(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 437 117 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **90314462.4**

(51) Int. Cl.5: **G03C 5/16**, G03C 7/30

(22) Date of filing: **31.12.90**

(30) Priority: **10.01.90 JP 2949/90**

(43) Date of publication of application:
17.07.91 Bulletin 91/29

(84) Designated Contracting States:
DE GB IT

(71) Applicant: **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome Shinjuku-ku
Tokyo(JP)

(72) Inventor: **Nagasaki, Satoru**
c/o Konica Corporation, 1 Sakuramachi
Hino-shi, Tokyo(JP)

(74) Representative: **Brock, Peter William et al**
URQUHART-DYKES & LORD 91 Wimpole Street
London W1M 8AH(GB)

(54) Light sensitive silver halide photographic material improved in diagnosic properties.

(57) Disclosed is a light-sensitive silver halide photographic material comprising:
a support;
a first light-sensitive unit comprising a first light-sensitive layer and a first non-light-sensitive layer; and
a second light-sensitive unit comprising a second light-sensitive layer and a second non-light-sensitive layer,
the first light-sensitive unit being provided on one side of the support and the second light-sensitive unit being provided on the other side of the support,
wherein a sensitivity of the first light-sensitive unit when exposure is effected only from the one side (sA), a sensitivity of the second light-sensitive unit when exposure is effected only from the other side (sB) and a sensitivity of the first light-sensitive unit when exposure is effected only from the other side (sA') satisfy the following equations:

(I) $sA/sA' > 4.0$

(II) $sA/sB = 1.5$ to 20

EP 0 437 117 A1

LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL IMPROVED IN DIAGNOSTIC PROPERTIES

BACKGROUND OF THE INVENTION

This invention relates to a light-sensitive silver halide photographic material for medical use excellent in sensitivity and sharpness, and also improved in diagnostic properties.

In recent years, in light-sensitive silver halide photographic materials, a higher level of photographic performances such as high sensitivity, excellent graininess, high sharpness and high covering power has been demanded. To cope with such demand, for example, various complicated technical means such as control of a crystal habit of a silver halide crystal itself, a grain size distribution or a distribution of iodine concentration in each grain have been studied and put to practical use.

Particularly, in light-sensitive silver halide photographic materials for medical use, since a minute change in a morbid state should be found accurately to improve diagnostic properties, sharpness of images after development is considered to be extremely important. For example, Japanese Unexamined Patent Publications No. 28827/1975, No. 185038/1982 and No. 158430/1989 disclose improvements in sharpness by incorporating a water-soluble dye in a light-sensitive layer and/or a layer adjacent thereto. However, according to these methods of the prior art, both of sensitivity and sharpness cannot be improved simultaneously, and there involves a drawback that when sharpness is improved, sensitivity is lowered. Accordingly, development of a technique which can improve sharpness without lowering sensitivity and also improve diagnostic properties has been strongly demanded.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a light-sensitive silver halide photographic material for medical use improved in sharpness without impairing sensitivity and also improved in diagnostic properties. Other objects of the present invention will be apparent from the following description.

The present inventors have studied intensively to improve sharpness, and consequently found that the above object can be accomplished by the method described below, to accomplish the present invention.

That is, the object of the present invention can be accomplished by:

(1) a light-sensitive silver halide photographic material comprising:

a support;

a first light-sensitive unit comprising a first light-sensitive layer and a first non-light-sensitive layer; and

a second light-sensitive unit comprising a second light-sensitive layer and a second non-light-sensitive layer,

said first light-sensitive unit being provided on one side of said support and said second light-sensitive unit being provided on the other side of said support,

wherein a sensitivity of said first light-sensitive unit when exposure is effected only from said one side (sA), a sensitivity of said second light-sensitive unit when exposure is effected only from said other side (sB) and a sensitivity of said first light-sensitive unit when exposure is effected only from said other side (sA') satisfy the following equations:

(I) $sA/sA' > 4.0$

(II) $sA/sB = 1.5$ to 20

(2) the light-sensitive silver halide photographic material described in (1), wherein a ratio of a covering power of the A surface to that of the B surface is 1 : 1.5 or more (that of the B surface is larger than that of the A surface), and

(3) the light-sensitive silver halide photographic material described in (1), wherein at least one of the light-sensitive silver halide photographic emulsion layer and the hydrophilic colloidal layer at the B surface side contains at least one water-soluble dye.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following, the present invention will be explained in more detail.

In the present invention, a sensitivity of a light-sensitive silver halide photographic material refers to a value determined according to the following method.

1. Exposure conditions

1-1. Fluorescent screen to be used (which varies depending on a light-sensitive wavelength of a film

used)

(a) In the case of a light-sensitive material having a sensitivity to blue region (a regular light-sensitive material)

Fluorescent screen mainly composed of $CaWO_4$ (e.g. a series of NR's manufactured by Konica Corporation)

(b) In the case of a light-sensitive material having a sensitivity to green region (an ortho light-sensitive material)

Fluorescent screen mainly composed of Gd_2O_2S activated with Tb (e.g. a series of KO's manufactured by Konica Corporation)

1-2. X-ray irradiation conditions

Voltage in tube:	70 Kvp
Current in tube:	100 mA
Time :	100 msec
Distance :	1.85 m
Grid :	unused

1-3. Exposure method

After a fluorescent screen is placed only on a back side of a cassette and a sample (film) is laminated thereon, exposure is effected through aluminum steps under the above conditions 1-2.

2. Development

Developing solution:	XD-90 (available from Konica Corporation)
Developing temperature:	35 °C
Fixing solution :	XF (Ditto)
Fixing temperature :	33 °C
Developing machine :	KX-500 (Ditto)

3. Method for measuring sensitivity

As for samples after development, a sample exposed only from an A surface side is divided into two pieces. From one piece, a B surface is removed for measuring sA, and from the other piece, an A surface is removed for measuring sB'. Next, also from a sample exposed only from a B surface side, an A surface and a B surface are removed in the same manner for measuring sB and sA', respectively. For four kinds of samples obtained, characteristic curves are measured, and from the characteristic curves obtained, reciprocals of exposure dosages required for obtaining a density of base density + fog density + 1.0 are determined to obtain sA, sB, sA' and sB'.

In the case of light-sensitive materials having sensitivities to red region and infrared region, an exposure method varies depending on each light-sensitive material.

The A surface and the B surface of the light-sensitive silver halide photographic material according to the present invention have a sensitivity of $sA/sA' > 4.0$, preferably 4.5 or more, more preferably 5.0 to 15.0.

Further, the sensitivity of the material is preferably sA/sB of 1.5 to 20, more preferably 2.5 to 10.

As a method for making a sensitivity difference between an emulsion on an A surface and that of an emulsion on a B surface, various methods can be mentioned. As one of the methods to do so, at least one of the light-sensitive silver halide photographic emulsion layer and the hydrophilic colloidal layer at the B surface side contains at least one water-soluble dye.

