross-over phenomenon. Of course, the higher the optical absorbance of the light-insensitive layer measured at the wavelength corresponding to the main emission peak of the phosphors, the better the image quality of the material, but at the same time the lower the sensitivity. Therefore, the man skilled in the art can choose the J-band absorbance by properly selecting the type and amount of spectral sensitizing dye adsorbed on the light-insensitive silver bromoiodide grains, the amount of water soluble iodide and bromide salts as hereinbefore described as well as the silver coating coverage according to the desired ratio between image quality (crossover) and sensitivity. Particularly useful optical absorbances are in the range from 0.3 to 1.50 read at the wavelength corresponding to the spectral emission maximum of the screens. The crossover reduction attained with the light-insensitive layer according to this invention is preferably at least 10%, more preferably at least 20% and most preferably at least 30% lower than the cross-over which can be obtained without said light-insensitive layer. Within such a range, lower values of absorbance provide X-ray elements having a high sensitivity and good image qualities. Higher values of absorbance provide X-ray materials having a good sensitivity and high image quality. The absorbance above does not consider the possible optical density of the base. As known to the man skilled in the art, this may contain a dye, usually an anthraquinone blue dye as described in US patents 3,488,195 and 3,948,664 and in GB patent 968,244, which can have an absorption in the spectral region of the light emitted by the screens. Since such a dye incorporated in the base which is impermeable to the photographic processing, cannot be decolorized, the quantity used and the absorbance resulting therefrom are very low, the latter being generally in the range from 0.03 to 0.20.

In addition to the capacity of the silver bromoiodide grains described above to reduce crossover, said grains are advantageous in that they can be readily removed (i.e., fixed) in processing with the undeveloped silver halide grains of the light-sensitive silver halide emulsion layer, thus avoiding any residual stain of the image bearing radiographic element.

While the light-insensitive silver bromoiodide emulsions heretofore described may be employed alone for crossover reduction, it is recognized that they can be employed in combination with conventional approaches for crossover reduction, if desired. A variety of approaches have been suggested to reduce crossover, as illustrated by Research Disclosure, Vol. 184, August 1979, Item 18431, Section V, here incorporated by reference.

Preferably, radiographic elements according to this invention having highly desirable image characteristics are those which employ in the light-sensitive silver halide emulsion layer low aspect ratio cubic silver halide grains having J-band spectral sensitizing dyes adsorbed on the surface of said silver halide grains in an amount substantially higher than that amount which substantially optimally sensitizes said grains, as described in European Patent Application 244,718.

Said substantially higher amount means a quantity which is required to obtain, in a double side coated radiographic element, a reduction of the cross-over exposure of at least 5% from the cross-over effect exhibited without such additional amount of dye. In quantitative terms, it generally means about 1.5 times the quantity minimally necessary to optimally sensitize the emulsion.

Said light-sensitive silver halide emulsions comprise a dispersing medium and low aspect ratio cubic silver halide grains. The term "cubic grains" according to the present invention is intended to include substantially cubic grains, that is silver halide grains which are regular cubic grains bounded by crystallographic faces (100), or which may have rounded edges and/or vertices or small faces (111), or may even be nearly spherical when prepared in the presence of soluble iodides or strong ripening agents, such as ammonia. The aspect ratio, that is the ratio of diameter to thickness, of said cubic silver halide grains is

lower than 8:1, preferably lower than 5:1 and most preferably is less than 3:1 and about 1:1. The silver halide grains may be of any required composition for forming a negative silver image, such as silver chloride, silver bromide, silver iodide, silver chloro-bromide, silver bromo-iodide and the like. Particularly good results are obtained with silver bromoiodide grains, preferably silver bromo-iodide grains containing
 5 about 0.1 to 15% moles of iodide ions, more preferably about 0.5 to 10% moles of iodide ions and still preferably silver bromo-iodide grains having average grain sizes in the range from 0.2 to 3 μ , more preferably from 0.4 to 1.5 μ .

Said cubic grain silver halide emulsions can be prepared by conventional methods, such as described in Research Disclosure, Vol. 176, December 1978, Item 17643. According to one preferred procedure, these
 10 emulsions can be prepared by a double jet precipitation process. Into a conventional reaction vessel for silver halide precipitation, equipped with an efficient stirring mechanism, is introduced a dispersing medium. Typically the dispersion medium initially introduced into the reaction vessel is about 10 to 50% by weight, preferably is about 20% by weight, based on the total weight of the dispersion medium present in the silver halide emulsion at the end of grain precipitation, the remaining portion of the dispersion medium being
 15 added after having removed the water soluble salts at the completion of silver halide precipitation. During precipitation, silver and halide salts are added to the reaction vessel by techniques well known in the precipitation of silver halide grains. Typically, an aqueous solution of a soluble silver salt, such as silver nitrate, is introduced into the reaction vessel concurrently with the introduction of the halide salts. A high pH, preferably a pH of about 9 to 11, in the reaction vessel favours the formation of the cubic grains. Said
 20 pH may be maintained during all the precipitation process or during part of said process. Particularly good results are obtained by precipitating about 10 to 30% by weight of the silver halide grains at a low pH, preferably from about 5 to 6, and the remaining silver halide grains at said high pH.

