United States Patent

[11] 3,630,744

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[73] Assignee **Gevaert-AGFA N.V. Mortsel, Belgium**
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[33] **Great Britain**
[31] **29,579/66**

[54] **SELECTIVELY DESENSITIZED SILVER HALIDE EMULSION MATERIALS**
4 Claims, No Drawings

[52] **U.S. Cl.** **96/101**
[51] **Int. Cl.** **G03c 1/36**
[50] **Field of Search** 96/101

[56] **References Cited**

UNITED STATES PATENTS

3,140,951	7/1964	Heseltine et al.	96/101
3,237,008	2/1966	Dostes et al.	96/101
3,250,618	5/1966	Stewart et al.	96/101

OTHER REFERENCES

Mees, Theory of Photographic Process, 2nd edition, 1954, The MacMillan Co., pages 421–422

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Assistant Examiner—Richard E. Fichter
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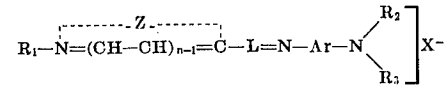
ABSTRACT: A photographic material containing a silver halide emulsion layer for recording information in the form of very short wavelength invisible electromagnetic radiation known as X-ray, wherein the sensitivity of said layer for ultra violet light and visible light is strongly reduced without substantially affecting the X-ray sensitivity of said material by incorporating therein an appropriate amount of a selective desensitizing compound according to the following general formula



wherein:

R_1 represents an alkyl group, an unsaturated aliphatic group, or an aryl group,

Z represents a heterocyclic nucleus of the thiazole series, benzothiazole series, naphthothiazole series, thiadiazole series, oxazole series, benzoxazole series, naphthoxazole series, selenazole series, benzoselenazole series, naphthoselenazole series, 2-quinoline series, pyrimidine series, quinoxaline series, quinazoline series, 1-phthalazine series, thionaphtheno [7,6-d]thiazole series, 2-pyridine series, and benzimidazole series,

L represents a methine radical,

Ar represents a bivalent aromatic radical,

n represents 1 or 2,

X^- represents an anion, but is not present when R_1 itself contains an anionic group, and

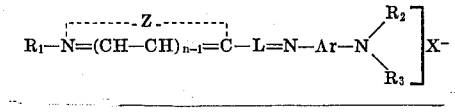
each of R_2 and R_3 represents alkyl, aryl, or R_2 and R_3 together represent the atoms necessary to close a heterocyclic nucleus is described.

SELECTIVELY DESENSITIZED SILVER HALIDE EMULSION MATERIALS

This invention relates to photographic elements for use in the recording of high-energy short wavelength electromagnetic radiation.

It is more particularly an object of the present invention to provide a photographic silver halide material the sensitivity of which for ultraviolet and visible light is very strongly reduced without substantial loss of X-ray sensitivity.

This object has been accomplished by providing a photographic material containing a silver halide emulsion layer for recording information in the form of very short wavelength invisible electromagnetic radiation known as X-ray, wherein the sensitivity of said layer for ultraviolet light and visible light is strongly reduced without substantially affecting the X-ray sensitivity of said material by incorporating therein an appropriate amount of a selective densitizing compound according to the following general formula:



wherein:

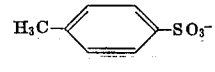
R_1 represents a substituent known in cyanine chemistry on the quaternated nitrogen atom of a heterocyclic nucleus, e.g. an alkyl radical including substituted alkyl of the type generally known in cyanine dye chemistry, such as C_1–C_5 alkyl including alkyl in substituted form, e.g. methyl, ethyl, n-propyl, n-butyl, n-amyl, isopropyl, isobutyl, β-hydroxethyl, β-acetoxyethyl, sulphoethyl, sulphopropyl, sulphobutyl, sulfatopropyl, sulfatobutyl, or a substituted alkyl group such as the group —A—CO—O—B—SO_2OH wherein A and B each represents a hydrocarbon group as described in the U.K. Pat. Specification No. 886,271 filed June 20, 1957 by Gevaert Photo-Producten N.V., or the group —A—W—NH—V—B, wherein A represents a methylene radical, an ethylene radical, a propylene radical or a butylene radical, B represents an alkyl group, an amino group, a substituted amino group and also a hydrogen atom in the case V is a single bond, and W and V each represents a —CO— radical, a —SO_2— radical or a single bond, but at least one of them is a —SO_2— radical as described in the U.K. Pat. Specification No. 904,332 filed July 5, 1957 by Gevaert Photo-Producten N.V., an unsaturated aliphatic radical, e.g. allyl, aralkyl including substituted aralkyl e.g. benzyl and carboxybenzyl, aryl including substituted aryl, e.g. phenyl and carboxyphenyl, a cycloalkyl radical such as cyclohexyl and cyclopentyl;