As another method, as a silver halide grain at the B surface side, one kind of grains with a small grain size is used, or when a plural kinds of grains are mixedly used, these grains are combinedly used so as to become an average grain size of the mixture small. Here, "small" means that the grain size of the B surface side is 70 to 80 % or less of that of the A surface side.

As the water-soluble dye, those generally known in the art can be employed.

In a preferred embodiment of the present invention, silver halide grains with a small grain size is used at the B surface side, and at least one of the above silver halide emulsion layer and the hydrophilic colloidal layer contains the dye as described above.

Next, a covering power mentioned in the present invention is a photographic density obtained by a predetermined amount of silver, and defined as described below.

Specifically, a covering power (C.P) is represented by the following formula:

C.P (covering power) = D/S x 1,000

S = Amount of silver (mg) per 100 dm^2 of one surface of light-sensitive material after development

D = Density of one surface of the light-sensitive material after development

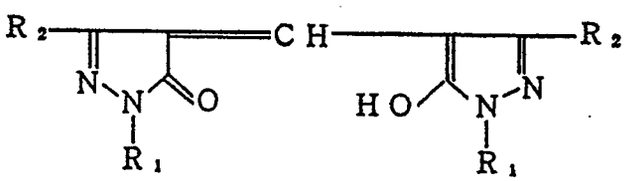
wherein the density (D) is a density obtained by measuring by means of a densitometer PDA-65 (trade name, manufactured by Konica Corporation) the light-sensitive material which has been exposed by using an incandescent lamp of 100 W at a voltage of 50 V for 3 seconds and developed by using XD-90 and XF (trade name, each available from Konica Corporation) and an automatic processor KX-500 (trade name, manufactured by Konica Corporation) at a developing temperature of 35 °C.

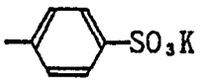
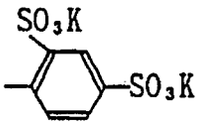
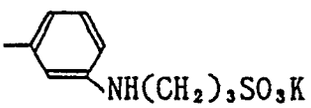
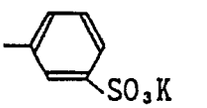
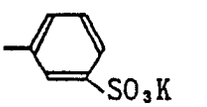
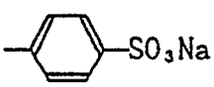
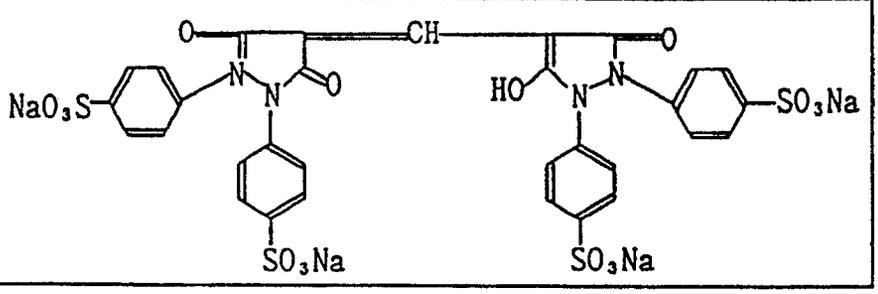
When a ratio of the covering power of the A surface to that of the B surface of the light-sensitive silver halide photographic material according to the present invention is 1 : 1.5 or more (the covering power of the B surface is larger than that of the A surface), preferably 1 : 1.5 to 5.0, more preferably 1 : 1.5 to 2.0, the effect of the present invention can be exhibited favorably.

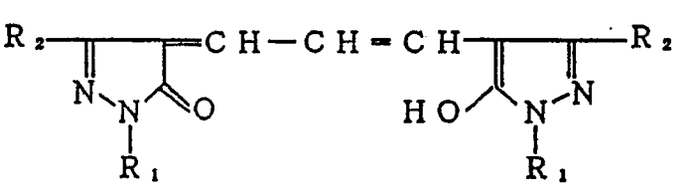
In the following, the dye which is used preferably in the present invention will be explained in more detail.

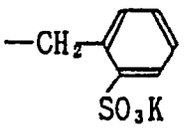
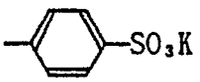
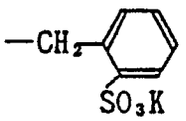
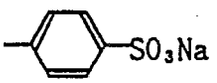
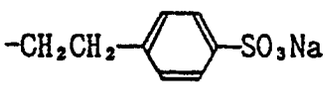
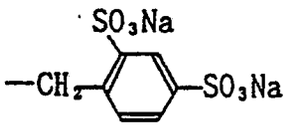
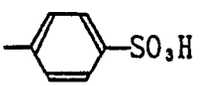
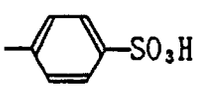
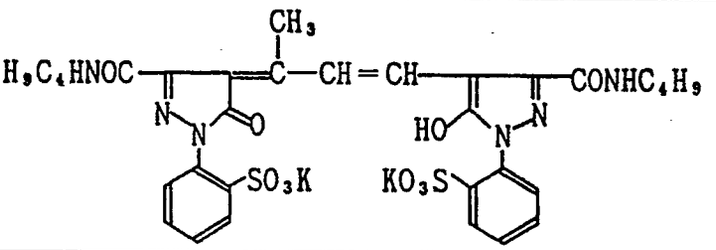
The dye which can be used in the present invention include, for example, arylidene dyes disclosed in U.K. Patents No. 584,609 and No. 1,210,252, U.S. Patents No. 2,538,008, No. 2,538,009, No. 2,688,541 and No. 4,420,555, styryl dyes disclosed in Japanese Patent Publications No. 3082/1953, No. 16594/1969 and No. 28898/1984, merocyanine dyes disclosed in U.S. Patents No. 3,486,897, No. 2,706,193, No. 3,260,601 and No. 4,035,190, cyanine dyes disclosed in U.S. Patents No. 2,843,486, No. 3,294,539 and No. 3,615,562, oxonol dyes disclosed in U.S. Patents No. 3,247,127, No. 3,469,985, No. 4,078,933, No. 2,533,472 and No. 3,379,533, azo dyes disclosed in U.S. Patent No. 3,671,254 and Japanese Unexamined Patent Publication No. 211043/1984 and azomethine dyes disclosed in U.K. Patents No. 750,031 and No. 2,014,598. Among them; preferred are dyes which can be decolored in a developing solution and a fixing solution containing a sulfite (e.g. arylidene dyes, styryl dyes, merocyanine dyes, cyanine dyes and oxonol dyes).

