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3,671,254

RADIOGRAPHIC ELEMENTS, COMPOUNDS AND PROCESSES

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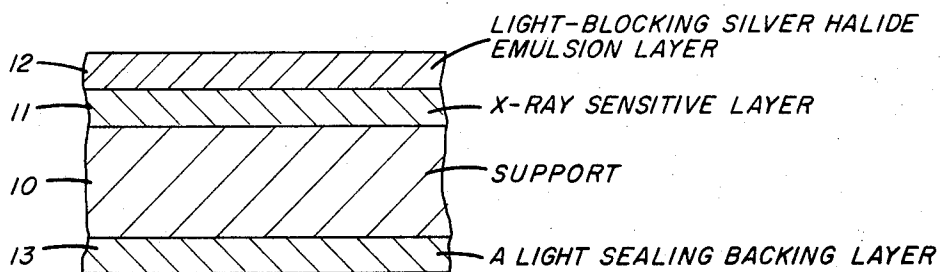


FIG. 1

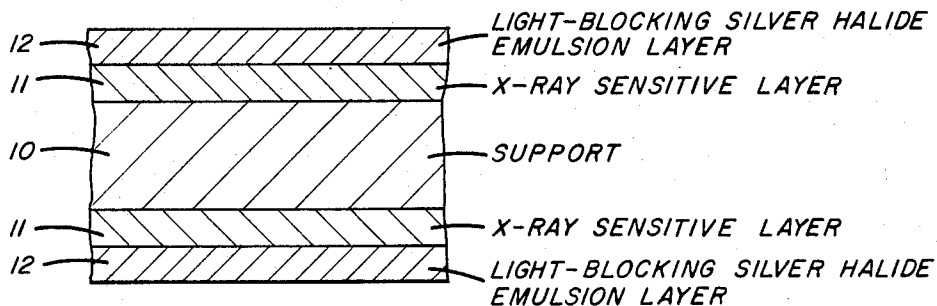


FIG. 2

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3,671,254

RADIOGRAPHIC ELEMENTS, COMPOUNDS AND PROCESSES

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23 Claims

ABSTRACT OF THE DISCLOSURE

A roomlight handling radiographic element or emulsion wherein the light-sensitive layer or layers thereof are protected from exposure to visible light; said element or emulsion comprising an X-ray-sensitive silver halide layer comprising a silver halide desensitizing compound such as a nitrothiazolinothiacyanine and a yellow dye, and coated upon said X-ray-sensitive layers a light-absorbing silver halide layer comprising a nitrogen-containing heterocyclic silver halide desensitizing compound and a yellow dye such as a phenylazopyrazol-5-one yellow dye. Processes for obtaining a radiographic image employing the roomlight handling radiographic elements and emulsions are disclosed.

Electromagnetic radiation-sensitive silver halide desensitized with a nitrothiazolinothiacyanine or containing a phenylazopyrazol-5-one yellow dye.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photographic elements and emulsions which are protected from visible light. In one aspect, this invention relates to photographic elements and emulsions which are desensitized toward visible light. In another aspect, this invention relates to photographic elements and emulsions containing a light-absorbing yellow dye. In another aspect, this invention relates to radiographic emulsions and elements which are highly suitable for handling and processing under conditions of ordinary roomlight illumination without exposure of the photosensitive layers thereof. In still another aspect, this invention relates to new yellow dyes capable of absorbing radiation of the visible spectrum. In yet another aspect, this invention relates to new desensitizing compounds capable of strongly depressing the light-sensitivity of silver halide without appreciably affecting its X-ray sensitivity. In still another aspect, this invention relates to the radiographic elements comprising an X-ray-sensitive silver halide layer and a light-absorbing silver halide layer, said element incorporating the new yellow dyes and the new silver halide desensitizers.

Description of the prior art

There have been various methods proposed in the art for protecting the light-sensitive layer or layers of photographic elements used in obtaining X-ray photographs. Certain of these photographic elements have been provided with an opaque protecting medium which is removed after exposing in a special processing bath. Such protective layers have not been entirely satisfactory because the layers are difficult to remove after exposure to X-rays and light-absorbing material is not always uniformly distributed throughout the medium. Other radiographic elements have been prepared using protective outer-layers, comprising a coating of chrome-yellow, Venetian red, and the like which forms a readily removable opaque protecting medium. This coating allows han-

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dling of the element in ordinary roomlight but is washed off prior to development so that development must of necessity be carried out in a darkroom. With any of the prior proposals for protecting the light-sensitive layer using an outer-protective opaque layer, there has also been the difficulty that these protective layers do not cover the edges of the film, and accordingly, light enters the film through these edges to produce edge-fog in the light-sensitive emulsion layer. To overcome this difficulty, it has been proposed to optically seal the edges of the film by applying a black colloid edge-coating or a sealing strip of opaque paper or fabric. It is apparent that the prior art has been unable to deduce a method for preparing a truly satisfactory roomlight handling photographic element. To meet the requirements of such an element, it should be stable to visible light exposure but have substantially unchanged sensitivity to X-ray radiation. The element should also be stable against edge-fog without requiring special treatment or expensive extra handling of separate film sheets to employ special optical sealers, light-blocking cassettes, etc. The roomlight handling elements should also be adapted to processing in conventional processing solutions without loss of optimum quality in the final result.

In U.S. Pat. 3,237,008 to Dostes and Pfaff issued Feb. 22, 1966, it is shown how to prepare a roomlight handling radiographic element which meets each of the above requirements while at the same time permits the operator to watch the complete development process under ordinary roomlight. The Dostes and Pfaff invention is accomplished by providing a radiographic element which comprises at least one X-ray-sensitive silver halide layer and coated thereupon a light-absorbing silver halide layer. Incorporated in each of the layers of the roomlight handling radiographic element is a combination of a nitrogen-containing heterocyclic silver halide desensitizing compound capable of depressing the light sensitivity of the silver halide without appreciably affecting the X-ray sensitivity, and a yellow dye which absorbs a substantial portion of the visible radiation to which the silver halide is sensitive, i.e., radiation between 350 and 500 m μ .

