United States Patent

[11] 3,615,643

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[73] Assignee **Fuji Photo Film Co., Ltd. Kanagawa, Japan**

[32] Priority **Jan. 8, 1969**
[33] **Japan**
[31] **44/1555**

[54] **DIRECT POSITIVE SILVER HALIDE EMULSION CONTAINING A DYE WITH AT LEAST ONE NAPTHO (2,3d) OXAZOLE NUCLEUS**

5 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **96/137, 96/138, 96/64**
[51] **Int. Cl.** **G03c 1/08, G03c 1/10**
[50] **Field of Search** 96/64, 137, 138, 107

[56] **References Cited**

UNITED STATES PATENTS

2,217,829	10/1940	Albers et al.	96/138
2,323,187	6/1943	Arens et al.	96/64
2,704,717	3/1955	Jones	96/137 X

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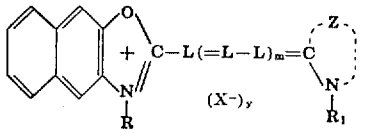
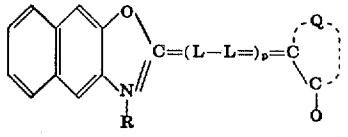
ABSTRACT: A fogged direct positive silver halide photographic emulsion containing a dye selected from the group represented by the following formulae:



and



wherein R and R_1, which may be the same or different, each represents an alkyl group, an alkoxyalkyl group, a hydroxyalkyl group, a carboxyalkyl group, a sulphoalkyl group, an allyl group, an aralkyl group, or a substituted aralkyl group, L is a methine chain or a methine chain substituted by alkyl or aryl groups; Z is an atomic group necessary to complete a 5- or 6-membered nitrogen containing heterocyclic nucleus; Q is an atomic group necessary to complete a 5- or 6-membered heterocyclic nucleus; *m* and *p* are individually 0, 1 or 2; X is an anion and *n* is 0 or 1.