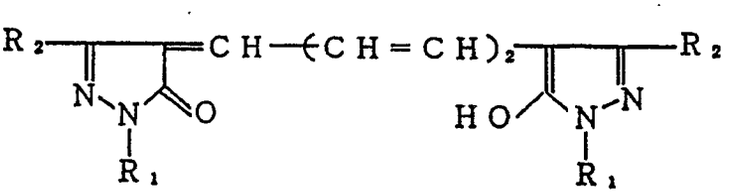
Specific examples of the dye to be used in the present invention are shown below, but the present invention is not limited to these examples.

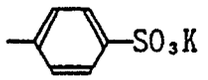
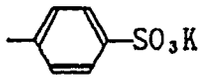
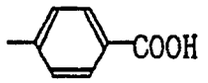


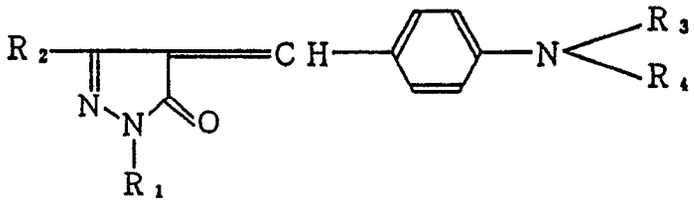
No.	R_1	R_2
1		$-NHCOC_4H_9$
2		$-NHCOC_6H_{13}$
3	$-(CH_2)_4SO_3K$	$-NHCOC_4H_9$
4	$-(CH_2)_2SO_3K$	$-CONHC_4H_9$
5		$-CONHC_4H_9(i)$
6		$-NHCO(CH_2)_7OH$
7		CH_3
8		$C_4H_9(t)$
9		

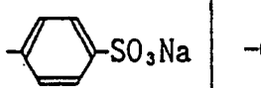
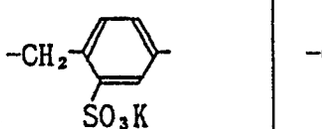
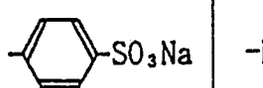
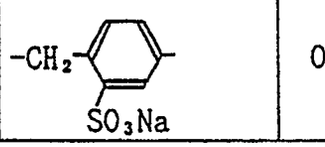


No.	R_1	R_2
10	$(CH_2)_3SO_3K$	$-CONHC_5H_{11}(i)$
11		$-CONHC_4H_9$
12		$-CONHC_4H_9$
13		$-CONHC_4H_9(i)$
14		$-CONHC_7H_{15}$
15		$-NHCOC_4H_9$
16		$-CONHC_5H_{11}$
17		$-CH_3$
18		$-COOH$
19		

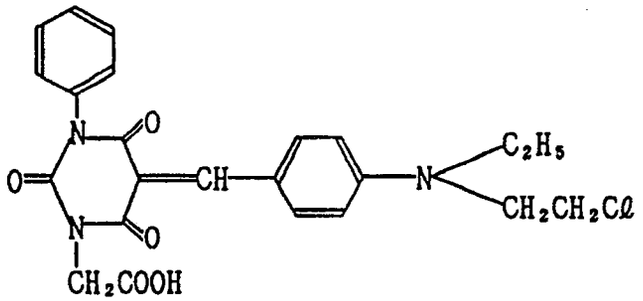


No.	R_1	R_2
20		—COOH
21		—$CONHC_4H_9$
22	—CH_2CH_2COOH	—$NHCOC_4H_9$(sec)
23	—$(CH_2)_3SO_3K$	—$CONHC_4H_9$(i)
24		—$NHCOC_4H_9$(i)

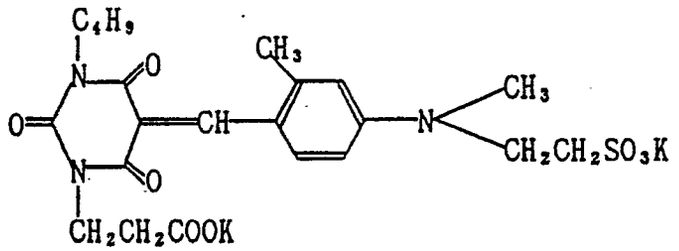


No.	R_1	R_2	R_3	R_4
25		$-OC_2H_5$	C_2H_5	$CH_2CH_2SO_3Na$
26		$-CH_3$	CH_2CH_2CN	CH_3
27		$-NHCH_3$	$-C_2H_5$	$-(CH_2)_2SO_3Na$
28	$-(CH_2)_3SO_3K$	CH_3	CH_3	CH_3
29		OC_2H_6	$-CH_2CH_2CN$	$-CH_2CH_2CN$

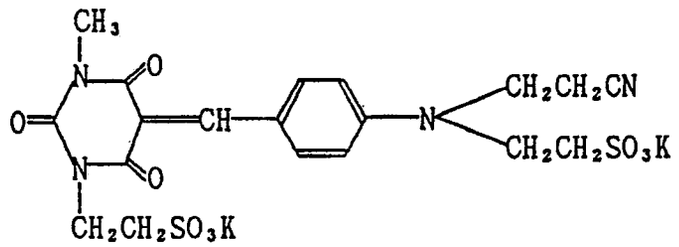
30

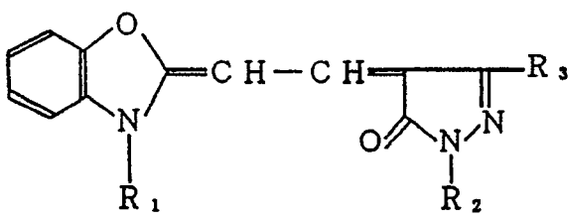


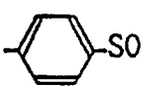
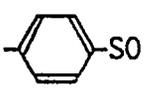
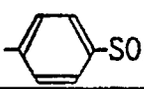
31



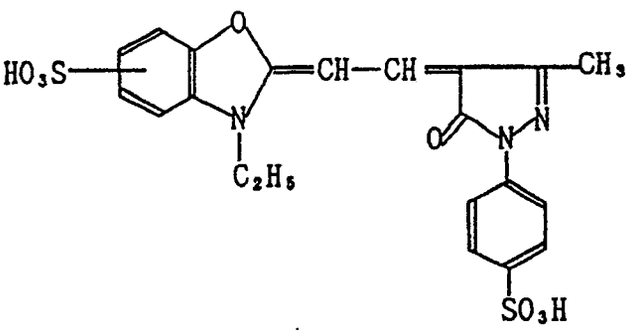
32



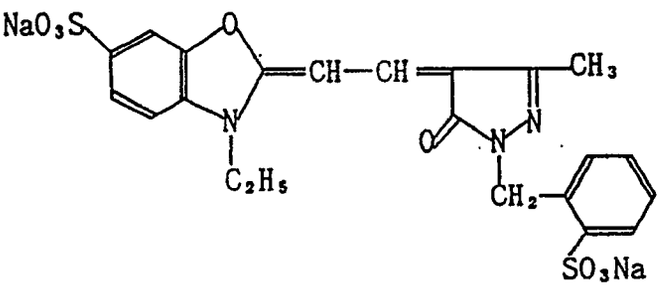


No.	R_1	R_2	R_3
33	$-(CH_2)_3SO_3K$	$-(CH_2)_3SO_3K$	$-NHCOCH_3$
34	$-(CH_2)_4SO_3Na$		$-OH$
35	$-(CH_2)_4SO_3Na$		$-CN$
36	$-C_2H_5$		$-CH_3$