Z represents the necessary atoms to complete a heterocyclic nucleus of the type used in the production of cyanine dyes, e.g. a nucleus of the thiazole series (e.g. thiazole, 4-methylthiazole, 4-methyl-5-carbethoxythiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4-(m-tolyl)-thiazole, 4-(p-bromophenyl)-thiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)-thiazole, 4(m-nitrophenyl)-thiazole, a nucleus of the benzoithiazole series (e.g. benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 6-sulphobenzothiazole, 4-phenybenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, 4,5,6,7-tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, 5,6-dimethylbenzothiazole), a nucleus of the naphthothiazole series (e.g. naphtho [2,1-d] thiazole, naphtho [1,2-d]-thiazole, 5-methoxynaphtho [1,2-d]-thiazole, 5-ethoxynaphtho[1,2-d]-thiazole, 8-methoxynaphtho[2,1-d]thiazole, 7-methoxynaphtho[2,1-d]-thiazole), a nucleus of the thionaphtheno[7,6-d]thiazole series (e.g. 7-methoxythionaphtheno[7,6-d]thiazole), a nucleus of the thiadiazole series (e.g. 4-phenylthiadiazole), nucleus of the oxazole series (e.g. 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5dimethyloxazole, 5-phenyloxazole), a nucleus of the benzoxazole series (e.g. benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole), a nucleus of the naphthoxazole series (e.g. naphtho[2,1-d]oxazole, naphtho[1,2-d]oxazole), nucleus of the selenazole series (e.g. 4-methylselenazole, 4-phenylselanazole), nucleus of the benzoselenazole series (e.g. benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, 4,5,6,7-tetrahydrobenzoselenazole), a nucleus of the naphthoselenazole series (e.g. naphtho[2,1-d]selenazole, naphtho[1,2-dselenazole), those of the 2quinoline series (e.g. quinoline, 3-methyl-quinoline, 5-methyl-quinoline, 7-methyl-quinoline, 8-methyl-quinoline, 6-chloro-quinoline, 8-chloro-quinoline, 6-methoxy-quinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.), a nucleus of the pyrimidine series, a nucleus of the quinoxaline series, a nucleus of the quinazoline series, a nucleus of the 1-phthalazine series, a nucleus of the 2-pyridine series (e.g. pyridine, 5-methylpyridine, 3-nitropyridine), a nucleus of the benzimidazole series (e.g. benzimidazole, 5,6-dichlorobenzimidazole, 5-chlorobenzimidazole, 5,6-dibromobenzimidazole, 5-chloro-6-aminobenzimidazole, 5-chloro-6-bromobenzimidazole, 5-phenylbenzimidazole, 5-fluorobenzimidazole, 5,6-difluorobenazimidazole, 5-cyanobenzimidazole, 5,6-dicyanobenzimidazole, 5-chloro-6-cyanobenzimidazole, 5-fluoro-6-cyanobenzimidazole, 5-acetylbenzimidazole, 5-chloro-6-fluorobenzimidazole, 5-carboxybenzimidazole, 7-carboxybenzimidazole, 5-carbethoxybenzimidazole, 7-carbethoxybenzimidazole, 5-sulphamylbenzimidazole, or 5-N-ethylsulphamybenzimidazole;