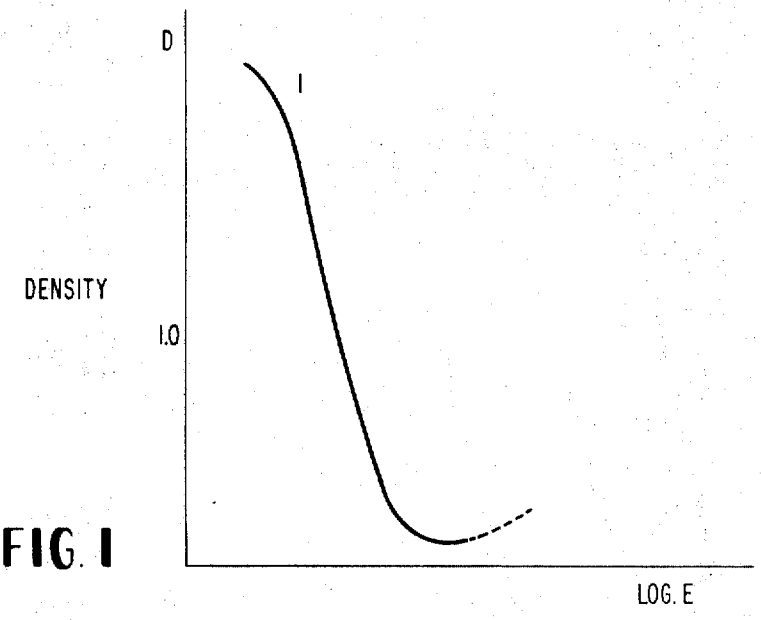


FIG. 1

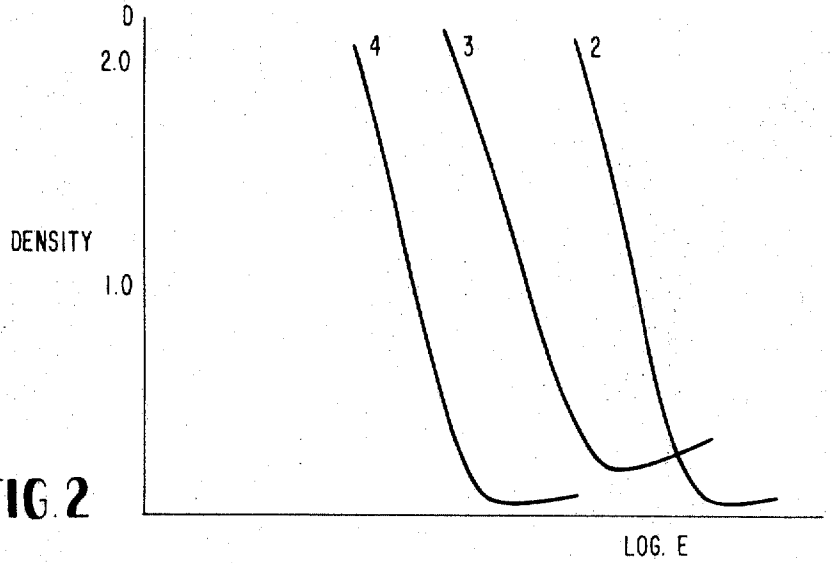


FIG. 2

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DIRECT POSITIVE SILVER HALIDE EMULSION CONTAINING A DYE WITH AT LEAST ONE NAPTHO (2,3d) OXAZOLE NUCLEUS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a silver halide photographic emulsion and, more particularly, a fogged direct positive photographic emulsion.

Description of the Prior Art

It is well known to add a sensitizing dye to a fogged silver halide photographic emulsion capable of directly giving a positive image through exposure and development in order to spectrally sensitize the silver halide photographic emulsion and to raise the overall sensitivity. During the same time, as is known, the contrast changes with the variety and amount of the sensitizing dye added although the overall sensitivity of the silver halide photographic emulsion is raised.

Generally, the overall sensitivity of a direct positive photographic emulsion is markedly raised by increasing the amount of sensitizing dye added thereto but, in many cases, the maximum density (D/max) and contrast are thereby decreased, often resulting in insufficient images.

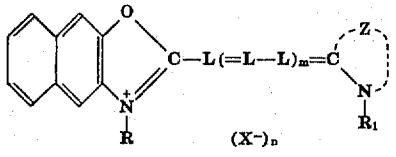
Furthermore, in some cases, when sensitizing a direct positive photographic emulsion by adding a sensitizing dye thereto, the overall sensitivity is raised but "re-reversal" is too large to give sufficient whiteness. "Re-reversal" means that the density increases after decreasing in the characteristic curve, as shown by the dotted portion of curve 1 in FIG. 1.

This "re-reversal" depends on the method of preparation of a silver halide emulsion and more remarkably on the variety of sensitizing dye added. Accordingly, a sensitizing dye causing a large "re-reversal" cannot be put to practical use as it is.

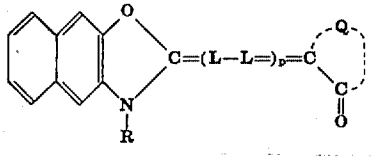
It is the principal object of the present invention to provide a high sensitivity, direct positive silver halide photographic emulsion possessing a low minimum density without "re-reversal," while holding a predetermined maximum density as well as high contrast.

SUMMARY OF THE INVENTION

The above-mentioned object can be accomplished by incorporating in a direct positive silver halide photographic emulsion a cyanine dye or a merocyanine dye represented by the following general formulas I and II, respectively:



(I)



(II)

wherein R and R_1 each represents an alkyl group such as methyl, ethyl, n-propyl, isobutyl and n-amyl, a substituted alkyl group such as β-methoxy-ethyl, β-hydroxyethyl, carboxymethyl, β-carboxyethyl, γ-carboxypropyl, β-sulfoethyl, γ-sulfopropyl, s-sulfobutyl, allyl (vinylmethyl), benzyl, β-phenylethyl and p-sulfophenylethyl, R and R_1 being the same or different groups; L is a methine chain such as $=CH-$ or $=CR_2-$ wherein R_2 is an alkyl group such as methyl or ethyl or an aryl group such as phenyl; Z is an atomic group necessary to complete a five-membered or six-membered nitrogen-containing heterocyclic nucleus, for example, oxazolines, oxazoles, benzoxazoles, naphthoxazoles, thiazolines, thiazoles, benzothiazoles, naphthothiazoles, selenazoles, benzoselenazoles, naphthoselenazoles, quinolines and pyridines, Q is an atomic group necessary to complete a five-membered or six-membered heterocyclic nucleus, for example, rhodanines, oxazolido-5-on-2-thiones, thiohydantoins, pyrazole-5-ones and thiobarbituric acids, m and p are 0, 1 or 2, x is an anion and n is 0 or 1.