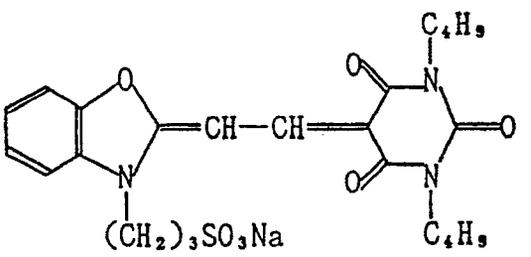
37



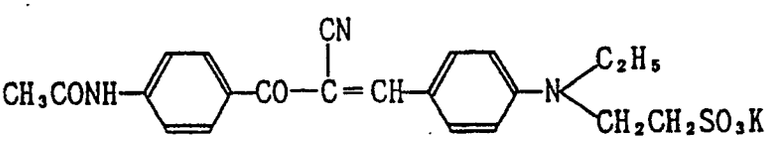
38



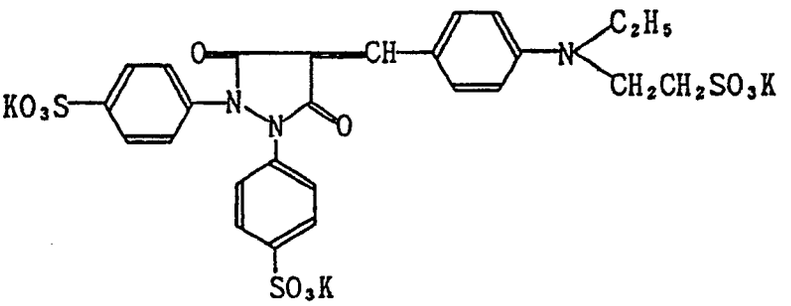
39



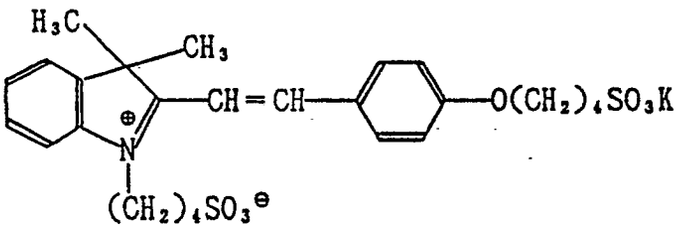
40



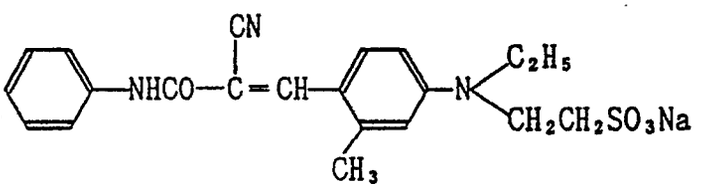
41



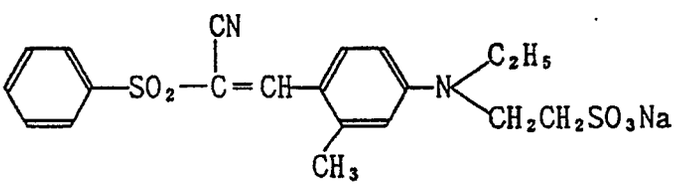
42



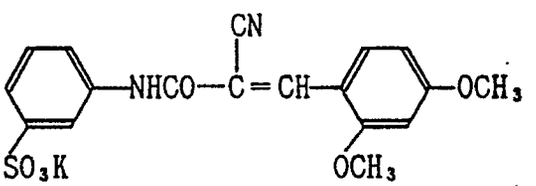
43



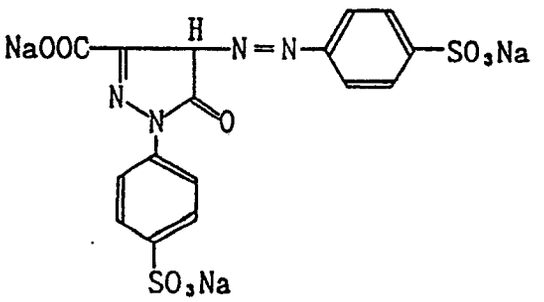
44



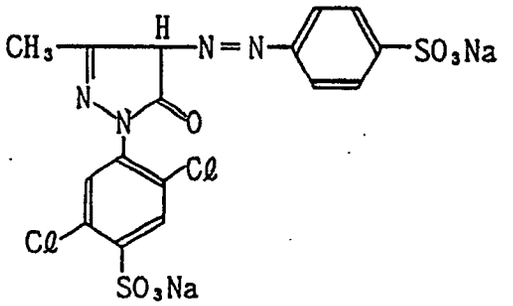
45



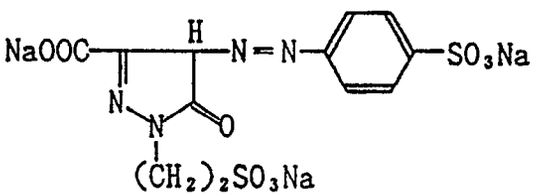
46



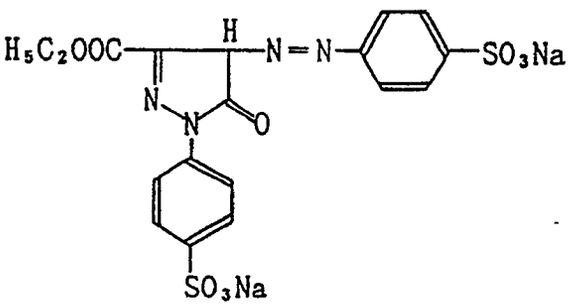
47



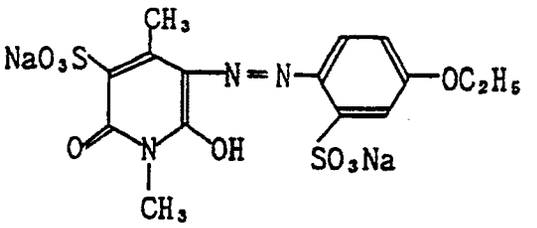
48



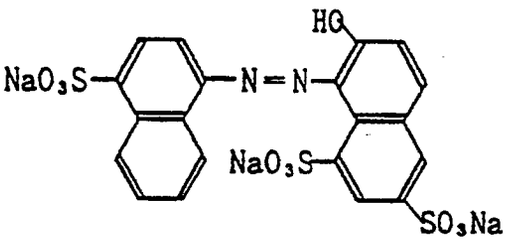
49



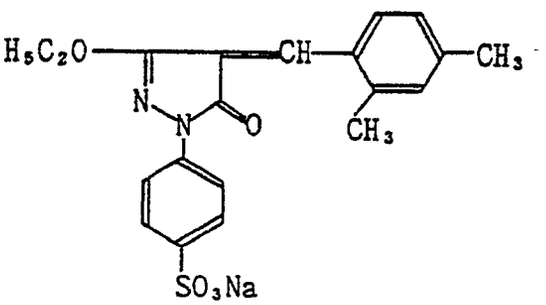
50



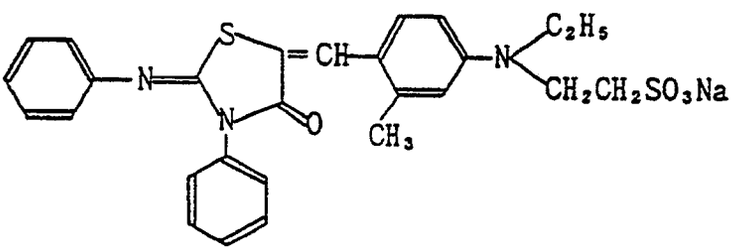
51



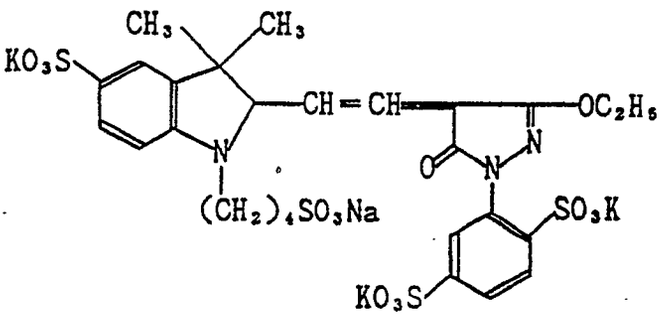
52



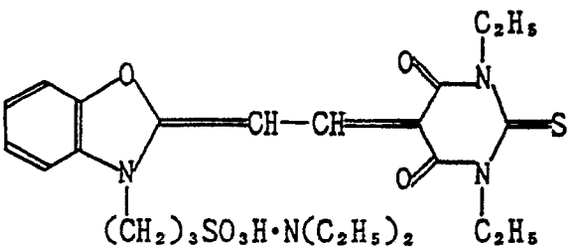
53



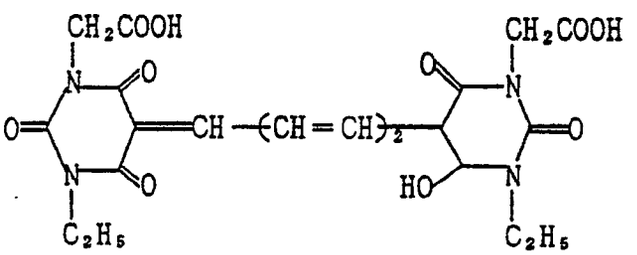
54



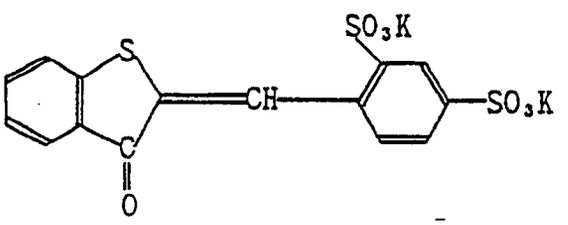
55



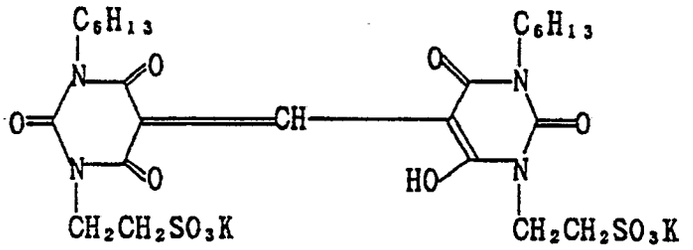
56



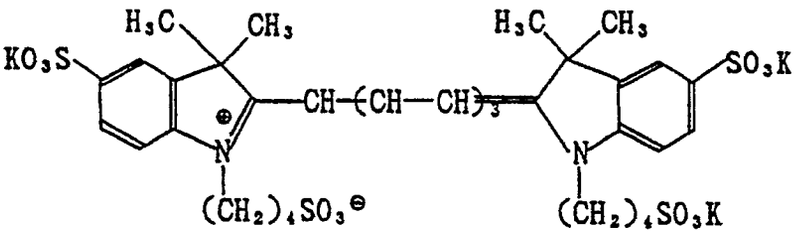
57



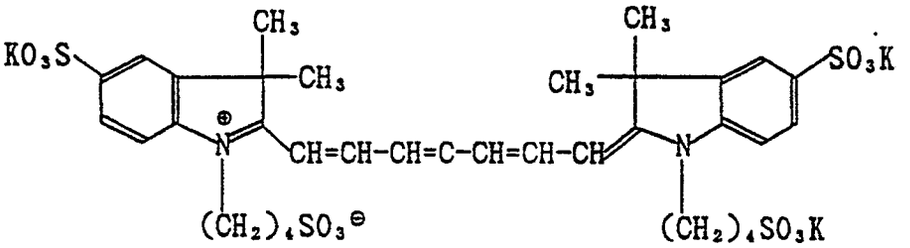
58



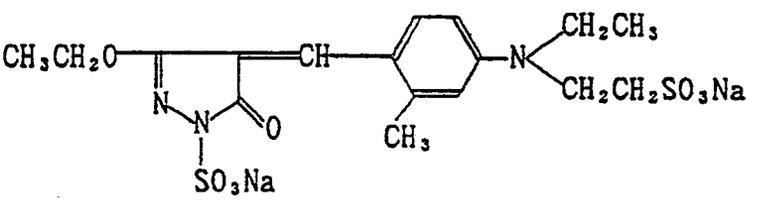