The dispersing medium for the silver halide grains can be chosen among those conventionally employed in the silver halide emulsions. Preferred dispersion media include hydrophilic colloids, such as
 25 proteins, protein derivatives, cellulose derivatives (e.g. cellulose esters), gelatin (e.g. acid or alkali treated gelatin), gelatin derivatives (e.g. acetylated gelatin, phthalated gelatin and the like), polysaccharides (e.g. dextran), gum arabic, casein and the like. It is also common to employ said hydrophilic colloids in combination with synthetic polymeric binders and peptizers such as acrylamide and methacrylamide polymers, polymers of alkyl and sulfoalkyl acrylates and methacrylates, polyvinyl alcohol and its derivatives,
 30 polyvinyl lactams, polyamides, polyamines, polyvinyl acetates, and the like.

The cubic grain silver halide emulsions may be chemically sensitized by any procedure known in the photographic art. The emulsion may be digested with active gelatins or with sulfur-containing compounds such as sodium thiosulfate, allylthiocyanate, allylthiourea, and the like. The silver halide emulsions may be sensitized by means of reductors, e.g. tin compounds as described in GB 789,823, polyamines and small
 35 amounts of noble metal compounds, such as gold, platinum, iridium, ruthenium and rhodium.

The cubic grain silver halide emulsions of the radiographic elements of the present invention are spectrally sensitized. According to the present invention, said spectral sensitizing dyes are employed in an amount substantially higher than that necessary to substantially optimally sensitize the cubic silver halide grains, preferably in an amount from two to eight times said optimum amount, more preferably in an
 40 amount from three to five times said optimum amount. Preferred amounts of spectral sensitizers in the photographic emulsion are in the range from 0.5 to 2 millimoles per mole of silver halide. More preferred quantities range from 0.6 to 1.2 millimoles per mole of silver halide.

It is known in the photographic art that photographic speed obtainable from the silver halide grains increases with the increasing concentration of the sensitizing dye until maximum speed is obtained with an
 45 optimum dye concentration, after that, further increases in dye concentration cause a decrease in the obtainable speed. The optimum amount of dye employed can vary depending upon the specific dye, as well as upon the size and aspect of the grains. Surprisingly, the amount of dye adsorbed on the surface of the low aspect ratio cubic grain silver halide emulsions of the light-sensitive layer can be increased beyond the optimum dye concentration to obtain in combination with the substantially light-insensitive J-band
 50 forming silver bromoiodide grains of the light-insensitive layer the full advantages of this invention, i.e. a reduced light scattering and cross-over exposure without a significant loss in speed.

The J-band sensitization dyes are preferably added to the low aspect ratio cubic grain silver halide emulsions in the presence of a water soluble iodide or bromide salt. The J-band sensitization is increased by the presence of said salts, increasing the strong coloration of the element before processing and
 55 consequently reducing the cross-over of exposing radiations by adding a smaller amount of dye. The residual stain after processing of the radiographic element also is lower. Said salts are more advantageously added to the silver halide emulsion before dye digestion, that is the pause following dye addition; said pause is preferably made at a temperature of 40 to 60°C for a time of about 50 to 150 minutes.

Typical water soluble salts include alkali metal, alkali earth metal and ammonium iodide and bromide such as ammonium, potassium, lithium, sodium, cadmium and strontium iodides and bromides. The amount of said water soluble iodide and bromide salts is advantageously lower than 100 mg per mole of silver, and preferably ranges from about 40 to about 70 mg per mole of silver.

5 Other radiographic elements according to this invention having highly desirable imaging characteristics are those which employ one or more light-sensitive high aspect ratio tabular grain emulsions or intermediate aspect ratio tabular grain emulsions, as disclosed in US Patents 4,425,425 and 4,425,426. Preferred tabular grain emulsions for use in the radiographic elements of this invention are those in which tabular silver halide grains having a thickness of less than 0.5 μm , preferably less than 0.3 μm and optimally less than 0.2 μm ,
10 have an average aspect ratio of greater than 5:1, preferably greater than 8:1 and optimally greater than 12:1 and account for greater than 50 percent, preferably greater than 70 percent and optimally greater than 90 percent of the total projected area of the silver halide grains present in the emulsion. It is specifically contemplated to provide double coated radiographic elements according to this invention in which tabular grain emulsion layers are coated nearer the support than nontabular grain silver halide emulsion layers to
15 reduce crossover, as illustrated in European Patent Application 84,637.

By employing light-sensitive low aspect ratio cubic grain silver halide or tabular grain silver halide emulsion layers as above described, which themselves reduce crossover, in combination with the light-insensitive low iodide silver bromiodide emulsion layer according to this invention, radiographic elements exhibiting extremely low crossover levels can be achieved while also achieving high photographic speed
20 and low residual stain.

The spectral sensitizing dyes can be used in the light-sensitive silver halide emulsion layers of the radiographic elements of this invention in combination among them or with other addenda, such as stabilizers, antifoggants, development modifiers, coating agents, brighteners and antistatic agents, which combination results in a supersensitization (that is, into a spectral sensitization higher than that which could
25 be obtained with any dye or addendum used alone or would result from the additive effect of the dyes and addenda). Mechanisms and compounds responsible for supersensitization are described for example in Photographic Science and Engineering, 18, 418-430, (1974). In particular advantageous results are obtained according to this invention by combining the spectral sensitizing dyes with a supersensitizing amount of a polymeric compound having amino-allylidene-malononitrile moieties, as described in US Pat. No. 4,307,183,
30 such as copolymers of a vinyl addition monomers and 3-diallyl-amino-allylidene-malononitrile monomer.

