Consommation et Corporations Canada | Consumer and Corporate Affairs Canada (21) (A1) 2,018,159
Bureau des brevets | Patent Office (22) 1990/06/04
Ottawa, Canada K1A 0C9 (43) 1990/12/15
(52) 96-194

(51) INTL.CL.[5] G03C-1/46; C03C-1/08; G03C-5/26

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Light-Sensitive Elements for Radiographic Use and Process for the Formation of an X-Ray Image

(72) Bussi, Giuseppe - Italy ;
Cavallo, Elio - Italy ;

(73) Minnesota Mining and Manufacturing Company - U.S.A. ;

(30) (IT) 20883-A/89 1989/06/15

(57) 30 Claims

Notice: The specification contained herein as filed

Light-Sensitive Elements For Radiographic Use And Process For the Formation of an X-Ray Image

ABSTRACT OF DISCLOSURE

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 a) substantially light-insensitive low iodide silver bromoiodide grains having an average grain size in the range of from 0.01 to 0.1 μm on which a spectral sensitizing dye is adsorbed to form a J-band, said dye adsorbed on said grains having a significant portion of its absorption in a region of the electromagnetic spectrum corresponding substantially to the spectral sensitivity of the silver halide emulsion, and b) dispersed zinc oxide particles.

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.

Light-Sensitive Elements For Radiographic Use And Process For the Formation of an X-Ray Image

FIELD OF THE INVENTION

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.

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 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 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 providing significant amplification factors.

The quality of the image obtained upon exposure and development of said radiographic elements is negatively affected by light scattering and crossover exposure. Light scattering occurs both in single and double-side emulsion layer coated radiographic materials. It is caused 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 layer and the support and, the light having been spread by the support, imagewise 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 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 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/or 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 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. That radiographic element comprises a transparent polyester base, 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 in the sensitivity of the light-sensitive element 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, into 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 long-time shelf storage, 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).

Additionally, FR 2,084,669 describes a double-side coated radiographic element comprising between the support and the silver halide emulsion layer, a light absorbing layer comprising dispersed particles of manganese dioxide. GB 2,075,208 describes a silver halide photographic material with improved antistatic properties comprising a support having in one layer thereon electrically conductive metal oxide particles dispersed in a binder, and US 4,574,115 describes a silver halide photographic material comprising a silver halide emulsion layer and a layer containing light-insensitive metal salt grains (such as, for example, silver halide grains or zinc oxide particles) on which a dye is adsorbed, wherein the absorption maximum of said dye is separated by 20 nm or more from the sensitization maximum of said emulsion layer located in a position farther from the light source than the layer containing said dye.

SUMMARY OF THE INVENTION

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 a) substantially light-insensitive low iodide silver bromoiodide grains having an average grain size in the range of from 0.01 to 0.1 µm on which a spectral sensitizing dye is adsorbed to form a J-band, said dye adsorbed on said grains having a significant portion of its absorption in a region of the electromagnetic spectrum corresponding substantially to the spectral sensitivity of the silver halide emulsion, and b) dispersed zinc oxide particles.

The combined action of absorption (from the J-band of the light-insensitive silver bromoiodide grains) and reflection (from the zinc oxide particles) of the light emitted by the X-ray intensifying screens 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, 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 a) substantially light-insensitive low iodide silver bromoiodide grains having an average grain size in the range of from 0.01 to 0.1 µm on which a spectral sensitizing dye is adsorbed to form a J-band, said dye adsorbed on said grains having a significant portion of its absorption in a region of the electromagnetic spectrum corresponding substantially to the spectral sensitivity of the silver halide emulsion, and b) dispersed zinc oxide particles.

The term "low iodide silver bromo-iodide grains" in the present invention means a total percentage of halide in the grains of from 0 mole percent to less than 10 mole percent iodide. Preferably the silver iodide provided by the silver bromoiodide 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 bromoiodide grains are substantially light-insensitive, that is they do not form any image upon conventional exposure (e.g. for an exposure of 10^{-2} seconds) 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 bromoiodide 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 bromoiodide 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 bathocromic 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, <u>Cyanine Dyes and Related Compounds</u>, John Wiley and Sons, 1964, Chapter XVII and by T. H. James, <u>The Theory of the Photographic Process</u>, 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):

$$R_1-\overbrace{N-(-CH=CH-)_p-C}^{Z_1}=\overset{R_3}{C}-(-\overset{R_4}{C}=\overset{R_5}{C})_m-\overbrace{C=(=CH-CH=)_q=N^+}^{Z_2}-R_2 \qquad (A^-)_k \quad (B^+)_l \qquad (I)$$