59



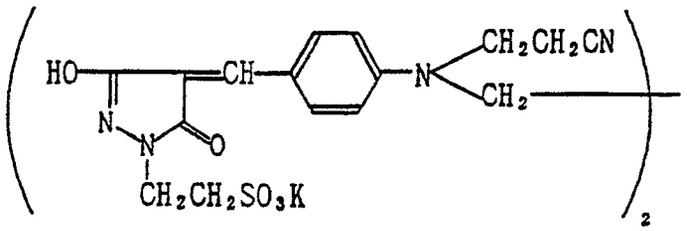
60



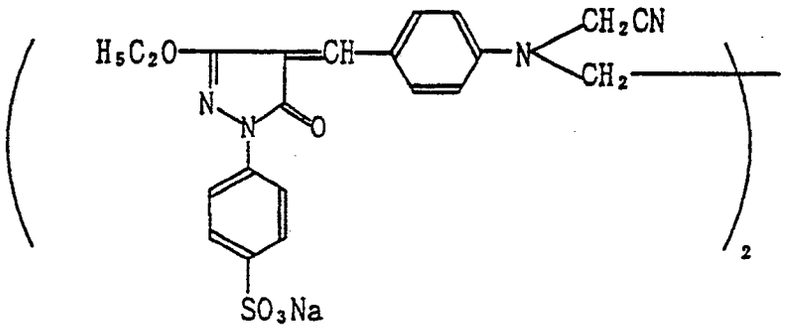
61



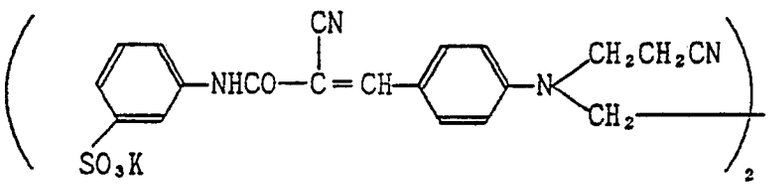
62



63



64



As a layer in which the dye as described above is to be contained, any layer may be selected, but the dye may be contained in at least one layer of a light-sensitive emulsion layer and other hydrophilic colloidal layers at the side where said emulsion layer is coated (e.g. non-light-sensitive layers such as an intermediate layer, a protective layer, a subbing layer and a mordant layer) or may be contained by dispersing therein. Preferably, the dye may be contained in a silver halide emulsion layer or a layer nearer to a support than the silver halide emulsion layer or in both of these layers.

The amount of the above dye to be added is preferably 0.2 mg/m^2 to 150 mg/m^2, more preferably 0.8 mg/m^2 to 50 mg/m^2.

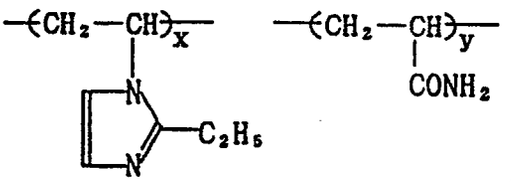