In addition to the features specifically described above, the photographic elements of this invention, in the light-sensitive silver halide emulsion layers or in other layers, can include additional addenda of conventional nature, such as stabilizers, antifoggants, brighteners, absorbing materials, hardeners, coating aids, plasticizers, lubricants, matting agents, antikinking agents, antistatic agents, and the like, as described
35 in Research Disclosure, Item 17643, December 1978 and in Research Disclosure, Item 18431, August 1979.

Preferred radiographic elements are of the type described in BE Patent 757,815 and in US Patent 3,705,858, i.e. elements wherein at least one light-sensitive silver halide emulsion layer is coated on both surfaces of a transparent support, the total silver coverage per surface unit for both layers being lower than about 6 g/m², preferably than 5 g/m². Such supports are preferably polyester film supports, such as
40 polyethylene terephthalate films. Generally said supports for use in medical radiography are blue tinted. Preferred dyes are anthraquinone dyes, such as those described in US Patents 3,488,195; 3,849,139; 3,918,976; 3,933,502; 3,948,664 and in UK Patents 1,250,983 and 1,372,668.

The exposed radiographic elements can be processed by any of the conventional processing techniques. Such processing techniques are illustrated for example in Research Disclosure, Item 17643, cited
45 above. Roller transport processing is particularly preferred, as illustrated in US Patents 3,025,779; 3,515,556; 3,545,971 and 3,647,459 and in UK Patent 1,269,268. Hardening development can be undertaken, as illustrated in US Patent 3,232,761.

As regards the processes for the silver halide emulsion preparation and the use of particular ingredients in the emulsion and in the light-sensitive element, reference is made to Research Disclosure 18,431
50 published in August 1979, wherein the following chapters are dealt with in deeper details:

IA. Preparation, purification and concentration methods for silver halide emulsions.

IB. Emulsion types.

IC. Crystal chemical sensitization and doping.

II. Stabilizers, antifogging and antifolding agents.

55 IIA. Stabilizers and/or antifoggants.

IIB. Stabilization or emulsions chemically sensitized with gold compounds.

IIC. Stabilization of emulsions containing polyalkylene oxides or plasticizers.

IID. Fog caused by metal contaminants.

- IIE. Stabilization of materials comprising agents to increase the covering power.
- IIF. Antifoggants for dichroic fog.
- IIG. Antifoggants for hardeners and developers comprising hardeners.
- IIH. Additions to minimize desensitization due to folding.
- 5 III. Antifoggants for emulsions coated on polyester bases.
- IIJ. Methods to stabilize emulsions at safety lights.
- IIK. Methods to stabilize x-ray materials used for high temperature. Rapid Access, roller processor transport processing.
- III. Compounds and antistatic layers.
- 10 IV. Protective layers.
- V. Direct positive materials.
- VI. Materials for processing at room light.
- VII. X-ray color materials.
- VIII. Phosphors and intensifying screens.
- 15 IX. Spectral sensitization.
- X. UV-sensitive materials
- XII. Bases

20

EXAMPLE 1

A reaction vessel equipped with a stirrer was charged with 7 L of water containing 70 g of gelatin and 25 4.5 ml of N/10 KBr. At 35° C a solution of 137 g KBr, 3.9 g KI and 23.5 g gelatin in 1.2 L of water and a solution of 200 g AgNO₃ in 1.2 L of water were added in 20 minutes according to conventional double jet techniques to the reaction vessel. The emulsion was washed in the conventional procedure. The silver bromiodide grains exhibited a mean diameter of 0.066 μ m and comprised 2 percent mole of silver iodide. The emulsion was added with KI in an amount of 400 mg/mole of silver and dye A in an amount of 5 g/mole 30 of silver, added with surfactants and hardeners and coated on both sides of a transparent blue tinted polyester support at 0.195 g/m² Ag per side (Film 1A).

Following the procedure described above a film (Film 1B) was prepared using a silver bromiodide emulsion having a mean diameter of 0.16 μ m and 2 percent mole of silver iodide, was prepared.

The following Table 1 reports the measure of J-band made with reference to the spectrophotometric 35 curve of each film in the region of 400 to 700 nm by measuring the absorbance at 549 nm, which corresponds to the dye absorbance J-band peak.

Table 1

40

Film	J-band
1A	0.61
1B	0.45

45

The J-band measurements demonstrate the major intensity of J-band peak with the use of a finer bromiodide emulsion.

50

EXAMPLE 2

Following the procedure described in example 1, the following silver halide (bromide, iodide or bromiodide) emulsions were prepared:

55

Emulsion	I%	mean diameter
2A	0	0.072 μm
2B	100	0.022 μm
2C	2	0.060 μm
2D	2	0.057 μm
2E	10	0.063 μm

Each emulsion was added with dye A in an amount of 5 g/mole of silver, added with surfactants and hardeners and coated on one side of a transparent blue tinted polyester support at 0.4 g/m² Ag.