The radiographic images prepared from the X-ray elements of Dostes and Pfaff are of excellent quality and show good image discrimination. The silver halide desensitizers are, however, desorbed from the silver halide grains during storage, especially when the temperature rises above normal room temperature, thereby causing a decrease in the desensitization of the silver halide grains to visible radiation. A second problem presented is the lack of uniformity in the decoloration of the X-ray film during processing. Normally the yellow dye used in each layer should be readily removed or decolorized in conventional processing solutions. However, it is found that the decoloration is not necessarily uniform and the decoloration depends in particular upon the temperature of the processing baths. In any event the processing solutions are contaminated by the yellow dyes and hence the processing lifetime of the developing solutions are thereby greatly shortened. It should be apparent that the art would greatly benefit if a desensitizer were found which remains adsorbed on the silver halide grains during storage thereby preventing the decrease in the desensitization of the silver halide grains to the visible light and allowing for greater storage life of photographic elements and if a yellow dye were known which does not dissolve in the processing baths, thereby not contaminating the processing solutions, and yet allow for processed radiographic elements to be clearly and unequivocally observable.

SUMMARY OF THE INVENTION

In accordance with this invention, there are provided novel photographic silver halide emulsions desensitized to

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visible electromagnetic radiations. There is provided further, photographic silver halide emulsions containing a novel light-absorbing yellow dye.

In a preferred embodiment of this invention, there are provided novel roomlight handling radiographic elements which do not show an increase in sensitivity to visible radiation during storage or increase in temperature, and which do not contaminate the processing baths during development but remain permanently and uniformly colored thereby allowing clear observation of the radiographic image. The improvements of the present invention are obtained by incorporating in an outer emulsion light-absorbing layer and in the inner-most light sensitive, X-ray sensitive emulsion layer a yellow dye which does not dissolve in the processing baths, and by incorporating in said inner emulsion layer a new desensitizer against visible light.

It is therefore an object of the present invention to provide a new yellow dye which will not dissolve in photographic processing solutions. A further object is to provide new silver halide desensitizing compounds. A further object is to provide a new silver halide desensitizing compound which is capable of strongly depressing the light sensitivity of silver halide without appreciably affecting the X-ray sensitivity of the silver halide grains. It is yet a further object to provide useful silver halide desensitizing compounds which strongly adhere to the silver halide grains. A still further object of the present invention is to provide a photographic element for X-rays which can be handled under conditions of ordinary roomlight illumination. Still a further object is to provide roomlight handling radiographic elements which are stable against edge-fog. A still further object is to provide radiographic elements which upon exposure can be processed in roomlight using conventional processing solutions. Another object is to provide roomlight handling radiographic elements which have light-absorbing outer protective layers which permit observation of image development under ordinary roomlight conditions. Another and still further object is to provide radiographic elements whose sensitivity to light does not increase during its shelf life. Other objects of this invention will become obvious to those skilled in the art from that which appears hereafter.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

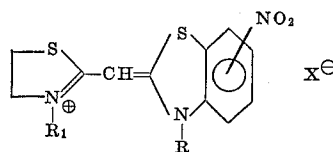
According to the present invention, it has been found that photographic emulsions comprising a hydrophilic colloid and electromagnetic radiation-sensitive silver halide layer can be strongly desensitized to visible radiations by incorporating a new silver halide desensitizer into said emulsion. In another embodiment of the invention, it has been found that light-blocking photographic emulsion and elements which do not contaminate processing solutions can be provided by incorporating a novel light-absorbing yellow dye in said emulsion. In another embodiment of this invention, it has been found that without modifying the structure of the radiographic element as disclosed in the aforementioned Dostes et al. patent, a superior product can be obtained by incorporating a new silver halide desensitizer and a new filter dye into a radiographic element comprising an outer light-absorbing layer and an inner light-sensitive, X-ray-sensitive emulsion layer. The new desensitizing compound is capable of greatly depressing the light sensitivity of the silver halide without appreciably affecting the X-ray sensitivity of said silver halide. Among the unexpected and unobvious properties of the new desensitizer is the fact that the new desensitizer remains adsorbed on the silver halide grains thereby ensuring a longer shelf life and a greater stability as compared with the prior art roomlight handling elements. The added stability of the roomlight-handling radiographic element is accomplished without affecting the removability of the desensitized silver halide grains from the layers of the radiographic elements in conventional processing baths. The

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new desensitizer is used only in the inner X-ray sensitive layers, whereas the desensitizers of the aforementioned Dostes et al. patent are employed in the overcoat in view of their ability to migrate rapidly into the baths during the processing operation. The yellow dye, which functions as a filter which absorbs visible light, is not readily removed from the emulsion layers. Upon processing the element, one obtains a radiogram having a black image upon a uniform yellow background.

By reference to the accompanying drawing, there can be seen the manner in which the roomlight handling radiographic elements of the invention can be prepared. FIG. 1 shows a sectional view of a photographic element having a light-sealing backing layer, whereas FIG. 2 shows an element which has an X-ray sensitive layer and a light-absorbing layer on each side of the single support.

The new desensitizing compounds which are employed in the practice of the invention are 3-alkyl-3'-alkyl nitrothiazolinothiacyanine halides. Suitable compounds can be represented by the structure

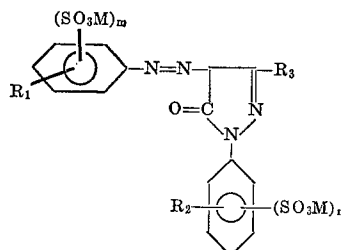


wherein X is halide such as chloride, bromine, or iodine and R_1 and R each are an alkyl group, for example, methyl, ethyl, propyl, butyl and the like. Examples of preferred nitrothiazolinothiacyanines are:

- 3-methyl-3'-methyl-6'-nitrothiazolinothiacyanine iodide
- 3-ethyl-3'-ethyl-6'-nitrothiazolinothiacyanine iodide
- 3-ethyl-3'-methyl-6'-nitrothiazolinothiacyanine iodide
- 3-butyl-3'-butyl-6'-nitrothiazolinothiacyanine chloride
- 3-ethyl-3'-ethyl-5'-nitrothiazolinothiacyanine iodide
- 3-ethyl-3'-methyl-5'-nitrothiazolinothiacyanine chloride
- 3-methyl-3'-methyl-6'-nitrothiazolinothiacyanine iodide and
- 3-butyl-3'-butyl-5'-nitrothiazolinothiacyanine chloride.