BRIEF DESCRIPTION OF THE DRAWINGS

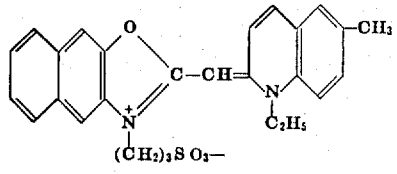
FIG. 1 represents the characteristic curve of a photographic emulsion undergoing the "re-reversal" phenomenon.

FIG. 2 represents the characteristic curves of photographic material containing no sensitizing dye, a conventional dye and the sensitizing dye of the present invention, respectively.

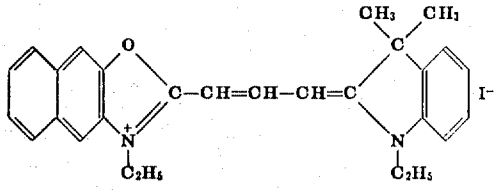
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Examples of the sensitizing dyes represented by the general formulas (I) or (II) are given below, and are merely illustrative, and not limiting, in nature.

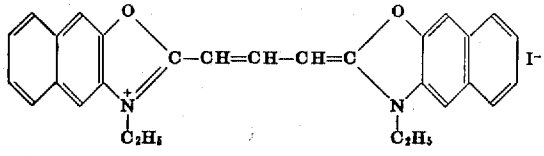
Dye 1



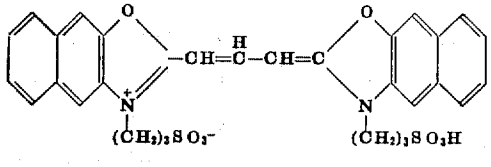
Dye 2



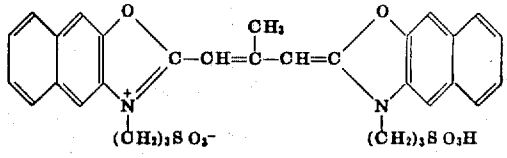
Dye 3



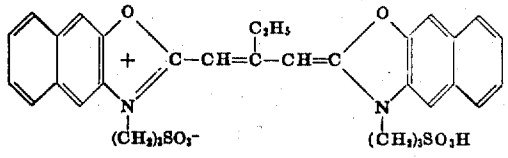
Dye 4



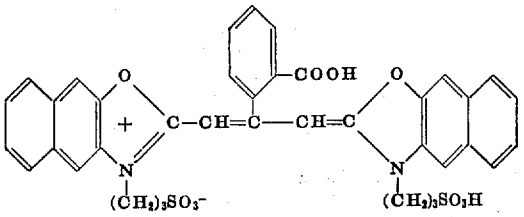
Dye 5



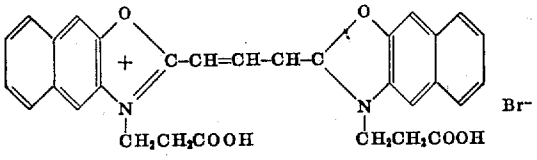
Dye 6



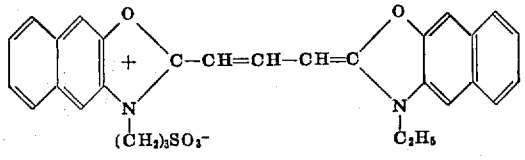
Dye 7



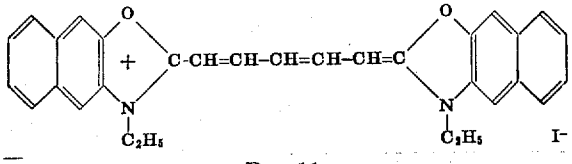
Dye 8



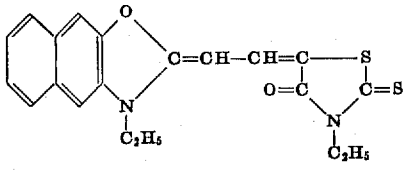
Dye 9