The following Table 2 reports the measure of J-band peak at 549 nm for each film.

Table 2

Film	Emulsion	J-band
2A	2A	0.40
2B	2B	0.37*
2C	2C	0.72
2D	2D	0.74
2E	2E	0.61

* J-band peak formed at 528 nm.

The J-band measurements demonstrate the major intensity of J-band peak with silver bromoiodide grains.

EXAMPLE 3

Following the procedure described in Example 2, several films were prepared similar to film 2D but using different amounts of dye A.

The following Table 3 reports the measure of J-band peak at 549 nm for each film.

Table 3

Film	Dye A amount	J-band
	g/mole Ag	
3A	2.5	0.53
3B	5.0	0.75
3C	7.5	0.84
3D	10.0	0.89

The J-band measurements demonstrate the increase of the J-band peak intensity obtained by increasing the amount of spectral sensitizing dye.

EXAMPLE 4

A light-sensitive cubic grain silver bromo-iodide gelatin emulsion (having 2.3% mole iodide) was prepared. Said emulsion comprised cubic grains having an average diameter of about 0.7 μm and an average aspect ratio of about 1:1. The emulsion was chemically sensitized with a sulfur compound and a

gold compound, and spectrally sensitized with 0.150 g/mole of silver of the green spectral sensitizing dye B and 208 mg/mole of silver of an (acrylamide-allylidene malononitrile) copolymer containing about 9% w/w of aminoallylidene malononitrile moieties. The emulsion, added with stabilizing and antifogging agents, surface active agents and gelatin hardeners, was coated on both sides of a subbed polyethylene terephthalate support base (blue tinted with an anthraquinone dye and having an optical density in green light of 0.13). The emulsion was coated at 2.35 g/m² silver and 1.9 g/m² gelatin per side. Each emulsion layer was finally covered with a protective gelatin layer at a gelatin coverage of 1.1 g/m². (Film 4A).

A light-insensitive fine grain silver bromo-iodide gelatin emulsion (having 2% iodide mole) was prepared. Said emulsion comprised grains having an average diameter of 0.057 μ m. The emulsion was added with 7.5 g/ mole of silver of the green spectral sensitizing dye A and 400 mg/mole of silver of potassium iodide. The emulsion was coated on both sides of the support base above at 0.1 g/m² silver and 1.25 g/m² gelatin per side. Both surfaces of the film thus obtained were coated with silver halide emulsion layers and protective layers as Film 4A above. (Film 4B).

The light-insensitive fine grain silver bromo-iodide gelatin emulsion of Film 4B above, added with 7.5 g/ mole of silver of the green spectral sensitizing dye A and 400 mg/mole of silver of potassium iodide, was coated on both sides of the support base above at 0.15 g/m² silver and 1.25 g/m² gelatin per side. Both surfaces of the film thus obtained were coated with silver halide emulsion layers and protective layers as Film 4A above. (Film 4C).

The light-insensitive fine grain silver bromo-iodide gelatin emulsion of Film 4B above, added with 7.5 g/ mole of silver of the green spectral sensitizing dye A and 400 mg/mole of silver of potassium iodide, was coated on both sides of the support base above at 0.2 g/m² silver and 1.25 g/m² gelatin per side. Both surfaces of the film thus obtained were coated with silver halide emulsion layers and protective layers as Film 4A above. (Film 4D).

Each film was interposed between two green emitting 3M Trimax™ T8 intensifying screens, then exposed through a laminated aluminium step wedge to X-rays of 300 mA and 80 kV for 0.15 seconds. After the exposure, the films were processed in a 3M Trimatic™ XP 507 roller transport processor. Processing consisted of 3M XAD/2 Developer for 24 seconds at 35° C, followed by fixing in 3M XAF/2 Fixer for 24 seconds at 30° C, washing in tap water for 22 seconds at 35° C and drying for 22 seconds at 35° C.

The sensitometric and image quality results are tabulated in the following table. Percent cross-over has been calculated by using the following equation:

$$\text{Percent Cross-over} = \frac{1}{\text{antilog } (\delta \log E)} \times 100$$

wherein $\delta \log E$ is the difference in sensitivity between the two emulsion layers of the same film when exposed with a single screen (the lower the percent of cross-over, the better the image quality). The measure of J-band was made referring to the spectrophotometric curve of the unexposed film in the region of 400 to 700 nm by measuring the absorbance at 549 nm, which correspond to the dye absorbance J-band peak near to the main emission peak of the phosphor of the screen.

Table 4

Film	Total Ag g/m ²	J-band*	Speed	Percent Crossover
4A	4.7	0	3.03	45
4B	4.9	0.32	2.85	27
4C	5.0	0.54	2.81	23
4D	5.1	0.71	2.79	18
4E**	7.1	0	2.70	19

*) J-band of the double side coated high-insensitive silver bromiodide layers.

**) 3M XUD Film: anticross-over film having an emulsion layer coated on both sides of the support base and a mordanted dye layer between each emulsion layer and the support, the total silver coverage of the film being 7.1 g/m².