L represents methine including substituted methine, e.g. a =CH—, =C(alkyl)—, =C(aryl)—, =C(aralkyl)—, =C—(COO-alkyl)—, =C—(CN)—, =C—(CO—alkyl)— or =C(CO—aryl)—radical;

Ar represents a bivalent aromatic radical, e.g. a phenylene radical,

n represents a positive integer 1 or 2, x^- represents an anion, e.g. Cl^-, Br^-, I^-, ClO_4^-, $CH_3SO_4^-$ and

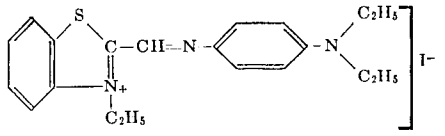


but X^- is not present when R_1 itself contains an anionic group, and

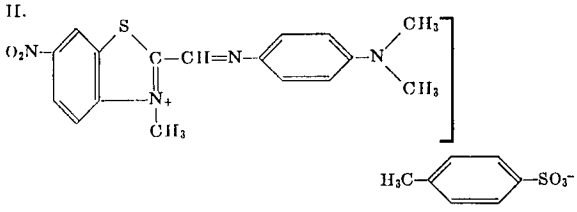
each of R_2 and R_3 represents alkyl including substituted alkyl, e.g. methyl, ethyl, propyl, butyl, benzyl, sulpho substituted alkyl, cyano substituted alkyl, halogen substituted alkyl, carbalkoxy substituted alkyl, carboxy substituted alkyl, a cycloalkyl radical such as cyclopentyl or cyclohexyl, aryl including substituted aryl e.g. phenyl, alkyl substituted phenyl, halogen substituted phenyl, nitro substituted phenyl, alkoxy substituted phenyl, or together the necessary atoms to close a heterocyclic nucleus e.g. a piperidine nucleus, a morpholine nucleus, a piperazine nucleus or a pyrrolidine nucleus.

Typical compounds included by the above general formula which have proved to be very selective desensitizers for the purpose of the invention are represented by the following structural formulae:

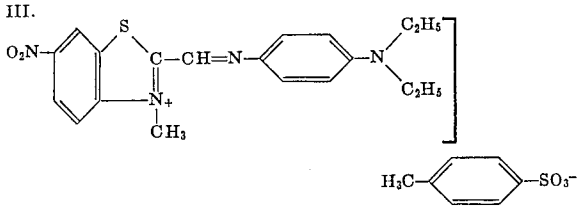
I.



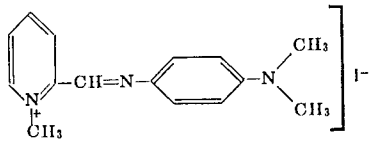
II.



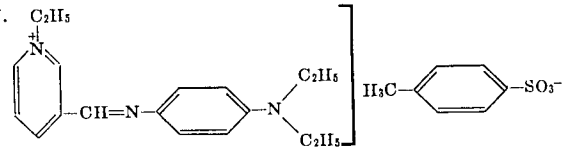
III.



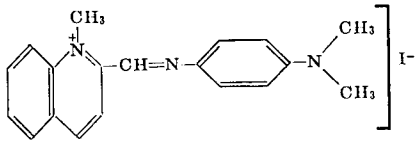
IV.



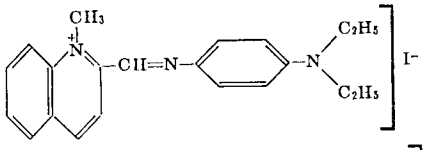
V.



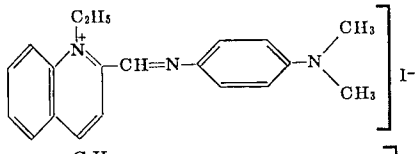
VI.



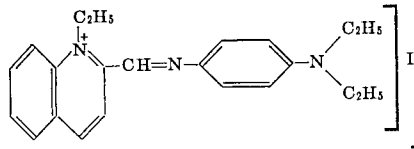
VII.