The new desensitizers of the present invention are conveniently prepared by methods referred to in, "The Cyanine Dyes and Related Compounds" by F. M. Hamer, Interscience Publishers, New York 1964, page 728. The preparation of 3-ethyl-3'-methyl-6'-nitrothiazolinothiacyanine is, for example, readily accomplished by reacting the methyl sulfate of 2-methylmercapto-3-methyl-6-nitrobenzothiazolium with the 2-methylthiazolinium ethyl paratoluene sulfonate.

The new yellow dyes which are employed in the practice of the invention are sulfophenyl phenylazopyrazol-5-ones having the structure:



wherein each of R_1 and R_2 is hydrogen, an alkyl group, such as methyl, butyl, amyl, hexyl and the like or alkoxy group such as methoxy, butoxy, amyloxy, hexoxy and the like, at least one of R_1 or R_2 is an alkyl or alkoxy

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group; R_3 is an alkyl or alkoxy group such as methyl, ethyl, propyl, butyl, and the like or methoxy, ethoxy, propoxy and the like; M is hydrogen, an alkali metal such as K, Na and the like, ammonium or substituted ammonium; and m and n are each equal to zero or one, at least one of m or n being equal to one. Illustrative of preferred filter-dyes which may be used in this invention are those wherein R_1 and R_2 can each be hydrogen or have from 4 to about 12 carbon atoms, at least one of R_1 and R_2 having from 4 to about 12 carbon atoms; R_3 has 1 to 4 carbon atoms, and R_1 , R_2 and $-\text{SO}_3\text{M}$ are in the ortho or para position. Another preferred group of filter-dyes are those wherein each of R_1 and R_2 are hydrogen or an alkyl or alkoxy group having from 4 to 6 carbon atoms, at least one of R_1 and R_2 being alkyl or alkoxy. Another preferred group of filter-dyes are those wherein each of R_1 and R_2 are hydrogen or have 5 or 6 carbon atoms at least one of R_1 or R_2 being an alkyl or alkoxy group. Still another preferred group of filter-dyes are those wherein R_1 is an alkoxy group of 5 or 6 carbon atoms, R_2 is hydrogen, m is equal to zero and R_1 and $-\text{SO}_3\text{M}$ are in the para position. Illustrative of the compounds useful in this invention are:

1-p-sulfophenyl-3-methyl-4-p-i-amyloxyphenyl-azopyrazol-5-one, sodium salt

1-p-sulfophenyl-3-methyl-4-p-n-amyloxyphenyl-azopyrazol-5-one, sodium salt

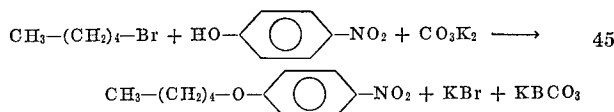
1-p-sulfophenyl-3-methyl-4-p-n-hexoxyphenyl-azopyrazol-5-one, sodium salt

1-p-sulfophenyl-3-methyl-4-p-n-butoxyphenyl-azopyrazol-5-one, sodium salt

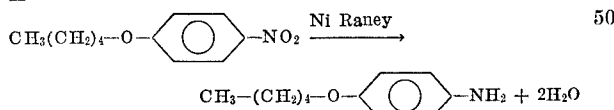
1-p-sulfophenyl-3-propyl-4-o-n-butylphenyl-azopyrazol-5-one, ammonium salt

The filter dyes are conveniently prepared by a three-step reaction, for example, the sodium salt of 1-p-sulfophenyl-3-methyl-4-p-n-amyloxyphenylazopyrazolone-5 is obtained according to the following equation:

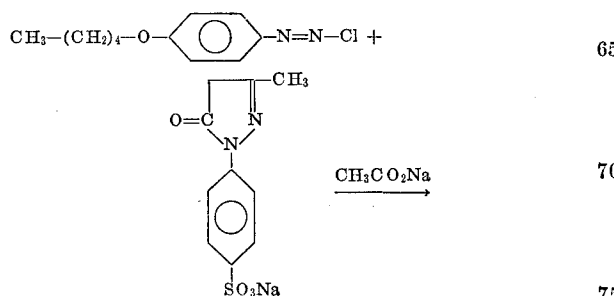
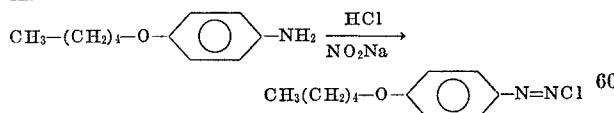
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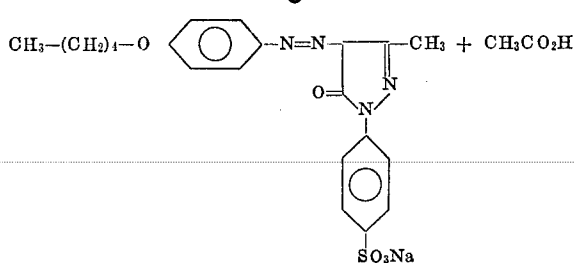
II



III

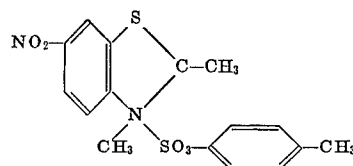


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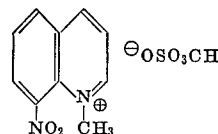


The visible-light absorbing dyes which are used with the desensitizing compounds in the silver halide layers should advantageously be dyes which are stable in a colloid carrier and should advantageously be nondiffusing. Suitable dyes should also be highly absorbent in regions of the spectrum to which the silver halide is sensitive, i.e. 350-500 $m\mu$, but should transmit the remainder of the visible spectrum freely so that it is possible to observe the progress of development under ordinary room-light. The most useful dyes are soluble in photographic gelatin and insoluble in the processing solutions.