EXAMPLE 5

A light-sensitive cubic grain silver bromo-iodide gelatin emulsion (having 2.3% mole iodide) was prepared. Said emulsion comprised cubic grains having an average diameter of about 0.7 μm and an average aspect ratio of about 1:1. The emulsion was chemically sensitized with a sulfur compound and a gold compound, and spectrally sensitized with 0.150 g/mole of silver of the green spectral sensitizing dye B and 208 mg/mole of silver of an (acrylamide-allylidene malononitrile) copolymer containing about 9% w/w of aminoallylidene malononitrile moieties. The emulsion, added with stabilizing and antifogging agents, surface active agents and gelatin hardeners, was coated on both sides of a subbed polyethylene terephthalate support base (blue tinted with an anthraquinone dye and having an optical density in green light of 0.13). The emulsion was coated at 2.23 g/m² silver and 1.9 g/m² gelatin per side. Each emulsion layer was finally covered with a protective gelatin layer at a gelatin coverage of 1.1 g/m². (Film 5A).

A light-insensitive fine grain silver bromo-iodide gelatin emulsion (having 2% mole iodide) was prepared. Said emulsion comprised grains having an average diameter of 0.16 μm . The emulsion was added with 5.0 g/mole of silver of the green spectral sensitizing dye A and 400 mg/mole of silver of potassium iodide. The emulsion was coated on both sides of the support base above at 0.2 g/m² silver and 1.25 g/m² gelatin per side. Both surfaces of the film thus obtained were coated with silver halide emulsion layers and protective layers as Film 5A above. (Film 5B).

A light-insensitive very fine grain silver bromiodide gelatin emulsion (having 2% mole iodide) was prepared. Said emulsion comprised grains having an average diameter of 0.066 μm . The emulsion was added with 5.0 g/mole of silver of the green spectral sensitizing dye A and 400 mg/mole of silver of potassium iodide. The emulsion was coated on both sides of the support base above at 0.2 g/m² silver and 1.25 g/m² gelatin per side. Both surfaces of the film thus obtained were coated with silver halide emulsion layers and protective layers as Film 5A above. (Film 5C).

A cubic grain silver bromo-iodide gelatin emulsion (having 2.3% mole iodide) was prepared. Said emulsion comprised cubic grains having an average diameter of about 0.7 μm and an average aspect ratio of about 1:1. The emulsion was chemically sensitized with a sulfur compound and a gold compound, and spectrally sensitized with 0.750 g/mole of silver of the green spectral sensitizing dye A, 60 mg/mole of silver of potassium iodide and 208 mg/mole of silver of a (acrylamide-allylaminoallylidene malononitrile) copolymer containing about 9% w/w of aminoallylidene malononitrile moieties. The emulsion, added with stabilizing and antifogging agents, surface active agents and gelatin hardeners, was coated on both sides of the subbed polyethylene terephthalate support base (blue-colored with an anthraquinone dye and having an optical density in green light of 0.13). The emulsion was coated at 2.25 g/m² silver and 1.9 g/m² gelatin per side. Each emulsion layer was finally covered with a protective gelatin layer at a gelatin coverage of 1.1 g/m². (Film 5D).

A light-insensitive fine grain silver bromo-iodide gelatin emulsion (having 2% mole iodide) was prepared. Said emulsion comprised grains having an average diameter of 0.16 μm . The emulsion was

added with 5.0 g/mole of silver of the green spectral sensitizing dye A and 400 mg/mole of silver of potassium iodide. The emulsion was coated on both sides of the support base above at 0.2 g/m² silver and 1.25 g/m² gelatin per side. Both surfaces of the film thus obtained were coated with silver halide emulsion layers and protective layers as Film 5D above. (Film 5E).

5 A light-insensitive very fine grain silver bromiodide gelatin emulsion (having 2% mole iodide) was prepared. Said emulsion comprised grains having an average diameter of 0.066 μ m. The emulsion was added with 5.0 g/mole of silver of the green spectral sensitizing dye A and 400 mg/mole of silver of potassium iodide. The emulsion was coated on both sides of the support base above at 0.2 g/m² silver and 1.25 g/m² gelatin per side. Both surfaces of the film thus obtained were coated with silver halide emulsion
10 layers and protective layers as Film 5D above. (Film 5F).

Each film was interposed between two green emitting 3M TrimaxTM T8 intensifying screens, then exposed through a laminated aluminium step wedge to X-rays of 300 mA and 80 kV for 0.15 seconds. After the exposure, the films were processed in a 3M TrimaticTM 507 roller transport processor. Processing consisted of 3M XAD/2 Developer for 24 seconds at 35°C, followed by fixing in 3M XAF/2 Fixer for 24
15 seconds at 30°C, washing in tap water for 22 seconds at 35°C and drying for 22 seconds at 35°C.

The sensitometric and image quality results are tabulated in the following table. Percent cross-over has been calculated by using the following equation:

$$20 \quad \text{Percent Cross-over} = \frac{1}{\text{antilog}(\delta \log E)} \times 100$$

wherein $\delta \log E$ is the difference in sensitivity between the two emulsion layers of the same film when exposed with a single screen (the lower the percent of cross-over, the better the image quality). The
25 measure of J-band was made referring to the spectrophotometric curve of the unexposed film in the region of 400 to 700 nm by measuring the absorbance at 549 nm, which correspond to the dye absorbance J-band peak near to the main emission peak of the phosphor of the screen.