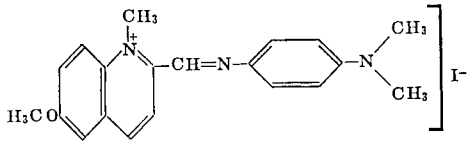
VIII.



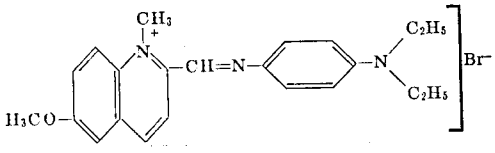
IX.



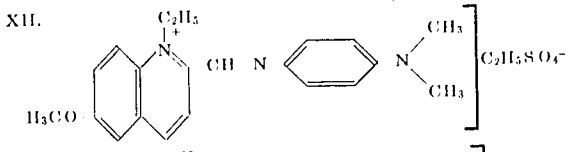
X,



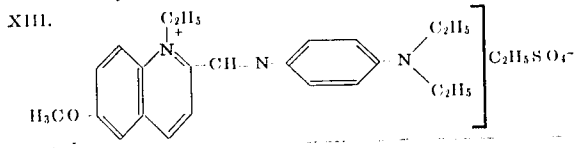
XI.



XII.



XIII.



The above compounds can be prepared according to techniques which are generally known to one skilled in the art of cyanine dye chemistry.

The quantity of desensitizing azomethine dye relative to silver halide for use according to the present invention has to be adapted depending upon the particular silver halide emulsion and the particular desensitizing compound used, the ratio of gelatin or other colloid binder to silver halide, the ingredients used e.g. stabilizers and the thermal treatment of the emulsion before coating.

In general it has been observed that amounts of 1 to 1,000 mg. of said azomethine dye per mole of silver halide are useful for obtaining the desired difference in sensitivity between visible light and X-rays. A preferred range of dye concentration lies between 1 and 100 mg. per mole of silver halide since thereby for a relatively strong reduction in visible light sensitivity the X-ray sensitivity of the emulsion is not substantially lowered.

By the wording "without substantially affecting the X-ray sensitivity" we understand that the sensitivity for X-rays does not diminish below 70 percent of the value it possesses without the addition of the desensitizing dye.

The azomethine desensitizing dyes used according to the present invention substantially lower the fog level of the developed material which is to be considered as a very interesting advantage.

Different type of silver halide, e.g. silver chloride, silver bromide, silver chlorobromide, silver chloroiodide and silver bromoiodide can be employed, although we have found that iodide containing bromide emulsions, preferably containing at most 2.5 mole percent iodide are especially useful for X-ray recording.

In order to decrease still further the sensitivity of the silver halide emulsions for ultraviolet light and visible radiation, an adequate amount of ultraviolet absorbing substance and dye e.g. a yellow dye may be used. The filter dye may be incorporated in the emulsion layer, topcoat or protective layer and/or in the base or a backing layer.

The desensitizing dyes used according to the present invention can be added to the light sensitive silver halide emulsion during different preparation steps of the light sensitive material. For example they can be incorporated therein by a separate addition, e.g. from a solution or dispersion, or they can be added as a mixture with one or more ingredients used in the formation of the silver halide grains, during the physical or chemical ripening or during another step preceding the coating of the emulsion. The desensitizing dyes can also be incorporated in a water-permeable layer adjacent to the silver halide emulsion layer, but have then to come by diffusion in working contact with the light sensitive silver halide.

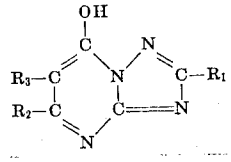
For the purpose of increasing the gradation and accelerating the development, the said desensitizing compounds are preferably used in combination with water-soluble alkylene oxide trialkylsulphonium products or polymers, e.g. as described in the U.S. Pat. Specification Nos. 1,970,578 of C. Scholler and M. Wittwer, issued Aug. 21, 1934, 2,240,472 of D. R. Swan, issued Apr. 29, 1941, 2,423,549 of Ferdinand Schulze, issued July 8, 1947, 2,441,389 of R. K. Blake, issued May 11, 1948, 2,531,832 of W. A. Stanton, issued Nov. 28,1950, 2,533,990 of R. K. Blake, issued Dec. 12, 1950 and the U.K. Pat. Specification Nos. 991,608 filed June 14, 1961