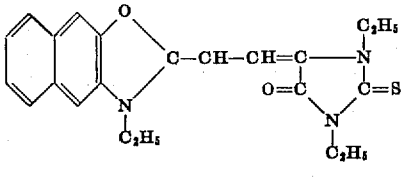
Dye 10



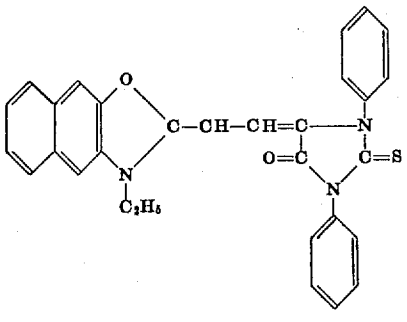
Dye 11



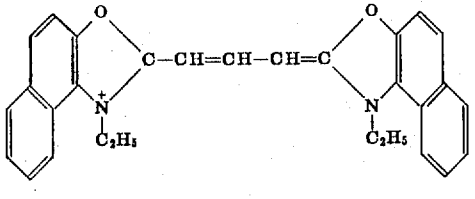
Dye 12



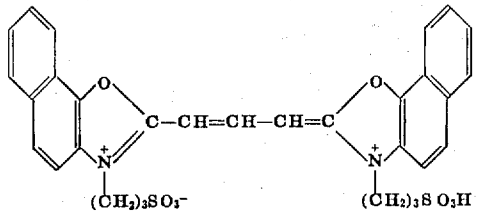
Dye 13



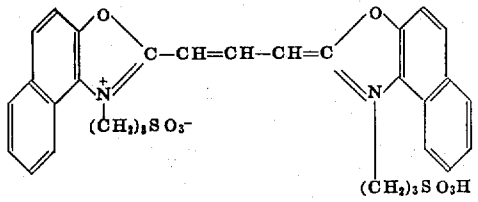
Comparison Dye A



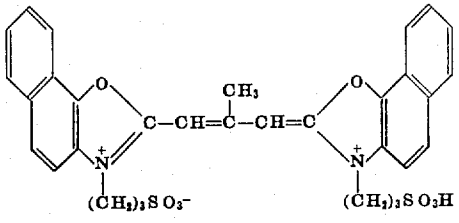
Comparison Dye B



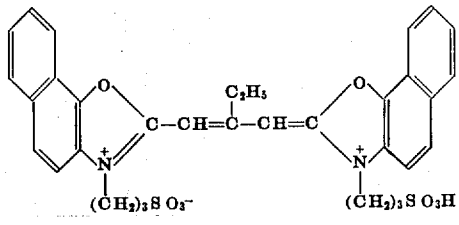
Comparison Dye C



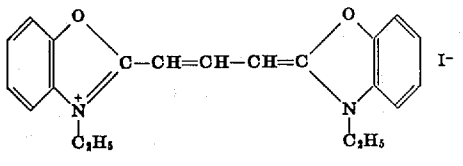
Comparison Dye D



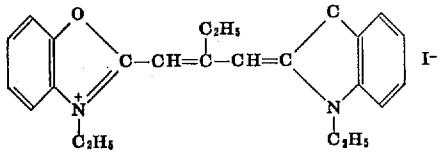
Comparison Dye E



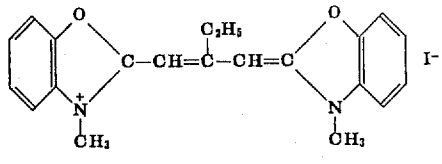
Comparison Dye F



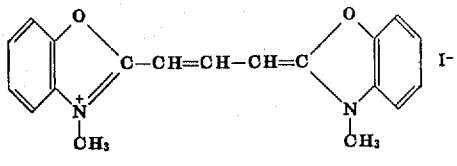
Comparison Dye G



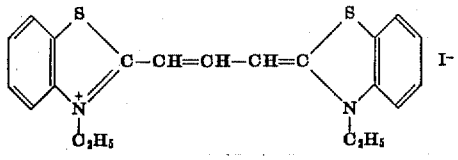
Comparison Dye H



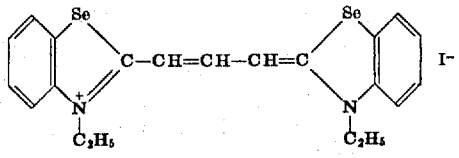
Comparison Dye I



Comparison Dye J



Comparison Dye K



It has already been disclosed in Japanese Patent publication No. 4125/1968, U.S. Pat. No. 2,323,187 and French Patent No. 1,520,822 that sensitizing cyanine dyes and merocyanine dyes are suitable for use to raise the spectral sensitivity of a direct positive silver halide photographic emulsion.