30 Table

Film	J-band*	J-band**	%Cross-over	Speed
A (Comp.)	--	0.98	50.5	3.07
B (Comp.)	0.454	1.33	29.1	2.91
35 C (Inv.)	0.601	1.61	23.3	2.84
D (Comp.)	--	1.26	36.6	3.11
E (Comp.)	0.454	1.68	20.1	3.01
F (Inv.)	0.601	1.95	15.2	3.01
40 G*** (Comp.)	--	1.70	16.2	2.69

* J-band of the underlayer.

** J-band of the total film.

*** 3M XUD Film: an anticross-over film having an emulsion layer coated on both the sides of the support base and a mordanted dye layer between each
45 emulsion layer and the support, the total silver coverage of the film being 7.1 g/m².

50 Claims

1. A light-sensitive silver halide element for use in radiography with X-ray intensifying screens comprising a transparent support base having coated on at least one of its sides a spectrally sensitized silver halide emulsion layer and, between the support base and the silver halide emulsion layer, a
55 hydrophilic colloid layer containing substantially light-insensitive silver halide grains on which a spectral sensitizing dye is adsorbed, said dye adsorbed on said grains having the absorption in a region of the electromagnetic spectrum corresponding substantially to the spectral sensitivity of the silver halide emul-

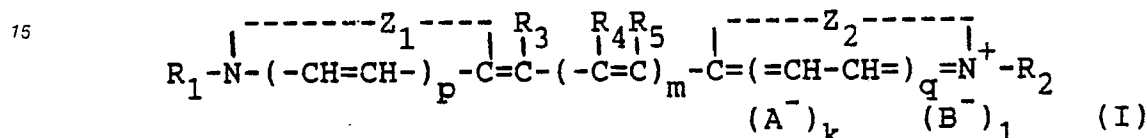
sion, characterized by the fact that said substantially light-insensitive silver halide grains are low iodide silver bromiodide grains having an average grain size in the range of from 0.01 to 0.1 μm adsorbed with said spectral sensitizing dye to form a J-band.

2. The light-sensitive element of claim 1, wherein said spectrally sensitized silver halide emulsion layer is coated on both sides of the transparent support base.

3. The light-sensitive element of claim 1, wherein said spectral sensitizing dye adsorbed on said substantially light-insensitive silver halide grains is a cyanine dye.

4. The light-sensitive element of claim 1, wherein said dye adsorbed on said substantially light-insensitive silver halide grains exhibits a J-band as a function of the adsorption having an absorbance of at least 0.30.

5. The light-sensitive element of claim 1, wherein said dye adsorbed on said substantially light-insensitive silver halide grains is represented by the following general formula (I):



wherein

Z₁ and Z₂, the same or different, each represents the elements necessary to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds,

R₁ and R₂, the same or different, each represents an alkyl group, an aryl group, an alkenyl group, or an aralkyl group,

R₃ represents a hydrogen atom,

R₄ and R₅, the same or different, each represents a hydrogen atom or a lower alkyl group,

p and q are 0 or 1,

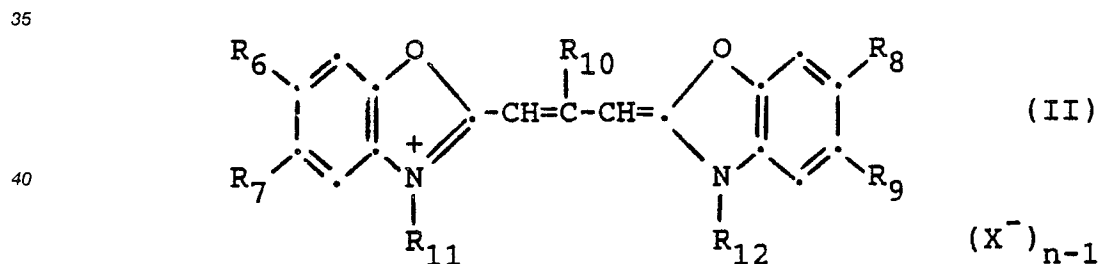
m is 0 or 1,

A is an anionic group,

B is a cationic group, and

k and l may be 0 or 1.

6. The light-sensitive element of claim 1, wherein said dye adsorbed on said substantially light-insensitive silver halide grains is represented by the following general formula (II):



wherein R₁₀ represents a hydrogen atom or a lower alkyl group, R₆, R₇, R₈ and R₉ each represents a hydrogen atom, a halogen atom, a hydroxy group, an alkoxy group, an amino group, an acylamino group, an acyloxy group, an alkoxy carbonyl group, an alkyl group, an alkoxy carbonylamino group or an aryl group, or, together, R₆ and R₇ and, respectively, R₈ and R₉ can be the atoms necessary to complete a benzene ring, R₁₁ and R₁₂ each represents an alkyl group, a hydroxyalkyl group, an acetoxyalkyl group, an alkoxyalkyl group, a carboxyl group containing alkyl group, a sulfo group containing alkyl group, a benzyl group, a phenetyl group or a vinylmethyl group, X⁻ represents an acid anion and n represents 1 or 2.