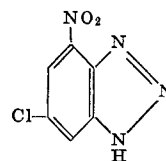
According to the invention, the new desensitizers when employed in roomlight handling radiographic elements, are incorporated only in the innermost X-ray-sensitive silver halide layer or layers. In the outer light-absorbing layers, there is employed nitrogen-containing heterocyclic desensitizers of U.S. Pat. 3,237,008. The compounds which are useful in the practice of the invention are represented by the following structural formula:



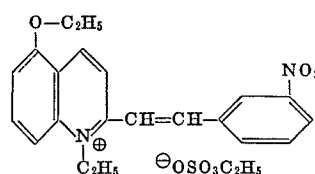
2-methyl-5-nitrobenzothiazole metho-p-toluenesulfonate



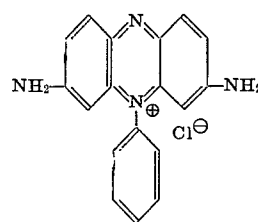
1-methyl-8-nitroquinolinium methosulfate



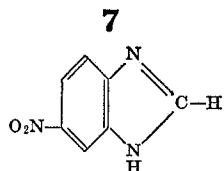
4-nitro-6-chlorobenzotriazole



6-ethoxy-2-(m-nitrostyryl) quinolinium ethethosulfate



3,7-diamino-5-phenyl-phenazinium chloride



5-nitrobenzimidazole

Additional useful nitrogen-containing heterocycles representative of the above classes comprise the following:

- 2-(o-nitrostyryl)-3-ethylbenzothiazolium iodide,
- 2-(o,p-dinitrostyryl)-benzothiazole,
- 6-nitro-benzo-1,2,3-triazole,
- 4-chloro-benzo-1,2,3-triazole,
- 5-chloro-benzo-1,2,3-triazole,
- 2-methyl-6-nitrobenzothiazole metho-p-toluene sulfonate,
- 2-(p-nitrostyryl)-quinoline metho-p-toluenesulfonate,
- 4-(p-nitrostyryl)-quinoline methiodide,
- 1-ethyl-7-nitro-quinolinium ethylsulfate,
- 1,3-diamino-5-methylphenazinium chloride,
- 1,3-diamino-5-benzylphenazinium chloride,
- 3,7-diamino-5-β-hydroxy-ethylphenazinium chloride,
- 5-chlorobenzimidazole,
- 2-methyl-5-chlorobenzimidazole,
- 2-mercaptobenzimidazole,
- 2-mercapto-6-chlorobenzimidazole.

The desensitizing compounds of the above type which can be advantageously employed in the practicing of our invention have been described in one or more of the following representative U.S. patents: 2,400,872 issued May 28, 1946; 2,541,472 issued Feb. 13, 1951; 2,939,789 issued June 7, 1960; 2,915,395 issued Dec. 1, 1959; and 2,066,099 issued Dec. 29, 1936.

In accordance with this invention the new desensitizing compounds can be employed in the inner-most layer, which is X-ray sensitive and also light sensitive, at a concentration in the order of from about 20 mg. to 500 mg. per mole of silver halide. At the higher concentrations, the silver halides of the X-ray-sensitive layer are desensitized not only to visible light but in part also to X-rays, whereas at the lower concentrations, the loss of sensitivity to X-rays is negligible. When employed in non-radiographic elements, the concentration is not limited since there is no concern as to desensitizing X-ray-sensitive silver halides. The light-absorbing dye is added to the gelatin in concentrations in the order from about 0.5 g. to about 100 g. per 150 g. of dry gelatin. The silver concentration in the innermost layer can vary from about 400 mg. to about 1 g. of silver per square foot.

The outer-light-absorbing protective layer normally comprises a silver halide emulsion layer more strongly desensitized than in the inner-most light-sensitive layer. In the outer-most layer, in accordance with the invention, an excess of desensitizing compound is employed in comparison to the concentration of desensitizing compound in the inner-most layer. The concentration of desensitizer in the outer-light-absorbing protective layer can be in the order of from about 20 mg. to 5.0 g. per mole of silver halide or more depending upon the extent of desensitization desired and upon the desensitizing compound employed. The visible light-absorbing dye is added in combination with the desensitizing compound in the emulsion in an amount of from about 0.5 g. to about 100 g. per 150 g. of dry gelatin. In the outer-light-absorbing emulsion layer a suitable concentration of silver per square foot can vary from about 100 to about 900 mg. of silver per square foot.

The outer-light protecting emulsion layer can comprise a silver halide emulsion which forms latent images predominantly inside the silver halide crystal, such as those described in Davy and Knott, U.S. Pat. 2,592,250 issued Apr. 8, 1952. Where emulsions of this type are used

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according to the invention desensitizing compounds of the type herein described are incorporated in an amount in the range from about 25 mg. to about 250 mg. per mole of silver halide. In such emulsion layers the light-absorbing dyes are contained in combination with desensitizing compounds in the range as indicated above for outer-light-absorbing layers.

Silver halide emulsions which form latent images predominantly inside the silver halide crystal are also referred to as internal image emulsions and have been described in Luckey et al., U.S. Pat. 2,996,382 issued on Aug. 15, 1961. The internal image emulsions which are useful according to our invention have little or no surface sensitivity. Such internal image emulsions, when measured according to normal photographic techniques by coating a test portion of the emulsion on a transparent support, exposing to a light-intensity scale having a fixed time between 0.01 and 1 second, bleaching 5 minutes in a 0.3 percent potassium ferricyanide solution at 65° F., and developing for about 5 minutes at 65° F. in developer B below, has a sensitivity, measured at a density of 0.1 above fog, appreciably greater (e.g., at least 1.4 log greater) than the sensitivity of an identical test portion which has been exposed in the same way and developed for 6 minutes at 68° F. in developer A below.

The developer compositions which are used in defining an internal image emulsion by comparison with a conventional surface image emulsion developer, compositions A and B are given hereinafter. Developer A is the usual type of surface image developer and developer B is an internal developer having high silver halide solvent activity.

The following developer compositions are used in the method of determining relative internal sensitivity of preferred emulsions:

(A)

	Grams
N-methyl-p-aminophenol sulfate -----	0.31
Sodium sulfite, desiccated -----	39.6
Hydroquinone -----	6.0
Sodium carbonate, desiccated -----	18.7
Potassium bromide -----	0.86
Citric acid -----	0.68
Potassium metabisulfite -----	1.5
Water to make 1.0 liter.	

(B)

	Grams
N-methyl-p-aminophenol sulfate -----	2.0
Sodium sulfite, desiccated -----	90.0
Hydroquinone -----	8.0
Sodium carbonate, monohydrate -----	52.5
Potassium bromide -----	5.0
Sodium thiosulfate -----	10.0
Water to make 1.0 liter.	