The dye can be introduced into a hydrophilic colloidal layer according to a conventional method. Specifically, the dye is prepared to be an aqueous solution having an appropriate concentration, and when an emulsion layer is colored, the aqueous solution of the dye may be added in a silver halide emulsion or an aqueous hydrophilic colloidal solution before coating, and then coated.

The dye according to the present invention may be carried within a layer by using a mordant.

For example, as a mordant which can make a dye nondiffusible by bonding at least one dye as described above to a mordant, compounds disclosed in, for example, U.S. Patents No. 2,548,564, No. 2,675,316, No. 2,795,519, No. 2,839,401, No. 2,882,156, No. 3,048,487, No. 3,184,309, No. 3,444,138, No. 3,445,231, No. 3,706,563, No. 3,709,690 and No. 3,788,855 can be preferably used.

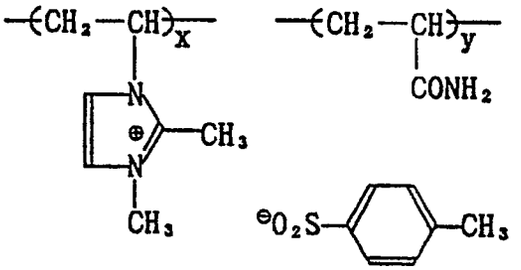
Specifically, the following compounds are included.

1 .



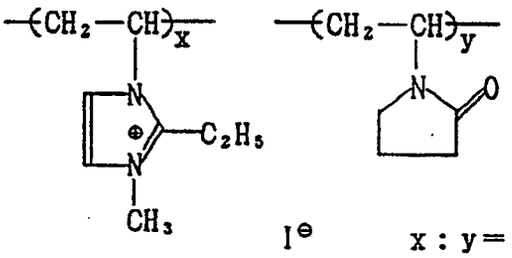
x : y = 25 : 75

2 .



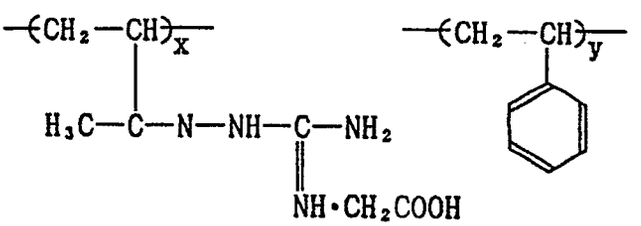
x : y = 25 : 75

3 .



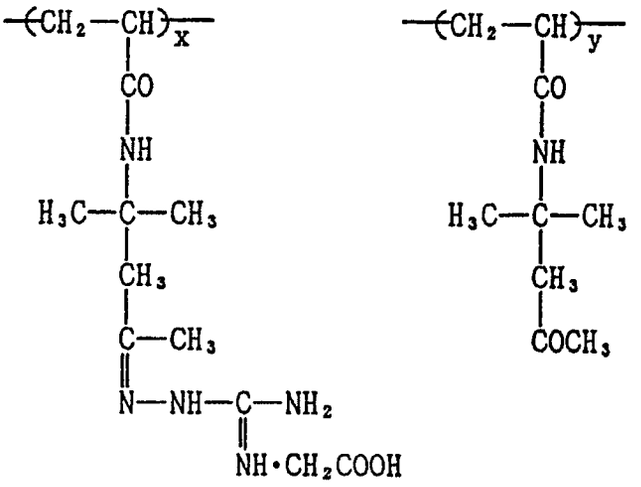
x : y = 66.7 : 33.3

4 .



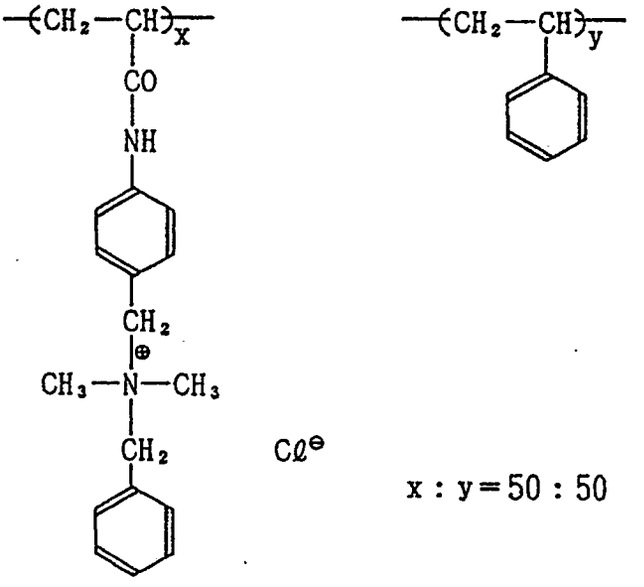
x : y = 66.7 : 33.3

5 .