by Kodak Ltd., 920,637 filed May 7, 1959, 945,340 filed Oct. 23, 1961, 940,051 filed Nov. 1, 1961 and 1,015,023 filed Dec. 24, 1962 all by Gevaert Photo-Producten N.V. For suitable development accelerating polymeric products of another type reference is made to our published Dutch Pat. application Nos. 6,614,230 filed Oct. 10, 1966 and 6,614,291 filed Oct. 11, 1966 . Other compounds which sensitize the photographic emulsion by development acceleration, and which can be used together with the selective desensitizing compounds applied according to the present invention are organic onium compounds and polyonium compounds, preferably of the ammonium or sulfonium type, e.g. quaternary tetra alkylammonium salts, alkyl-pyridinium salts, bis-alkylene pyridinium salts, alkylquinolinium salts, and trialkylsolphonium salts.

The selective desensitizing compounds can further be combined with chemical sensitizers known in the art e.g. sulfur-containing compounds such as allyl isothiocyanate, allyl thiourea, or sodium thiosulfate, reducing compounds such as the tin compounds described in the Belgian Pat. Specification Nos. 493,464 filed Jan. 24, 1950 and 568,687 filed June 18, 1958 both by Gevaert Photo-Producten N.V., the imino-aminomethane sulfinic acid compounds described in the British Pat. Specification No. 798,823 filed Dec. 11, 1956 by Mullard Ltd., or noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium compounds.

The desensitizing compounds used according to the present invention can also be used in combination with known stabilizing agents for silver halide emulsions, e.g. mercury compounds, sulfur compounds such as 1-phenyl-2-tetrazoline-5-thion, the compounds described in the Belgian Pat. Specification No. 571,916 and 571,917 both filed Oct. 10, 1958 by Gevaert Photo-Producten N.V., either or not in combination with chemically sensitizing and stabilizing cadmium salts in the light sensitive material as well as in the developer.

Together with the above-mentioned ingredients, derivatives of tetra-azaindenes, e.g. having the following general formula can be used as fog-inhibiting compounds in the light sensitive material:



wherein:

each of R_1 and R_2 represents a hydrogen atom, an alkyl, an aralkyl, or an aryl radical, and

R_3 represents a hydrogen atom, an alkyl, a carboxy, or an alkoxy-carbonyl group.

The selective desensitized silver halide emulsions can be applied by usual coating techniques to any type of support known in silver halide photography e.g. paper, cellulose triacetate or polyester resin support.

The following examples illustrate the present invention without however limiting it thereto.

Example 1

An ordinary coarse-grained silver bromoiodide (2 mole percent iodide) emulsion of the type normally used in radiography, which had been chemically sensitized to its optimum speed was divided into two portions. One portion was then treated with a desensitizing compound of the structural formula I above, the other portion of the emulsion remained untreated and served as a control. Each of the portions of the emulsions was then coated on an ordinary cellulose triacetate film base, and the coatings dried. The films obtained were then divided in two identical strips one of which was exposed to 80 kilovolt X-rays through an aluminum step wedge and the other strip was exposed through a grey-wedge to an incandescent bulb emitting in the visible region of the spectrum, and provided with a filter to correct its emission spectrum towards the normal spectrum of daylight. Each strip was then developed for 4 minutes in the following developer at 20° C.

p-monomethylaminophenol sulfate	4 g.
anhydrous sodium sulfite	65 g.
hydroquinone	10 g.
anhydrous sodium carbonate	45 g.
potassium bromide	5 g.
water	1,800 cc.

After development, the strips were fixed, washed and dried in the usual manner.

The relative speeds (in percent of the control) of the strips exposed to 80 kv. X-rays and visible light respectively were then measured at a density of 1.00 above fog.