Suitable internal image emulsion are described in Davey and Knott, U.S. Pat. 2,592,250 issued Apr. 8, 1952. Other emulsions which can be used in the outer-most layers of the present invention comprise, for example, relatively insensitive silver chlorobromide and silver bromoiodide emulsions.

The methods of incorporating the desensitizing compounds and visible light-absorbing materials in silver halide emulsions are well known to those skilled in the art. The desensitizing compounds can be directly dispersed in the emulsions, or they can be dissolved in water (or in organic solvents, such as methanol, ethanol, etc., where the water-solubility is not sufficiently great) and added in the form of their solutions. While the visible light-absorbing dyes can be directly dispersed in the emulsions, it is convenient to add the same in the form of solutions in appropriate solvents. Methanol, ethanol, pyridine, and the like have proved satisfactory. Mixtures of solvents, e.g., pyridine diluted with methanol or acetone, can also be used. According to the invention the desensitizing compounds and the visible light-absorbing

dye are dispersed in the finished emulsions and should be uniformly distributed throughout the emulsion. The following procedure is satisfactory:

Stock solutions of the desensitizing compounds and visible light-absorbing dye are prepared by dissolving the same in appropriate solvents as described above. The desired amount of stock solution of the dye (or desensitizing compounds) is slowly added to the liquid gelatino-silver halide emulsion with stirring. Stirring is continued until the dye is thoroughly incorporated in the emulsion. Then the desired amount of the stock solution of the desensitizing compound (or dye, if the desensitizing compound has been added first) is slowly added to the emulsion, while stirring. Stirring is continued until the second solution is thoroughly incorporated. The treated emulsion can then be coated out on a suitable support, such as glass, cellulose derivative film, resin film, or paper, to suitable thicknesses and allowed to dry. Most usually the roomlight handling radiographic elements of our invention are duplicated, i.e., coated on either side of a support with the light-sensitive, X-ray-sensitive emulsion layer being the innermost layer, and the light protecting outer layer being coated as a second layer on either side of the support. The details of such coating methods are well known to those skilled in the art and have been described in U.S. Pat. 1,947,160 issued Feb. 13, 1934.

The coating thickness of the innermost light-sensitive, X-ray-sensitive layer of the multilayer radiographic elements prepared according to the invention can vary widely, but in general, thicknesses from about 0.4 to about 1.2 units, can be used. The thicknesses of the outer-protective layers are not critical and can depend more upon the concentration of the light diffusing, e.g. silver halide, and absorbing materials per square foot of coated surface.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for illustrating this invention.

EXAMPLE I

To a high contrast coarse-grained silver bromide gelatin emulsion having a low iodide content of the type normally used in radiography and containing 150 gm. of dry gelatin per mole of silver halide is added 150 mg. of 3'-methyl-3-ethyl-6'-nitrothiazolinethiacyanine iodide per mole of silver halide and 3 g. of 1-p-sulfophenyl-3-methyl-4-p-hexoxyphenylazopyrazol-5-one sodium salt per 150 g. of dry gelatin. The emulsion is coated at 90° F. on both sides of a cellulose triacetate base to obtain a coverage of 900 mg. silver per square foot on each side.

Over each of the emulsion layers is applied a layer of non-chemically sensitized fine-grain bromide gelatin emulsion incorporating therein 1 g. of 4-nitro-6-chlorobenzotriazole per mole of silver halide and 30 g. of 1-p-sulfophenyl-3-methyl-4-p-n-hexoxyphenylazopyrazol-5-one for 150 g. of dry gelatin. The overcoat is coated at a coverage of 104 mg. of silver per square foot per side. An anti-abrasion layer is then coated over the light-absorbing emulsion layer and the element is dried.

The resulting film is exposed to an 80 kv. X-ray source under roomlight illumination, developed for 5 minutes at 20° C., fixed and washed. All of the steps for processing the roomlight handling radiographic element of this example are carried out under both inactinic safe light illumination and 50 lux artificial light illumination.

A control sample is prepared which is identical to the above prepared film, except said control sample does not contain any desensitizer, filter dye or absorbing overcoat. The control sample is exposed and developed in the same manner as the new film.

The radiogram obtained from the new film produced by this example is of good quality and does not show

evidence of edge fog. The results for the new film and the control sample are summarized in Table I.

TABLE I

Film	Inactinic light			50 lux artificial light		
	Speed	Gamma	Fog	Speed	Gamma	Fog
Control	100	4.5	0.02	Black	4.0	0.02
New film	89	4.5	0.02	89	4.5	0.02

EXAMPLE II

A conventional cellulose acetate film base is coated with a typical coarse-grain silver bromide gelatin X-ray sensitive emulsion which is desensitized with 43.5 ml. of 4-nitro-6-chlorobenzotriazole(I) and to which is added 25 g. of 3-carboxy-1-(1'-sulfophenyl)-4-(4'-sulfophenylazo)-5 pyrazolonedisodium salt (II) per mole of silver halide. The silver content of the coating is 882 mg. per square foot. As an outer-light-absorbing layer a fine-grain, silver bromide gelatin emulsion strongly desensitized with 900 mg. of compound (I) and containing 80 g. of compound (II) per mole of silver halide is coated over each of the light-sensitive, X-ray-sensitive layers at a thickness to give 540 mg. of silver per square foot. This film, identified in Table II as A, is typical of the X-ray films disclosed in U.S. Pat. 3,237,008.

A film, identified as Film B in Table II, is prepared in the manner of Example 1.

After drying, the coated films are cut into strips and stored. Upon removal from storage, the film strips are exposed to a tungsten lamp of 400 watts, at 2,850° K. for 100 seconds, at a distance of 75 cm. and developed at 20° C., for 5 minutes and fixed in a conventional fixing bath. The results are summarized in Table II.