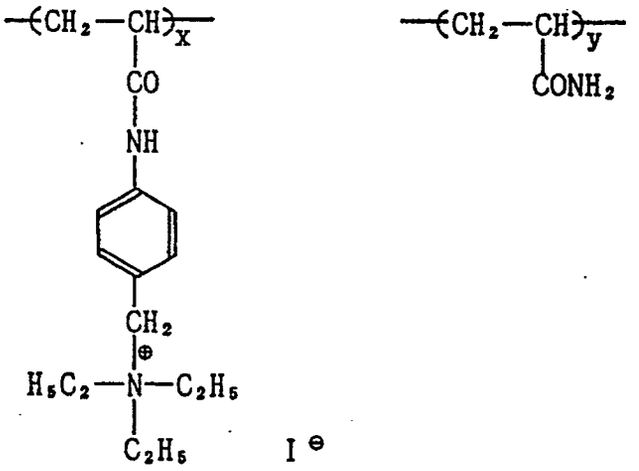
x : y = 75 : 25

6 .



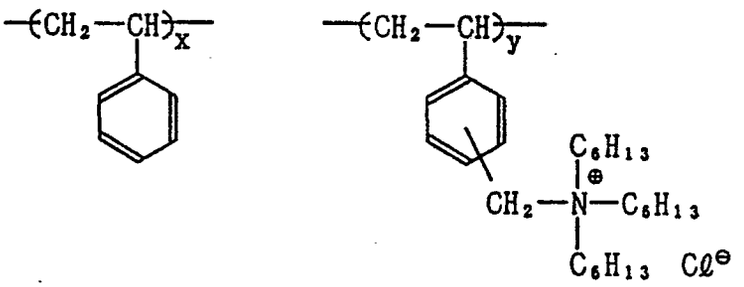
x : y = 50 : 50

7.



x : y = 50 : 50

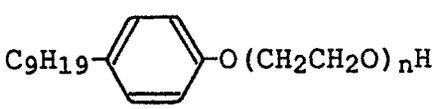
8.



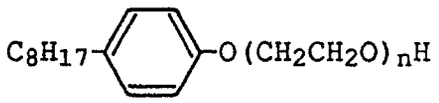
x : y = 50 : 50

In the present invention, as a nonionic surfactant to be used when employed as a mordant layer, nonionic surfactants known in the art may be used.

Specific examples of the nonionic surfactant useful in the present invention are shown below.



(n = 15 to 30)



(n = 10)

$C_{12}H_{25}O(CH_2CH_2O)_nH$

(n = 10 to 15)

$C_8H_{17}O(CH_2CH_2O)_nH$

(n = 10 to 20)

The hydrophilic colloidal layer mentioned in the present invention refers to a hydrophilic layer provided in layers of a light-sensitive silver halide photographic material, and refers to various layers which contain a binder component such as gelatin and are necessary for a light-sensitive material for photography such as a silver halide emulsion layer, a protective layer, an intermediate layer, an antihalation layer, a filter layer, a development controlling layer, an UV absorbing layer and a prime-coating layer.

In the most preferred embodiment of the present invention, on one surface of a polyethylene terephthalate film support of which both surfaces have been subjected to a subbing treatment, a high sensitivity silver halide emulsion layer is coated as an A surface, and a protective layer containing gelatin as a binder component is provided thereon.

Next, on the opposite surface thereof, a low sensitivity silver halide emulsion layer having a sensitivity different from that of the A surface is coated as a B surface. In said emulsion layer, the water-soluble dye according to the present invention may be added and contained, and further, a hydrophilic colloidal layer (e.g. a gelatin layer containing a dye or a mordant layer on which a dye is carried) may be provided above or under said emulsion layer.

The emulsion to be used in the light-sensitive silver halide photographic material of the present invention may be any silver halide such as silver iodobromide, silver iodochloride and silver iodochlorobromide, but silver iodobromide is preferred since a light-sensitive material having a particularly high sensitivity can be obtained.

The silver halide grains in the photographic emulsion may have any shape such as cube, octahedron and tetradecahedron which grow in an isotropic manner, or polyhedral crystal such as sphere and twin having defects in phases or a mixture or complex thereof. The silver halide grains may have a grain size of from 0.1 μm (fine particles) or less to 20 μm (big particles).

The emulsion to be used in the light-sensitive silver halide photographic material of the present invention can be prepared according to the known method. For example, the emulsion can be prepared according to "1. Emulsion Preparing Method (Emulsion Preparation and types)" disclosed at pp. 22 to 23 of Research Disclosure (RD) No. 17643 (December, 1978) and the method disclosed at p. 648 of RD No. 18716 (November, 1979).

As a preferred embodiment of the present invention, a monodispersed emulsion in which silver iodide exists locally internally of its grain can be mentioned. The monodispersed emulsion herein mentioned refers to silver halide grains wherein, for example, when an average grain diameter is measured according to the conventional method, at least 95 % of the grains in terms of the grain number or weight have a grain diameter preferably within ± 40 %, more preferably within ± 30 % of the average grain size. A grain size distribution of the silver halide may be a narrow distribution as in the case of a monodispersed emulsion or a wide distribution as in the case of a polydispersed emulsion.

Crystalline structure of the silver halide may comprise different silver halide compositions at an inner portion and an outer portion.

As a preferred embodiment of the present invention, the emulsion is a core/shell type monodispersed emulsion having a clearly two-layered structure comprising a core portion with a high iodine content and a shell layer with a low iodine content.

An amount of silver iodide in the portion with a high iodine content of the present invention is 20 to 40 mole %, particularly preferably 20 to 30 mole %.

A method for preparing such a monodispersed emulsion is known in the art, and disclosed in, for example, Journal of Photographic Science, vol. 12, pp. 242 to 251 (1963), Japanese Unexamined Patent

Publications No. 36890/1973, No. 16364/1977, No. 142329/1980 and No. 49938/1983, U.K. Patent No. 1,413,748, and U.S. Patents No. 3,574,628 and No. 3,655,394.

As the monodispersed emulsion as described above, particularly preferred is an emulsion in which a seed crystal is used as a growth nucleus and grains are grown by supplying a silver ion and a halide ion. Further, a method for obtaining a core/shell emulsion is disclosed in detail in, for example, U.K. Patent No. 1,027,146, U.S. Patents No. 3,505,068 and No. 4,444,877, and Japanese Unexamined Patent Publication No. 14331/1985.

The silver halide emulsion to be used in the present invention may be a tabular grain having an aspect ratio of 5 or more.

Such a tabular grain have advantages that improvement in spectral sensitizing efficiency and improvement in graininess and sharpness of images can be accomplished, and it can be prepared according to the methods disclosed in, for example, U.K. Patent No. 2,112,157, and U.S. Patents No. 4,439,520, No. 4,433,048, No. 4,414,310 and No. 4,434,226.