TABLE 1

	Mg. per mole of silver halide	Exposure to 80 kv. X-rays: Fog	Exposure to 80 kv. X-rays: Relative speed (percent)	Exposure to visible light: Relative speed (percent)
Structural formula of dye—				
I	None	0.16	100	100
	13	0.02	96	15

Example 2

Example 1 is repeated but with a silver bromoiodide emulsion containing 2.5 mole percent iodide and with a dye of structural formula VIII. The sensitometric results are listed in table 2.

TABLE 2

	Mg. per mole of silver halide	Exposure to 80 kv. X-rays: Fog	Exposure to 80 kv. X-rays: Relative speed (percent)	Exposure to visible light: Relative speed (percent)
Structural formula of dye—				
VIII	None	0.08	100	100
	13	0.01	92	15.2

Example 3

The foregoing examples were repeated with a silver bromoiodide emulsion containing 0.35 mole percent iodide and with dyes as indicated in the following table 3 wherein the results obtained are listed.

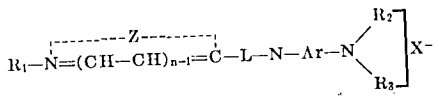
TABLE 3

	Mg. per mole of silver halide	Exposure to 80 kv. X-rays: Fog	Exposure to 80 kv. X-rays: Relative speed (percent)	Exposure to visible light: Relative speed (percent)
Structural formula of dye—				
	None	0.14	100	100
VI	3	0.03	98	21
VI	20	0.01	91	3.8
VII	10	0.03	105	23
VIII	3	0.03	101	33
VIII	10	0.02	95	20
IX	3	0.02	112	60
IX	10	0.03	105	36
X	6	0.02	98	13.5
X	15	0.01	95	6.8
XI	3	0.03	102	45
XI	10	0.03	100	32

We claim:

1. A photographic material comprising an X-ray sensitive silver halide emulsion layer, containing a desensitizing compound, which decreases the sensitivity to ultra violet radiation and visible light of the emulsion layer to a greater extent than its sensitivity to X-rays wherein said compound is used in said

emulsion layer in an amount of from about 1 to 100 mg. per mole of silver halide such as not to decrease the X-ray sensitivity of the emulsion layer below about 70 percent of its inherent value and retaining the desensitization of the emulsion to ultraviolet and visible light and wherein said compound corresponds with the general formula:



wherein:

R_1 represents an alkyl group, an unsaturated aliphatic group, or an aryl group,

Z represents the necessary atoms to complete a heterocyclic nucleus of the thiazole series, benzothiazole series, naphthothiazole series, thiadiazole series, oxazole series, benzoxazole series, naphthoxazole series, selenazole series, benzoselenazole series, naphthoselenazole series, 2-quinoline series, pyrimidine series, quinoxaline series, quinazoline series, 1-phthalazine series, thionaphtheno[7,6-d]thiazole series, 2-pyridine series, and benzimidazole series,

L represents a methine radical,

Ar represents a bivalent aromatic radical,

n represents 1 or 2,

X^- represents an anion, but is not present when R_1 itself contains an anionic group, and

each of R_2 and R_3 represents alkyl aryl, or R_2 and R_3 together represent the atoms necessary to close a heterocyclic nucleus.

2. A photographic material according to claim 1 wherein in the general formula:

R_1 represents C_1—C_5 alkyl,

Z represents the necessary atoms to complete a nucleus of the 2-quinoline series or a nucleus of the benzothiazole series,

L represents a methine radical,

Ar represents a p-phenylene radical,

n represents 1,

X^- represents an anion, but is not present when R_1 itself contains an anionic group, and

each of R_2 and R_3 represents alkyl.

3. A photographic material according to claim 1 wherein the silver halide emulsion layer contains in addition to the said desensitizing compound a water-soluble alkylene oxide condensation product as developing accelerator and a mercury compound as stabilizing agent.

4. A photographic material according to claim 2 wherein the silver halide emulsion layer contains in addition to the said desensitizing compound a water-soluble alkylene oxide condensation product as developing accelerator and a mercury compound as stabilizing agent.

* * * * *