TABLE II

X-ray film	Fog after 12 months of storage	Desensitization to visible light (Log E) storage period (month)				
		0	3	6	9	12
A	0.60	-4.5	-4.3	-4.1	-3.8	-3.7
B	0.06	-4.5	-4.5	-4.5	-4.4	-4.4

EXAMPLE III

An X-ray film is prepared in the same manner as in Example I except there is added 0.1 g. of 3'-methyl-3-ethyl-6'-nitrothiazolinethiacyanine iodide per mole of silver halide instead of 0.15 g. and 4 g. instead of 3 g. of 1-p-sulfophenyl - 3 - methyl-4-p-n-hexoxyphenylazopyrazol-5 one sodium salt per 150 g. of dry gelatin. A control film is prepared in the same manner as in Example I. The control and the new film are exposed and processed in the same manner as in Example I.

The results are summarized in Table III.

TABLE III

X-ray film	Inactinic light			50 lux artificial light		
	Speed	Gamma	Fog	Speed	Gamma	Fog
Control	100	4.5	0.02	Black	4.4	0.05
New film	100	4.5	0.03	100	4.4	0.74

EXAMPLE IV

This example illustrates the manner of preparation of a yellow dye of the invention.

In a flask of one liter equipped with a mechanical agitator and a reflux condenser there is introduced 55.6 g. of para nitrophenyl, 55.2 g. of the anhydrous potassium carbonate 66.0 g. of hexylbromide and 400 ml. of anhydrous acetone and heated under reflux for about 96 hours. The solvent is removed under vacuum and 400 ml. of water are added. The solution is extracted 2 times with 200 ml. respectively of benzene. The benzene extracts are combined and washed 3 times with 200 ml. of a solution of 10% sodium hydroxide. Benzene is heated and the remaining oil is distilled under vacuum.

Sixty-seven (67 g.) grams of the obtained para-n-hexoxynitrobenzene is mixed with 100 ml. of methanol in the presence of 2 g. of Raney Nickel and catalytically reduced at 50° C. under 22 lbs. of pressure for 1 hour. Upon filtering and heating the solvent under vacuum and distilling, one obtains as the residue para n-hexoxyaniline.

In a one-liter flask sitting in a cooling medium, supplied with mechanical agitator, a thermometer and a dropping funnel there is introduced 57.9 g. of p-n-hexoxyaniline, 300 ml. of water and 75 ml. of concentrated hydrochloric acid. To the above solution, over a period of from 50 to about 60 minutes 21 g. of sodium nitrite in 30 ml. of water is introduced very slowly while continuously maintaining the temperature below 0° C. Upon completing the introduction of the sodium nitrite, the solution is agitated for 30 minutes. Into a two-liter flask equipped with a mechanical agitator and a thermometer 76.2 g. of p-sulfophenylmethylpyrazalone is dissolved in a solution of sodium hydroxide. To the solution is added 90 g. of sodium acetate. The diazonium prepared and obtained in the above step is then introduced while maintaining the mixture at a temperature from 0 to 5° C. A yellow colored product falls out immediately.

The mixture is cooled and agitated for 2 hours. The dye, which is like gum, is filtered while still wet and put in 400 ml. of acetic acid. The mixture is heated to boiling then cooled and filtered. The dye is re-crystallized in acetic acid and dried under vacuum at a temperature of about 40° C. to about 50° C. One hundred seventy-three grams (173 g.) of the yellow dye was obtained with a yield of 69.5%.

The dye is in a form of an orange powder and melts and decomposes at about 250° C. The molecular coefficient of adsorption in water shows an epsilon of 22.200 with a maximum of absorption at 416-419 m μ .

EXAMPLE V

This example describes the typical method for the preparation of the desensitizers. In a 6-liter 3-necked flask there is introduced 3 liters of anhydrous pyridine, 1.060 kg. of methyl sulfate of 3-methyl-2-methyl mercapto-6-nitrobenzothiazolium and .905 kg. of ethyl paratoluene sulfonate of 2-methyl-thiazolienium. The mixture is stirred and heated at 100° for about 20 minutes and then cooled to 0° whereupon a dye crystallizes out. The mixture is filtered. The solid is suspended in 3 liters of ethanol and refluxed. It is then added a solution of 675 g. of sodium iodide dissolved in 3 liters of triethanolamine, agitated for 30 minutes, filtered and heated in warm alcohol. One obtains 730 g. of 3-ethyl-3'-methyl-6'-nitrothiazolinethiacyanineiodide.

The invention can be further described by reference to the accompanying drawing. In FIG. 1 the support is coated with a light-sensitive, X-ray-sensitive layer 11 which has coated thereon a light-absorbing silver halide emulsion layer 12 which prevents the exposure of the light-sensitive layer 11 during roomlight handling of the radiographic element. On the back side of the element, there is coated a light-sealing backing layer 13. The backing layer suitably employed in the invention must be an antihalation layers which dissolves smoothly in photographic developers and which do not disintegrate and contaminate conventional developer solutions, such as described in U.S. Pat. 2,327,828 issued Aug. 24, 1943.

In FIG. 2 of the accompanying drawing the support 10 is coated on each side with an X-ray-sensitive, light-sensitive layer 11 and superimposed on each of the light-sensitive layers are the light-absorbing silver halide emulsion layers 12. In roomlight handling element of the types shown in FIG. 2, a light-sealing backing layer is not used since the outer protective layers protect the inner-most layer 11 from visible light exposure.

The X-ray film of my invention is particularly useful in dentistry and in industrial radiography.

Any of the useful photographic addenda may be incorporated into X-ray-sensitive emulsion layer.

As indicated, heretofore, the X-ray-sensitive emulsion layers are coated upon a support. Typical film supports are cellulose nitrate, cellulose ester, polyvinyl acetal, polystyrene, polyethylene, terephthalate, other polyesters, and the like. Supports such as cards or paper which are coated with alphaolefin polymers, particularly polymers of alpha-olefins containing 2 or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene co-polymers, and the like, give good results.

The thickness of said support can vary as well known in the art in order to practice effectively my invention.

The silver halide emulsions used with this invention can comprise silver chloride, silver bromide, silver bromiodide, silver chlorobromiodide or mixtures thereof. The emulsions may be coarse or fine grain and can be prepared by any of the well-known procedures, e.g. single jet emulsions, double jet emulsions, such as Lippman emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al., U.S. Pat. 2,222,264 issued Nov. 4, 1940; Illingsworth U. S. Pat. 3,320,069 issued May 15, 1967; and McBride U.S. Pat. 3,271,157 issued Sept. 6, 1966. Surface image emulsions may be used or internal image emulsions such as those described in Davey et al. U.S. Pat. 2,592,250 issued Apr. 8, 1952. The emulsions may be regular grain emulsions such as the type described in Klein and Moisar, J. Phot. Sci., vol. 12, No. 5, Sept./Oct., 1964, pp. 242-251. With respect to the X-ray-sensitive layers particularly good results are obtained with gelatino silver bromiodide emulsions in which the average grain size of the silver bromiodide crystal is in the range of about 0.5 to about 5 microns.