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 substituetd 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,

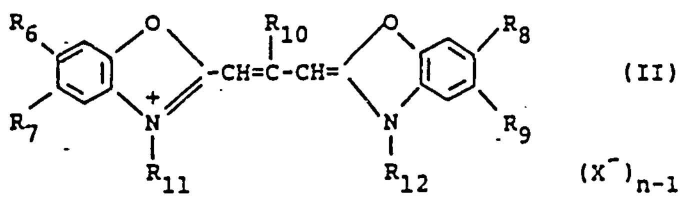
R_4 and R_5 can be the same or different and represent a hydrogen atom or a lower alkyl group of from 1 to 4 carbon atoms,

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 Z_1 and Z_2 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 R_1 and R_3, R_2 and R_5, or R_1 and R_2 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):



(II)

wherein

R_{10} represents a hydrogen atom or a lower alkyl group of from 1 to 4 carbon atoms (e.g. methyl, and ethyl),

R_6, R_7, R_8 and R_9 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, R_6 and R_7 and, respectively, R_8 and R_9 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),

R_{11} and R_{12} 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 vinylmethyl 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 R_6, R_7, R_8, R_9, R_{10}, and R_{11} 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 R_6, R_7, R_8 and R_9 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_2H_5	H	5-Cl	H	5'-Cl	$(CH_2)_3SO_3^-$	$(CH_2)_3SO_3H$	-	1
B**	C_2H_5	H	5-Cl	H	5'-C_6H_5	$(CH_2)_3SO_3^-$	$(CH_2)_2CH(CH_3)SO_3H$	-	1
C	CH_3	H	5-OCH_3	H	5'-OCH_3	C_2H_5	$(CH_2)_3SO_3^-$	-	1
D	C_2H_5	6-CH_3	5-Cl	H	5'-Cl	$(CH_2)_4SO_3$	$(CH_2)_3SO_3H$	-	1
E	C_2H_5	H	5-Cl	H	5'-Cl	C_2H_5	C_2H_5	I	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 bromoiodide, 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 bromoiodide 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 bromoiodide 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 bromoiodide grains can be chosen among those conventionally employed in the silver halide emulsions. Preferred dispersion media include hydrophilic colloids, such as proteins, protein derivatives, celluiose derivatives (e.g. cellulose esters), gelatin (e.g. acid or alkali treated gelatin), gelatin derivatives (e.g. acetylated gelatin, phthalated gelatin and the like), polysaccarides (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 ultrafiltration. Such substantially light-insensitive silver bromiodide grains are not chemically sensitized nor substantially physically ripened.

In the present invention, the hydrophilic colloid layer coated between the support base and the silver halide emulsion layer comprises, in combination with the light-insensitive very fine low iodide silver bromoiodide grains having adsorbed on their surface J-band forming spectral sensitizing dyes, dispersed metal oxide particles. These are preferably metal oxides which are removed during development processing steps (development, fixing, etc.). From the point of view of the dye being removed and decolored during the processing, zinc oxide is particularly preferred. The particle size of the zinc oxide particles used in the present invention is not particularly restricted, but it is generally in the range of from 0.05 to 5 µm (average diameter), preferably from 0.1 to 1 µm. The amount of zinc oxide particles used in the present invention is not particularly limited, but is selected depending upon the desired reflecting action and the desired transparency of the developed radiographic element; it is generally in a range of from 0.1 to 10 g/m^2, and preferably from 0.5 to 3 g/m^2.

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-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 µm, more preferably from 0.4 to 1.5 µm. The emulsions are coated on the base at a total silver coverage comprised in the range from about 3 to 6 grams 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 screens so as to be exposed to the radiations emitted b 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 sensitized to the wavelength region of the light emitted by the screens. Sensitization is performed by using spectral sensitizers 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 phosphors 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 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 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 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 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 bromoiodide grains as hereinbefore described.

The hydrophilic colloid layer containing the substantially light-insensitive very fine grain low iodide silver bromoiodide emulsions and the dispersed zinc oxide particles 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 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 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 and the dispersed zinc oxide particles 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 and the dispersed zinc oxide particles 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 µm. Within such a range, as known in the art, a lower thickness, e.g. between 0.05 to 0.5 µm, is used when the layer works as a sublayer and a higher thickness, e.g. between 1 and 2 µm, is used when the layer works as a 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.

an extrusion coating technique.