In the case of the spectral sensitization of a direct positive photographic emulsion with a sensitizing dye, however, the photographic characteristics of reversal, that is, spectral sensitivity, contrast, minimum density and re-reversal, differ with the variety of sensitizing dyes. This is unlike the spectral sensitization of the ordinary nonfogged emulsion. It is found that these photographic characteristics differ remarkably depending on the difference of structure, i.e., heterocyclic ring, or a sensitizing dye.

In the case where an ordinary sensitizing cyanine dye or merocyanine dye is incorporated into a direct positive silver halide photographic emulsion, there is a tendency for an increase of spectral sensitivity to be accompanied by a lowering of contrast, an increase of minimum density and an increase of "re-reversal."

As will be apparent from the examples described below, a direct positive silver halide photographic emulsion sensitized with a dye having at least one naphtho (2,3d) oxazole nucleus represented by the general formula (I) or (II) has more excellent characteristics, such as higher sensitivity, less re-reversal and lower minimum density than an emulsion sensitized with a dye having no naphtho (2,3 d) oxazole nucleus, for example, benzoxazole, benzothiazole, naphtho (2,1 d) oxazole or naphtho (1,2) oxazole nucleus. A high-sensitive direct positive silver halide photographic emulsion can be obtained by incorporating a sensitizing dye represented by the general formula (I) or (II) into a direct positive silver halide photographic emulsion. The thus-sensitized emulsion is particularly suitable for use in the copying of documents.

Ordinarily it is preferable to add a dye of the general formula (I) or (II) to an emulsion in the form of a solution in a suitable solvent such as water, methanol or ethanol.

The amount of the dye to be added to a direct positive silver halide emulsion is substantially the same as in ordinary silver halide nonfogged emulsions, i.e., 0.5–50 mg. per kg. of the emulsion. One or more of the dyes may be used.

Silver salts such as silver chloride, silver bromide, silver chlorobromide, silver chloroiodide, silver iodobromide and silver chloroiodobromide may be used as the emulsion in the present invention.

The emulsifying and physical ripening of the silver halide emulsion used in the present invention are carried out in a manner similar to that employed for ordinary emulsions but, before emulsifying or during the physical ripening, a salt of a Group VIII metal, such as iridium or rhodium, may be added thereto. The silver halide emulsion used in the present invention is fogged to its maximum density by light or by adding a chemical fogging agent thereto. Such a chemical fogging agent must fog the silver halide without attacking it. Ordinarily, thiourea dioxide, stannous chloride, formaldehyde, or hydrazine may be used. After the fogging, the pH and pAg are controlled, as the occasion demands, and a solution of the dye of the present invention is then added to the emulsion with sufficient agitation and then coated onto a support. Ordinary additives such as coating aids and hardeners may be added to the emulsion.

The following may be employed as the support: glass, a cellulose derivative film, a synthetic resin film or baryta paper.

The following examples further illustrate the present invention and are not intended to limit the same in any manner.

EXAMPLE I

A silver chloroiodobromide emulsion (iodine 1.3 mol percent, bromine 2.4 mol percent) was fogged with hydrazine dihydrochloride and the pH and pAg were respectively adjusted to 5.6 and 6.7. A predetermined amount of a dye solution having a concentration of 1×10^{-3} mol/l was added to the emulsion, stirred adequately, applied to a cellulose triacetate base and dried. The resulting silver halide direct positive photographic light-sensitive material was exposed through a step wedge by means of a sensitometer. The light-sensitive material was then developed with the following developer:

DEVELOPER

metol —4 g.
hydroquinone —10 g.
anhydrous sodium sulfite —60 g.
anhydrous sodium carbonate —2.5 g.
mater to make —1 l.

The developed material was fixed with an ordinary sodium thiosulfate-containing fixing solution, washed with water and dried. Measurement of the optical density was carried out by means of a densitometer. The results are shown in table 1.

The sensitivity is represented by a relative value of the reciprocal of the amount of exposure required for giving a density of from one to 100 times the sensitivity of an emulsion to which no sensitizing dye is added.