The X-ray-sensitive emulsions described herein can be chemically sensitized with compounds of the sulfur group, noble metal salts such as gold salts, reduction-sensitized with reducing agents, and combinations of these. Furthermore, the X-ray-sensitive emulsion layers can be hardened with any suitable hardener or combination such as aldehyde hardeners, aziridine hardeners, hardeners which are derivatives of dioxane, vinyl sulfones, oxypolysaccharides, such as oxystarch, oxy plant gums, inorganic hardeners such as chromium salts, and the like.

The silver halide coatings of the radiographic and other elements useful in this invention can contain any of the hydrophilic, water-permeable binding materials suitable for this purpose. Suitable materials include gelatin, colloidal albumen, polyvinyl compounds, cellulose derivatives, acryl amide polymers and the like, alone or in combination and mixtures. The binding agents for the emulsion layer of the radiographic and other photographic elements can also contain dispersed polymerized vinyl compounds. Certain of these compounds are disclosed, for example, in U.S. Pats. 3,142,568 of Nottorf issued July 28, 1964; 3,193,386 of White issued July 6, 1965; 3,062,672 of Houck et al. issued Nov. 6, 1962; and 3,220,844 of Houck et al. issued Nov. 30, 1965; and include the water-insoluble polymers and latex co-polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, or the like.

The X-ray-sensitive radiographic silver halide coatings and other photographic silver halide coatings can also contain additional additives, particularly those known to be beneficial in photographic emulsions. For example, they can contain speed-increasing compounds, for example, "onium" salt, such as quaternary ammonium ternary sulfonium salts, polyalkylene glycols, thioethers and the like. The photographic silver halide coatings can be stabilized with mercury compounds, azindenes quaternary benzo-thiazolium compounds, hydroxy substituted aromatic compounds, and the like.

The photographic silver halide emulsions or coatings used in my invention can also contain non-ionic, anionic and/or amphoteric coating aids. Some useful coating aids

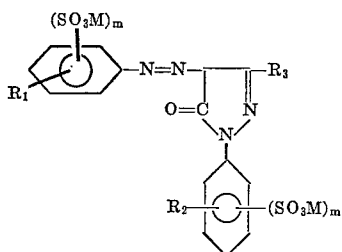
include, for example, saponin, alkyl substituted aryl oxy alkylene ethyl sulfonates of the type described in U.S. Pat. 2,600,831 issued June 17, 1952, maleopimarates of the type described in U.S. Pat. 2,823,123 issued Feb. 11, 1958, taurine derivatives of the type described in U.S. Pat. 2,739,891 issued on Mar. 27, 1956, and alkyl aminopropionates of the type described in U.S. Pat. 3,113,816 issued May 19, 1964. Typical of still other good coating aids and surfactants which can be employed in the emulsions used with the screens of this invention include the alkylphenoxy poly(hydroxyalkylene oxides) such as alkylphenoxy poly(glycidols) having from about 5 to about 12 glycidol units, for example, such as those disclosed in British Pat. 1,022,878 issued Mar. 16, 1966, to Olin Mathieson. The emulsions and radiographic combinations used and described herein can contain incorporated developing agents such as polyhydroxy benzenes, aminophenols and 1,3-pyrazolidones.

The radiographic silver halide emulsions and other photographic emulsions can contain various protective overcoats such as those which comprise colloidal silica in an overcoat comprising gelatin and at least one other hydrophilic colloid, including gelatin-compatible acrylic polymers which improve various physical characteristics and optical clarity.

This invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. In a photographic element comprising a support having coated thereon at least one X-ray sensitive gelatino-silver halide emulsion layer comprising a silver halide desensitizing compound and a yellow dye, and coated on said X-ray-sensitive layer at least one light-absorbing gelatino-silver halide emulsion layer comprising a nitrogen-containing heterocyclic silver halide desensitizing compound distinct from said desensitizing compound in the X-ray-sensitive silver halide emulsion layer, and a yellow dye, said yellow dye being absorbent in the regions of the visible spectrum in which said gelatino-silver halide emulsion is sensitive and capable of transmitting the remainder of the visible spectrum, the improvement wherein said desensitizer contained in the X-ray-sensitive silver halide emulsion is a 3-alkyl-3'-alkyl-6'-nitrothiazolinothiacyanine present in desensitizing concentration and said yellow dye, present in visible-light absorbing concentration, is a compound having the structural formula



wherein each R_1 and R_2 is hydrogen, an alkyl or alkoxy group of from about 4 to about 12 carbon atoms with the condition that at least one of R_1 or R_2 is an alkyl or an alkoxy group; R_3 is an alkyl or alkoxy group of from 1 to about 4 carbon atoms; M is hydrogen, an alkali metal, ammonium, or substituted ammonium; and m and n are equal to zero or one with the condition that at least one of m or n be equal to one.

2. In a photographic element as in claim 1 wherein said desensitizer contained in the X-ray-sensitive silver halide emulsion layer is present in a range of from about 0.02 g. to about 0.5 g. per mole of silver, said desensitizer present in the light-absorbing gelatino-silver halide emulsion layer is present in a range of from about 20 mg. to about 5 g. per mole of silver and said yellow dye is present

in each layer in a range of from about 0.5 g. to about 100 g. per 150 g. of dry gelatin.

3. In a photographic element as in claim 1 wherein the support is coated on both sides with said X-ray-sensitive gelatino-silver halide emulsion layers, said emulsion layers having thereon, said light-absorbing gelatino-silver halide emulsions.

4. In a photographic element as in claim 1 wherein said nitrogen-containing heterocyclic compound is 4-nitro-6-chlorobenzotriazole.

5. In a photographic element as in claim 1 wherein R_1 , R_2 and each $-SO_3M$ group are in the ortho or para position.

6. In a photographic element as in claim 1 wherein each of R_1 and R_2 is hydrogen or an alkoxy or alkyl group having from 4 to 6 carbon atoms.