The sharp absorption band (J-band) shown by the spectral sensitizing dye adsorbed on the light-insensitive silver bromoioide 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. The presence of the zinc oxide particles has the aim of reflecting the light emitted by the intensifying screens and therefore of avoiding or reducing the decrease of sensitivity of the material. 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 or bromide salts as hereinbefore described as well as the silver coating coverage and the amount of zinc oxide particles according to the desired ratio between image quality (crossover) and sensitivity. Particularly useful optical absorbances are in the range from 0.3 to 2.0, 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 absorbance 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. The base may contain a dye, as previously described.

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 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 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 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 advantagaously 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.

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, 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 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 bromoiodide emulsion layer according to this invention, radiographic elements exhibiting extremely low crossover levels can be achieved while also achieving high photographic speed 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 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-allilydene-malononitrile moieties, as described in US Pat. No. 4,307,183, 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 in Research Disclosuro, 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 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 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 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.

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.

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.
IV. Protective layers.
V. Direct positive materials.
VI. Materials for processing at room light.
VII. X-ray color materials.
VIII. Phosphors and intensifying screens.
IX. Spectral sensitization.
X. UV-sensitive materials
XII. Bases

EXAMPLE 1

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, spectrally sensitized with 0.750 g/mole of silver of the green spectral sensitizing dye A and added with KI in an amount of 60 mg/mole of silver. 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 2.2 g/m² silver and 1.6 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 1A).

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 0.06 µm. The emulsion was added with 5.5 g/ mole of silver of the green spectral sensitizing dye A and 400 mg/mole of silver of potassium iodide. The emulsion was added with a dispersion of fine particles of zinc oxide having a mean diameter of 0.5 µm, prepared by dispersing zinc oxide in gelatin in the presence of anionic dispersing agents with the aid of a high speed stirrer, in an amount such as to have 1,080 g of zinc oxide per mole of silver. The emulsion was coated on both sides of the support base above at 0.1 g/m^2 silver, 1 g/m^2 zinc oxide and 1.5 g/m^2 gelatin per side. Both surfaces of the film thus obtained were coated with silver halide emulsion layers and protective layers as Film 1A above. (Film 1B).

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 measurement of the 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 corresponds to the dye absorbance J-band peak near to the main emission peak of the phosphor of the screen.

Table 1

Film	Total Ag g/m²	J-band*	Speed	Percent Crossover
1A	4.4	1.35	3.09	34
1B	4.6	1.76	3.10	17
1C**	7.1	1.70	2.75	17

*) J-band of the double side coated light-insensitive silver bromoiodide 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 2

A radiographic film (Film 2A) was prepared similar to Film 1A of Example 1 having a total silver coverage of 4.24 g/m².

Radiographic films (Films 2B, 2C and 2D) according to the present invention were prepared similar to Film 1B of Example 1 respectively having a total silver coverage of 4.61 g/m², 0.1 g/m² of light-insensitive silver bromo-iodide grains per side and 0.5 g/m² of zinc oxide per side (Film 2B), a total silver coverage of 4.57 g/m², 0.1 g/m² of light-insensitive silver bromo-iodide grains and 1 g/m² of zinc oxide per side (Film 2C), a total silver coverage of 4.54 g/m², 0.1 g/m² of light-insensitive silver bromo-iodide grains per side and 1.5 g/m² of zinc oxide per side (Film 2D).

Radiographic films (Films 2E, 2F and 2G) according to the present invention were prepared similar to Film 1B of Example 1 respectively having a total silver coverage of 4.80 g/m², 0.2 g/m² of light-insensitive silver bromo-iodide grains per side and 0.5 g/m² of zinc oxide per side (Film 2E), a total silver coverage of 4.76 g/m², 0.2 g/m² of light-insensitive silver bromo-iodide grains per side and 1 g/m² of zinc oxide per side (Film 2F), a total silver coverage of 4.7 g/m², 0.2 g/m² of light-insensitive silver bromo-iodide grains per side and 1.5 g/m² of zinc oxide per side (Film 2G).

Radiographic films (Films 2H and 2I) were prepared similar to Film 1B of Example 1 respectively having a total silver coverage of 4.59 g/m², 0.1 g/m² of light-insensitive silver bromo-iodide grains per side and no zinc oxide (Film 2H), a total silver coverage of 4.85 g/m², 0.2 g/m² of light-insensitive silver bromo-iodide grains per side and no zinc oxide (Film 2I).