TABLE 1

Sample No.	Dye	Addition amount of dye solution per 100 g. of emulsion (ml.)	Sensitivity	Minimum density
(1)	None		100	0.05
(2)	Dye 1	2	240	0.06
(3)	Dye 2	2	675	0.07
(4)	Dye 7	4	1,660	0.10
(5)	Dye 8	4	1,590	0.09
(6)	Dye 9	4	2,760	0.06

EXAMPLE II

A procedure similar to that described in example I was repeated except that a silver chloroiodide (iodine 1.3 mol percent) was used in place of the silver chloroiodobromide. The results are shown in table 2.

TABLE 2

Test No.	Dye	Addition amount of dye solution per 100 g. of emulsion (ml.)	Sensitivity	Minimum density
a	None		100	0.05
b	Dye 4	1	2,770	0.05
c	B (comparison)	1	283	0.22
d	C (comparison)	1	250	0.11
e	Dye 5	1	2,000	0.66
f	D (comparison)	1	437	0.11
g	Dye 6	1	3,640	0.05
h	E (comparison)	1	215	0.07
i	Dye 3	4	1,590	0.07
j	A (comparison)	4	250	0.15

It is evident from table 2 that the dyes having a naphtho (2,3 d) oxazole nucleus produce higher sensitivities and smaller minimum densities than the dyes having a naphtho (2,1 d) oxazole nucleus or a naphtho (1,2 d) oxazole nucleus.

EXAMPLE III

A silver chloroiodobromide emulsion (iodine 1.0 mol. percent, bromine 30 mol percent) was fogged with hydrazine dihydrochloride and the pH and pAg were respectively adjusted to 5.6 and 6.7. A predetermined amount of a solution of sensitizing dye having a concentration of 1×10^{13} mol/l was added to the emulsion, stirred adequately and applied to a cellulose triacetate base. After drying, the resulting photographic material was exposed through a step wedge by means of a sensitometer. The material after exposure was developed at 20° C. for 2 minutes with the following developer. The developer was used within 6 hours after preparation.

Developer

anhydrous sodium sulfite —30 g.
paraformaldehyde —7.5 g.
potassium metabisulfite —2.6 g.
boric acid —7.5 g.
hydroquinone —22.5 g.
potassium bromide —1.6 g.
water to make —1 l.

The results are shown in table 3, in which tests *a'* to *f'* employ emulsions obtained from the same batch, and tests *g'* to *j'* employ emulsions obtained from another batch.

TABLE 3

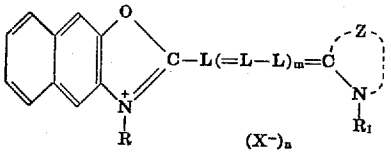
Test No.	Dye	Addition amount of dye solution per 100 g. of emulsion (ml.)	Sensitivity	Gamma	Minimum density
a'	None		100	4.2	0.05
b'	Dye 3	1	1,010	4.1	0.06
c'	G (comparison)	1	320	3.2	0.17
d'	H (comparison)	1	280	2.8	0.18
e'	I (comparison)	1	355	3.2	0.17
f'	K (comparison)	1	195	2.3	0.25
g'	None		100	4.1	0.04
h'	Dye 8	2	2,890	4.1	0.04
i'	J (comparison)	2	1,520	3.5	0.06
j'	F (comparison)	2	892	3.8	0.08

In FIG. 2, curves 2, 3 and 4 are the characteristic curves of *a'*, *c'* and *b'* in table 3, respectively.

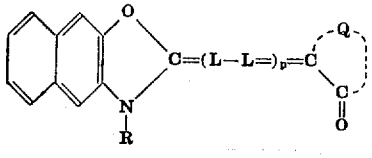
What is claimed:

1. A fogged direct positive silver halide photographic emulsion containing at least one cyanine for merocyanine-sensitizing dye, said dye having at least one naptho (2,3 d) oxazole nucleus.