7. The light-sensitive element of claim 1, wherein said substantially light-insensitive silver halide grains are used in an amount of from 0.05 to 0.5 g/m².

8. The light-sensitive element of claim 1, wherein said dye adsorbed on said substantially light-insensitive silver halide grains is used in an amount of from 25 to 100 percent of monolayer coverage of the surface of said substantially light-insensitive silver halide grains.

9. The light-sensitive element of claim 1, wherein said spectral sensitizing dye adsorbed on said substantially light-insensitive silver halide grains is added to said substantially light-insensitive silver halide grains in reactive association with a water soluble iodide or bromide salt.

10. The light-sensitive element of claim 1, wherein the silver halide emulsion layer is spectrally sensitized to the green light of the visible spectrum.

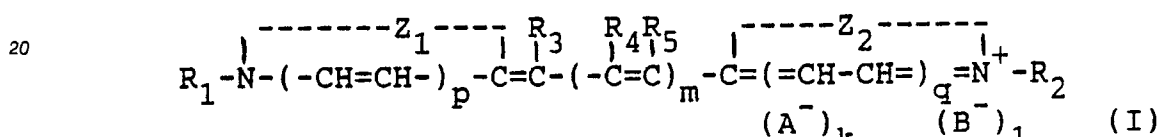
11. The light-sensitive element of claim 1, wherein the silver halide emulsion layer comprises low aspect ratio cubic silver halide grains and a spectral sensitizing dye adsorbed on the surface of said cubic silver halide grains exhibiting a J-band as a function of the adsorption having an absorbance of at least 0.5.

12. The light-sensitive element of claim 11, wherein said spectral sensitizing dye is adsorbed on the
10 surface of said cubic silver halide grains in an amount substantially higher than amount which substantially
optimally sensitizes said cubic grains.

13. The light-sensitive element of claim 11, wherein the silver halide is a silver bromo-iodide having an average grain size in the range from 0.2 to 1.5 μm .

14. The light-sensitive element of claim 11, wherein said J-band spectral sensitizing dye is a cyanine
15 dye.

15. The light-sensitive element of claim 11, wherein said dye adsorbed on said silver halide grains is represented by the following general formula (I):



25 wherein

Z₁ and Z₂, the same or different, each represents the elements necessary to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds,

R₁ and R₂, the same or different, each represents an alkyl group, an aryl group, an alkenyl group, or an aralkyl group,

30 R₃ represents a hydrogen atom,

R₄ and R₅, the same or different, each represents a hydrogen atom or a lower alkyl group,

p and q are 0 or 1,

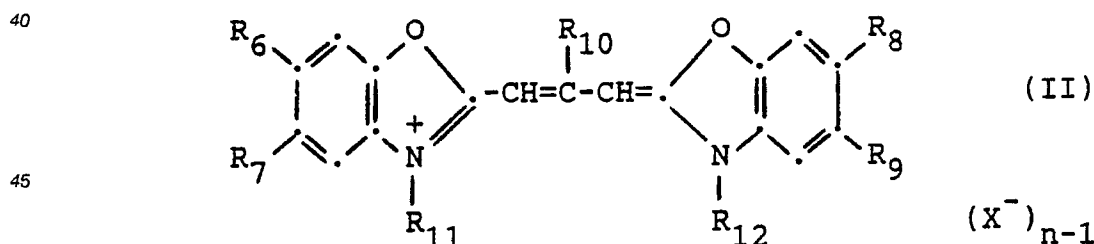
m is 0 or 1,

A is an anionic group.

25 B is a cationic group, and

k and l may be 0 or 1.

16. The light-sensitive element of claim 11, wherein said dye adsorbed on said silver halide grains is represented by the following general formula (II):



wherein R₁₀ represents a hydrogen atom or a lower alkyl group, R₆, R₇, R₈ and R₉ each represents a
50 hydrogen atom, a halogen atom, a hydroxy group, an alkoxy group, an amino group, an acylamino group,
an acyloxy group, an alkoxycarbonyl group, an alkyl group, an alkoxycarbonylamino group or an aryl group,
or, together, R₆ and R₇ and, respectively, R₈ and R₉ can be the atoms necessary to complete a benzene
ring, R₁₁ and R₁₂ each represents an alkyl group, a hydroxyalkyl group, an acetoxyalkyl group, an
alkoxyalkyl group, a carboxyl group containing alkyl group, a sulfo group containing alkyl group, a benzyl
55 group, a phenetyl group or a vinylmethyl group, X⁻ represents an acid anion and n represents 1 or 2.

17. The light-sensitive element of claim 11, wherein said spectral sensitizing dye is adsorbed on the surface of the cubic silver halide grains in an amount of two to eight times the amount sufficient to optimally sensitize said grains.

19. The light-sensitive element of claim 11, wherein said spectral sensitizing dye is added to the cubic silver halide grains in reactive association with a super-sensitizer.

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24. The light-sensitive element of claim 21, wherein said dye adsorbed on the surface of said tabular silver halide grains is represented by the following general formula (I):



Z₁ and Z₂, the same or different, each represents the elements necessary to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds.