Radiographic films (Films 2L, 2M and 2N) were prepared similar to Film 1B of Example 1 respectively having a total silver coverage of 4.38 g/m², 0.5 g/m² of zinc oxide per side and no light-insensitive silver bromo-iodide grains (Film 2L), a total silver coverage of 4.33 g/m², 1 g/m² of zinc oxide per side and no light-insensitive silver bromo-iodide grains (Film 2M), a total silver coverage of 4.33 g/m², 1.5 g/m² of zinc oxide per side and no light-insensitive silver bromo-iodide grains (Film 2N).

Samples of the films above, after storage at 50°C for 15 hours, were exposed and processed as described in Example 1.

The following Table reports the results of speed and percent crossover.

Table 2

Film	Total Ag (g/m²)	Speed	Percent Crossover
2A	4.24	2.59	39
2B	4.61	2.62	21
2C	4.57	2.62	20
2D	4.54	2.68	17
2E	4.80	2.53	15
2F	4.76	2.57	14
2G	4.71	2.61	13
2H	4.59	2.52	24
2I	4.85	2.49	15
2L	4.38	2.71	33
2M	4.33	2.77	29
2N	4.33	2.78	26

The result show how the radiographic films of the present invention offer advantages in cross-over reduction without loss of sensitivity.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

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 hydrophilic colloid layer containing a) substantially light-insensitive low iodide silver bromoiodide grains having an average grain size in the range of from 0.01 to 0.1 µm on which a spectral sensitizing dye is adsorbed to form a J-band, 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, and b) dispersed zinc oxide particles.

2. The light-sensitive element of claim 1, wherein spectrally sensitized silver halide emulsion layers are 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):

$$R_1-\overbrace{N-(-CH=CH-)_p-C}^{Z_1}=\overset{R_3}{\overset{|}{C}}-(-\overset{R_4}{\overset{|}{C}}=\overset{R_5}{\overset{|}{C}})_m-\overbrace{C=(=CH-CH=)_q=N^+}^{Z_2}-R_2 \quad (A^-)_k \cdot (B^+)_l \qquad (I)$$

wherein

Z_1 and Z_2, the same or different, each represents the elements necessary to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds,

R_1 and R_2, the same or different, each represents an alkyl group, an aryl group, an alkenyl group, or an aralkyl group,

R_3 represents a hydrogen atom,

R_4 and R_5, the same or different, each represents a hydrogen atom or a lower alkyl group,

p and q are 0 or 1,

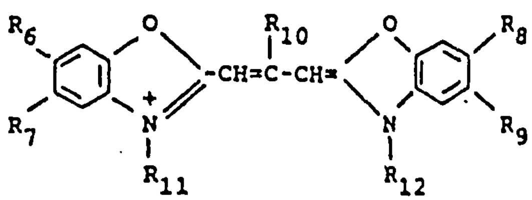
m is C or 1,

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):



(II)

$(X^-)_{n-1}$

wherein R_{10} represents a hydrogen atom or a lower alkyl group, R_6, R_7, R_8 and R_9 each represents a 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, R_6 and R_7 and, respectively, R_8 and R_9 can be the atoms necessary to complete a benzene ring, R_{11} and R_{12} 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 bromoiode grains are used in an amount of from 0.05 to 1.0 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 said zinc oxide particles have a particle size of from 0.1 to 1 µm.

11. The light-sensitive element of claim 1, wherein said zinc oxide particles are used in an amount of from 0.5 to 3 g/m².

12. The light-sensitive element of claim 1, wherein

the silver halide emulsion layer is spectrally sensitized to the green light of the visible spectrum.

13. 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.

14. The light-sensitive element of claim 13, wherein said spectral sensitizing dye is adsorbed on the surface of said cubic silver halide grains in an amount substantially higher than the amount which substantially optimally sensitizes said cubic grains.

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

16. The light-sensitive element of claim 13, wherein said J-band spectral sensitizing dye is a cyanine dye.

17. The light-sensitive element of claim 13, wherein said dye adsorbed on said silver halide grains is represented by the following general formula (I):

$$R_1-\overbrace{N-(-CH=CH-)_p-C}^{Z_1}=\overset{R_3}{C}-(-\overset{R_4}{C}=\overset{R_5}{C})_m-\overbrace{C=(=CH-CH=)_q=N^{+}}^{Z_2}-R_2 \quad (A^-)_k \quad (B^+)_l \qquad (I)$$

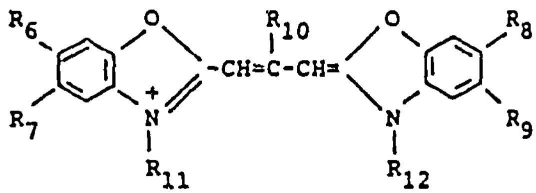
wherein

Z_1 and Z_2, the same or different, each represents the elements necessary to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds,

R_1 and R_2, the same or different, each represents an alkyl group, an aryl group, an alkenyl group, or an aralkyl

group,
R_3 represents a hydrogen atom,
R_4 and R_5, 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.