2. The fogged direct positive silver halide photographic emulsion as in claim 1, where said dye is selected from the group represented by the following formulas



and

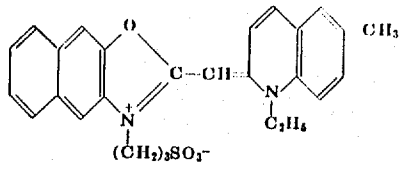


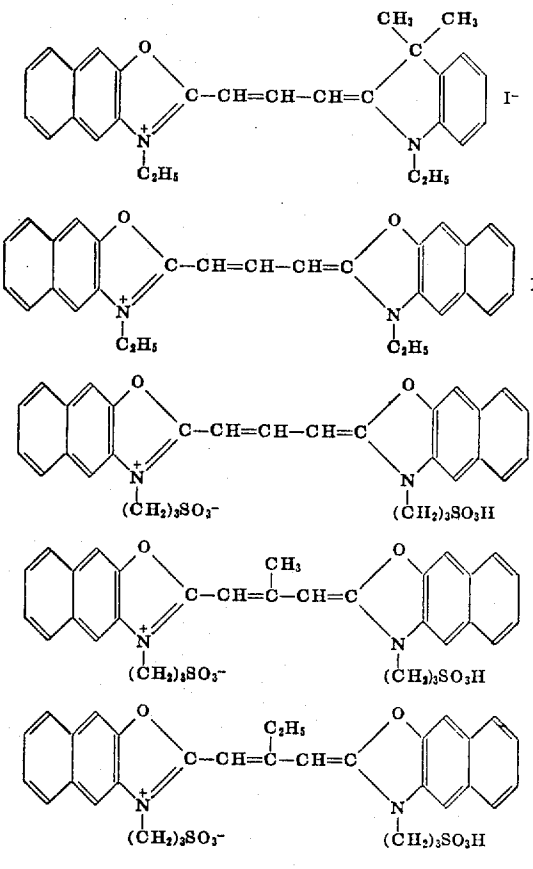
wherein R and R_1, which may be the same or different, each represents an alkyl group, an alkoxyalkyl group, a hydroxyalkyl group, a carboxyalkyl group, a sulphoalkyl group, an allyl group, an aralkyl group, or a substituted aralkyl group; L is a methine chain or a methine chain substituted by alkyl or aryl groups; Z is an atomic group necessary to complete a five- or six-membered nitrogen containing heterocyclic nucleus; Q is an atomic group necessary to complete a five- or six-membered heterocyclic nucleus; m and p are individually 0, 1 or 2; X is an anion and n is 0 or 1.

3. The fogged direct positive silver halide photographic emulsion as in claim 2, wherein said nitrogen-containing heterocyclic nucleus is selected from the group consisting of oxazolines, oxazoles, benzoxazoles, naphthoxazoles, thiazolines, thiazoles, benzothiazoles, naphthothiazoles, selenazoles, benzoselenazoles, napthoselenazoles, quinolines and pyridines, and wherein said heterocyclic nucleus is selected from the group consisting of rhodanines, oxazolido-5-on-2-thiones, thiohydantoines, pyrazole-5-ons and thiobarbituric acids.

4. A photographic element comprising a support having thereon at least one layer of the fogged direct positive silver halide emulsion of claim 1.

5. A fogged direct positive silver halide photographic emulsion containing from 0.5 to 50 mg. per kg. of emulsion, of a dye selected from the group consisting of compounds represented by the following formulas:





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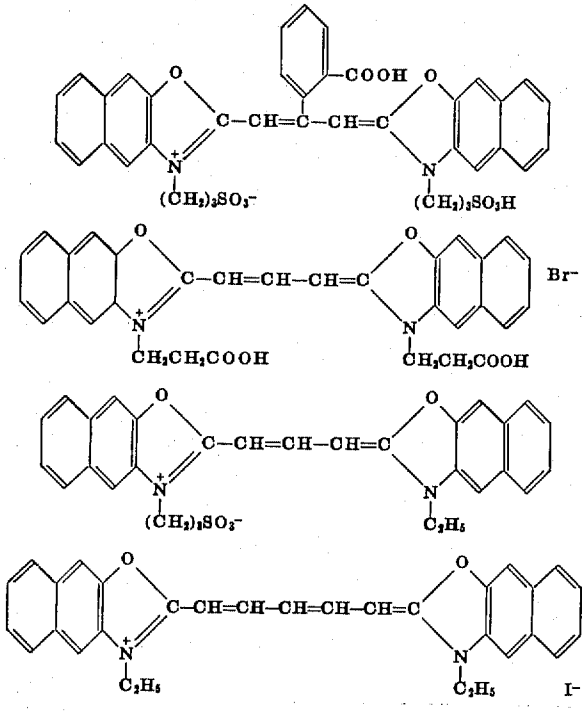

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