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R₄ and R₅, the same or different, each represents a hydrogen atom or a lower alkyl group,

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A is an anionic group, B is a cationic group, and

25. The light-sensitive element of claim 21, wherein said dye adsorbed on silver halide grains is represented by the following general formula (II):

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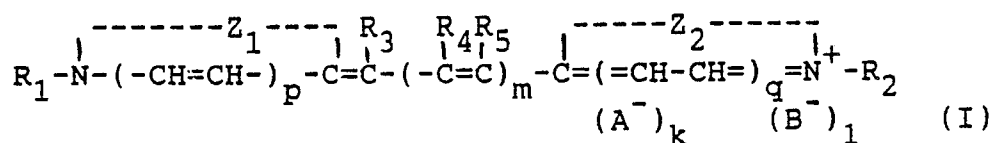
26. The light-sensitive element of claim 21, wherein the dye adsorbed on the surface of said tabular silver halide grains is used in an amount of from 25 to 100 percent of monolayer coverage of the surface of said tabular silver halide grains.

27. The light-sensitive element of claim 21, wherein said silver halide is silver bromide or silver bromoiodide.

28. A substantially light-insensitive silver halide emulsion comprising silver halide grains on which a spectral sensitizing dye is adsorbed, characterized by the fact that said silver halide grains are low iodide silver bromoiodide grains having average grain size of from 0.01 to 0.1 μm adsorbed with said spectral sensitizing dye to form a J-band.

29. The substantially light-insensitive silver halide emulsion of claim 28, wherein said spectral sensitizing dye adsorbed on said substantially light-insensitive silver halide grains is a cyanine dye.

30. The substantially light-insensitive silver halide emulsion of claim 28, wherein said dye adsorbed on said substantially light-insensitive silver halide grains is represented by the following general formula (I):



wherein

Z₁ and Z₂, the same or different, each represents the elements necessary to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds,

R₁ and R₂, the same or different, each represents an alkyl group, an aryl group, an alkenyl group, or an aralkyl group,

R₃ represents a hydrogen atom,

R₄ and R₅, the same or different, each represents a hydrogen atom or a lower alkyl group,

p and q are 0 or 1,

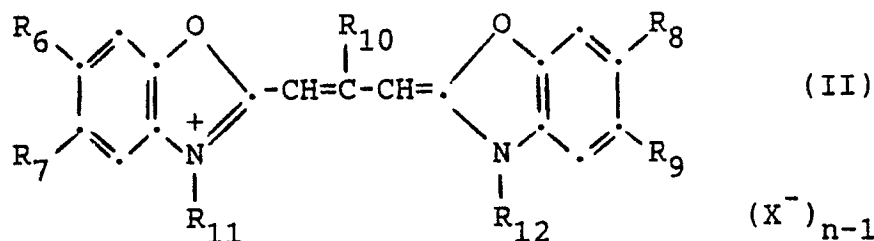
m is 0 or 1,

A is an anionic group,

B is a cationic group, and

k and l may be 0 or 1.

31. The substantially light-insensitive silver halide emulsion of claim 28, wherein said dye adsorbed on said substantially light-insensitive silver halide grains is represented by the following general formula (II):



wherein R₁₀ represents a hydrogen atom or a lower alkyl group, R₆, R₇, R₈ and R₉ each represents a hydrogen atom, a halogen atom, a hydroxy group, an alkoxy group, an amino group, an acylamino group, an acyloxy group, an alkoxy carbonyl group, an alkyl group, an alkoxy carbonylamino group or an aryl group, or, together, R₆ and R₇ and, respectively, R₈ and R₉ can be the atoms necessary to complete a benzene ring, R₁₁ and R₁₂ each represents an alkyl group, a hydroxyalkyl group, an acetoxyalkyl group, an alkoxyalkyl group, a carboxyl group containing alkyl group, a sulfo group containing alkyl group, a benzyl group, a phenetyl group or a vinylmethyl group, X⁻ represents an acid anion and n represents 1 or 2.

32. The substantially light-insensitive silver halide emulsion of claim 28, wherein said dye adsorbed on said substantially light-insensitive silver halide grains is used in an amount of from 25 to 100 percent of monolayer coverage of the surface of said substantially light-insensitive silver halide grains.

33. The substantially light-insensitive silver halide emulsion of claim 28, wherein said spectral sensitizing dye adsorbed on said substantially light-insensitive silver halide grains is added to said substantially light-insensitive silver halide grains in reactive association with a water soluble iodide or bromide salt.

34. A process for forming an X-ray image which includes:

(a) exposing to X-rays through X-ray intensifying screens a spectrally sensitized silver halide element comprising coated on at least one side of a transparent support base at least a spectrally sensitized silver halide emulsion layer and, between the base and a silver halide emulsion layer, a hydrophilic colloid layer
5 containing substantially light-insensitive silver halide grains on which a spectral sensitizing dye is adsorbed, said dye adsorbed on said grains having the absorption in a region of the electromagnetic spectrum corresponding substantially to the spectral sensitivity of the silver halide emulsion,

(b) developing,

(c) fixing with thiosulfate ions, and

10 (d) washing with water,

characterized by the fact that said substantially light-insensitive silver halide grains are low iodide silver bromiodide grains having average grain size in the range of from 0.01 to 0.1 μm adsorbed with said spectral sensitizing dye to form a J-band.

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