18. The light-sensitive element of claim 13, wherein said dye adsorbed on said silver halide grains is represented by the following general formula (II):



(II)

$(X^-)_{n-1}$

wherein R_{10} represents a hydrogen atom or a lower alkyl group, R_6, R_7, R_8 and R_9 each represents a 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, R_6 and R_7 and, respectively, R_8 and R_9 can be the atoms necessary to complete a benzene ring, R_{11} and R_{12} 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.

19. The light-sensitive element of claim 13, 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.

20. The light-sensitive element of claim 13, wherein said spectral sensitizing dye is added to the cubic silver halide grains in reactive association with a water soluble iodide or bromide salt.

21. The light-sensitive element of claim 13, wherein said spectral sensitizing dye is added to the cubic silver halide grains in reactive association with a supersensitizer.

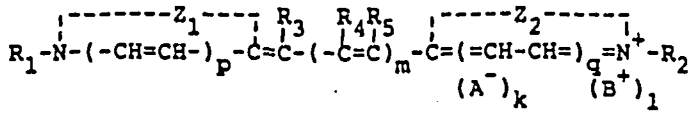
22. The light-sensitive element of claim 13, wherein said spectral sensitizing dye is added to the cubic silver halide grains in reactive association with a supersensitizing amount of a polymeric compound having an amino-allylidene-malononitrile moiety.

23. The light-sensitive element of claim 1, wherein the silver halide emulsion layer comprises tabular silver halide grains having a thickness of less than 0.5 μm and an average aspect ratio of at least 5:1 accounting for at least 35 percent of the total projected area of said silver halide grains present in said silver halide emulsion layer and a spectral sensitizing dye adsorbed on the surface of said tabular silver halide grains.

24. The light-sensitive element of claim 23, wherein said spectral sensitizing dye adsorbed on the surface of said tabular silver halide grains exhibits a J-band as a function of the adsorpticn having an absorbance of at least 0.5.

25. The light-sensitive element of claim 24, wherein said J-band spectral sensitizing dye is a cyanine dye.

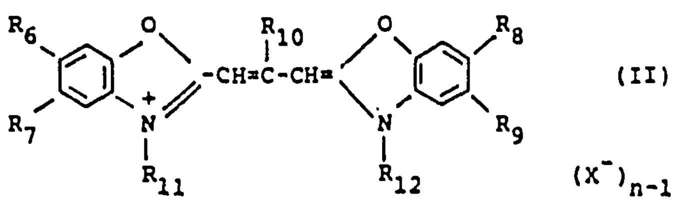
26. The light-sensitive element of claim 23, wherein said dye adsorbed on the surface of said tabular silver halide grains is represented by the following general formula (I):



(I)

wherein
Z_1 and Z_2, the same or different, each represents the elements necessary to complete a cyclic nucleus derived from basic heterocyclic nitrogen compounds,
R_1 and R_2, the same or different, each represents an alkyl group, an aryl group, an alkenyl group, or an aralkyl group,
R_3 represents a hydrogen atom,
R_4 and R_5, 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.

27. The light-sensitive element of claim 23, wherein said dye adsorbed on the surface of said tabular silver halide grains is represented by the following general formula (II):



(II)

wherein R_{10} represents a hydrogen atom or a lower alkyl group, R_6, R_7, R_8 and R_9 each represents a 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, R_6 and R_7 and, respectively, R_8 and R_9 can be the atoms necessary to complete a benzene ring, R_{11} and R_{12} 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.

28. The light-sensitive element of claim 23, 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.

29. The light-sensitive element of claim 23, wherein said silver halide is silver bromide or silver bromo-iodide.

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

(1) 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 containing a) substantially light-insensitive silver bromo-iodide grains, having average grain size in the range from 0.01 to 0.1 µm, on which a spectral sensitizing dye is adsorbed to form a J-band, 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 and b) dispersed zinc oxide particles,

(2) developing,

(3) fixing with thiosulfate ions, and

(4) washing with water.