7. In a photographic element as in claim 1 wherein each of R_1 and R_2 is hydrogen or an alkoxy or alkyl group having 5 or 6 carbon atoms.

8. In a photographic element as in claim 7 wherein R_1 is an alkoxy group in the para position, R_2 is hydrogen and m equals zero.

9. In a photographic element as in claim 1 wherein R_1 is an alkoxy group in the para position, R_2 is hydrogen, m equals zero, and $-SO_3M$ is in the para position.

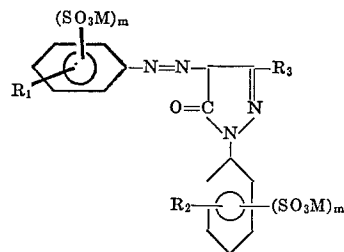
10. In a photographic element as in claim 1 wherein said light-absorbing silver halide layer comprises silver halide which forms latent images predominantly inside the silver halide crystals.

11. In a photographic element as in claim 10 wherein said nitrogen-containing heterocyclic silver halide desensitizing compound is present in the light-absorbing silver halide layer in a range of from about 25 mg. to about 250 mg. per mole of silver halide.

12. In a photographic element as in claim 1 wherein said desensitizer in the X-ray-sensitive layer is 3-ethyl-3'-methyl-6'-nitrothiazolinothiacyanine halide, said nitrogen-containing heterocyclic compound in the light-absorbing layer is 4-nitro-6-chlorobenzotriazole and said yellow dye is 1-p-sulfophenyl-3-methyl-4-p-n-hexoxyphenylazopyrazol-5-one, sodium salt.

13. In a photographic element as in claim 12 wherein said light-absorbing layer comprises silver halide which forms latent images predominantly inside the silver halide crystals.

14. X-ray-sensitive gelatino-silver halide emulsion comprising a 3-alkyl-3'-alkyl-6'-nitrothiazolinothiacyanine iodide in a desensitizing concentration and a dye in visible-light absorbing concentration having the structural formula:



wherein each R_1 and R_2 is hydrogen, an alkyl or alkoxy group of from about 4 to about 12 carbon atoms with the condition that at least one of R_1 or R_2 is an alkyl or an alkoxy group; R_3 is an alkyl group or alkoxy group of from 1 to 4 carbon atoms; M is hydrogen, an alkali metal, ammonium or substituted ammonium; and m and n are each equal to zero or one with the condition that at least one of m or n be equal to one.

15. An X-ray-sensitive gelatino-silver halide emulsion as in claim 14 wherein said 3-alkyl and 3'-alkyl groups can have from 1 to 8 carbon atoms and each of R_1 and R_2 have from 4 to 6 carbon atoms and are in the ortho or para position.

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16. An X-ray-sensitive gelatino-silver halide emulsion as in claim 14 wherein said 3-alkyl and 3'-alkyl groups have from 1 to 3 carbon atoms and each of R_1 and R_2 is hydrogen or an alkoxy or alkyl group having 5 or 6 carbon atoms.

17. An X-ray-sensitive gelatino-silver halide emulsion as in claim 14 wherein each of R_1 and R_2 is hydrogen or an alkoxy group.

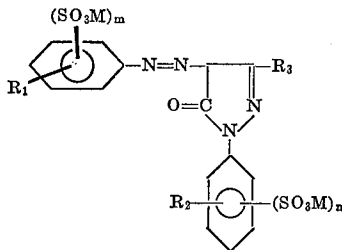
18. An X-ray-sensitive gelatino-silver halide emulsion as in claim 17 wherein R_1 has 5 or 6 carbon atoms and is in the para position, R_2 is hydrogen, m equals zero and $-\text{SO}_3\text{M}$ is in the para position.

19. An X-ray-sensitive gelatino-silver halide emulsion comprising 3-ethyl-3'-methyl-6'-nitrothiazolinothiacyanine iodide in a desensitizing concentration and 1-*p*-sulfophenyl-3-methyl-4-*p*-*n*-hexoxyphenylazopyrazol-5-one, sodium salt in visible light absorbing concentration.

20. In a process for producing a radiographic image, said process comprising (a) exposing in room light a roomlight handling radiographic element, and (b) developing said element in roomlight in a radiographic silver halide developing solution, the improvement wherein said element comprises an X-ray-sensitive silver halide emulsion of claim 14.

21. In a photographic emulsion comprising a hydrophilic colloid, at least one electromagnetic radiation-sensitive silver halide and a desensitizer to visible radiation, the improvement wherein said desensitizer is a 3-alkyl-3'-alkyl-6'-nitrothiazolinothiacyanine halide.

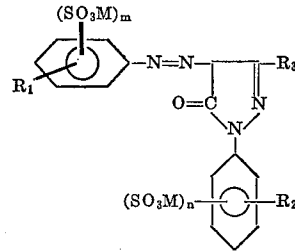
22. A photographic emulsion as in claim 21 additionally comprising a yellow dye having the structural formula



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wherein each R_1 and R_2 is hydrogen, an alkyl or alkoxy group of from about 4 to about 12 carbon atoms with the condition that at least one of R_1 or R_2 is an alkyl or an alkoxy group; R_3 is an alkyl or alkoxy group of from 1 to about 4 carbon atoms; M is hydrogen, an alkali metal, ammonium, or substituted ammonium; and m and n are each equal to zero or one with the condition that at least one of m or n be equal to one.

23. In a photographic emulsion comprising a hydrophilic colloid, at least one electromagnetic radiation sensitive silver halide and a yellow dye, the improvement wherein said yellow dye is represented by the structural formula



wherein each R_1 and R_2 is hydrogen, an alkyl or alkoxy group of from about 4 to about 12 carbon atoms with the condition that at least one of R_1 or R_2 is an alkyl or alkoxy group; R_3 is an alkyl or alkoxy group of from 1 to about 4 carbon atoms; M is hydrogen, an alkali metal, ammonium or substituted ammonium; and m and n are each equal to zero or one with the condition that at least one of m or n be equal to one.

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| 40 | NORMAN G. TORCHIN, Primary Examiner | | |
| | R. FICHTER, Assistant Examiner | | |
| | U.S. Cl. X.R. | | |
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