The above emulsion may be any emulsion of a surface latent image type in which an latent image is formed on a grain surface, an internal latent image type in which a latent image is formed internally of a grain or a type in which a latent image is formed both on a grain surface and internally of a grain. In the emulsion, during physical ripening or preparation of grains, cadmium salt, lead salt, zinc salt, thallium salt, iridium salt or complex salt thereof, rhodium salt or complex salt thereof and iron salt or complex salt thereof may be used. For removing soluble salts, the emulsion may be subjected to a noodle washing method, a flocculation sedimentation method or an ultra-filtration method. As a preferred washing method, there may be included, as particularly preferred desalting methods, a method of using an aromatic hydrocarbon type aldehyde resin containing sulfo group as disclosed in Japanese Patent Publication No. 16086/1960 and a method of using exemplary compounds G3 and G8 of a coagulating polymeric agent as disclosed in Japanese Unexamined Patent Publication No. 158644/1988.

In the emulsion according to the present invention, in the step of before and after the step of physical ripening or chemical ripening, various additives for photography can be used. As the additives known in the art, compounds disclosed in, for example, Research Disclosure No. 17643 (December, 1978) and Research Disclosure No. 18716 (November, 1979) are included. Kinds of the compounds disclosed in these two Research Disclosures and pages are shown below.

Additive	RD-17643 Page	RD-17643 Class	RD-18716 Page Class
Chemical Sensitizer	23	III	648, light upper column
Sensitizing dye	23	IV	648, right column to 649, left column
Development accelerator	29	XXI	648, right upper column
Antifoggant	24	VI	649, right lower column
Stabilizer	24	VI	
Antistaining agent	25	VII	650, left to right column
Image stabilizer	25	VII	
UV absorber	25 to 26	VIII	649, right column to 650, left column
Filter dye	25 to 26	VIII	
Brightener	24	V	
Hardener	26	X	651, left column
Coating aid	26 to 27	XI	650, right column
Surfactant	26 to 27	XI	650, right column
Plasticizer	27	XII	650, right column
Lubricant	27		
Antistatic agent	27	XII	650, right column
Matte agent	28	XVI	650, right column
Binder	26	IX	651, left column

As a support which can be used in the light-sensitive material according to the present invention, those disclosed on p. 28 of RD No. 17643 and in the left column of p. 647 of RD No. 18716 can be mentioned.

A suitable support is a plastic film. Generally, for enhancing adhesiveness of the support to a coating layer, a prime-coating layer may be provided on a surface of the support or a surface of the support may be subjected to corona discharging or UV ray irradiation. On one surface or both surfaces of the support thus treated, the emulsion according to the present invention can be coated.

The present invention can be applied to all light-sensitive silver halide photographic materials, but it is particularly suitable for high sensitivity black and white light-sensitive materials.

When the present invention is applied to X-ray radiography for medical use, for example, a fluorescent screen composed mainly of a fluorescent substance which emits near ultraviolet light or visible light by irradiating transmissive radiation is employed. It is desired to bring the fluorescent screen close contact with both surfaces of the light-sensitive material comprising the emulsion of the present invention coated on both surfaces thereof and then to effect exposure.

The transmissive radiation herein mentioned refers to an electromagnetic wave with high energy such as X-ray and gamma ray.

The fluorescent screen includes a fluorescent screen comprising a fluorescent component composed mainly of calcium tungstate or a fluorescent screen composed mainly of a rare earth compound activated by terbium.

EXAMPLES

In the following, the present invention is described by referring to Examples. As a matter of course, the present invention is not limited by Examples as described below at all.

Example 1

Monodispersed grains of silver iodobromide containing 2.0 mole % of silver iodide with an average grain size of 0.2 μm were used as nuclei, and silver iodobromide containing 30 mole % of silver iodide was grown at pH 9.3 and pAg 7.5. Subsequently, at pH 7.8 and pAg 8.9, equimolar amounts of potassium bromide and silver nitrate were added to prepare monodispersed emulsion grains (A) with an average grain size of 1.50 μm, (B) with that of 1.20 μm, (C) with that of 0.70 μm and (D) with that of 0.41 μm, respectively, so that all the monodispersed emulsion grains obtained were silver iodobromide grains with an average silver iodide content of 2.3 mole. These emulsions were subjected to desalting to remove excessive salts according to the conventional coagulation method. Specifically, to the emulsions maintained at 40 °C were added a formalin condensate of sodium naphthalenesulfonate and an aqueous solution of magnesium sulfate to effect coagulation. After a supernatant liquid was removed, pure water up to 40 °C was added and then an aqueous solution of magnesium sulfate was added again to effect coagulation, followed by removing a supernatant liquid.

Among the emulsions obtained, (A), (B) and (C) were chemically ripened by adding 2.4×10^{-3} mole of ammonium thiocyanate per mole of silver, an optimum amount of chloroauric acid and hypo, and then stabilized by adding 2×10^{-2} mole of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

To the three kinds of the emulsions obtained were added emulsion additives described below, water-soluble dyes shown in Table 1 and lime-treated gelatin to prepare emulsion coating solutions shown below.

The water-soluble dye was added in the emulsion coating solution for the side of the B surface.

Coating solution 1:	a solution in which a mixing ratio of (A):(B):(C) is 20.0:40.0:40.0
Coating solution 2:	a solution in which a mixing ratio of (A):(B) is 33.3:66.7
Coating solution 3:	a solution comprising only (C)
Coating solution 4:	a solution in which a mixing ratio of (A):(B) is 40.0:60.0
Coating solution 5:	a solution in which a mixing ratio of (A):(B) is 20.0:80.0

Further, a protective film coating solution having a composition shown below was prepared.

The respective coating solutions obtained were coated by two slide hopper type coaters simultaneously on both surfaces of a polyethylene terephthalate base with a thickness of 175 μm subjected to a subbing treatment so as to have a constitution as shown in Table 1, followed by drying for 2 minutes and 50 seconds, to obtain Samples No. 1 to No. 16.

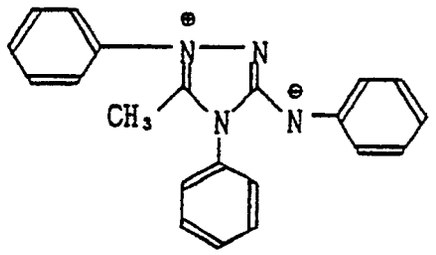
Silver amounts of both A and B surfaces were made 56 mg/dm^2, respectively.

For the samples obtained, according to a method as described below, sensitivities (sA, sA', sB, sB' and Sw) and MTF were measured, and diagnostic properties were evaluated.

The results are shown in Table 1. As a fluorescent screen, NR-160 (manufactured by Konica Corporation) was employed.

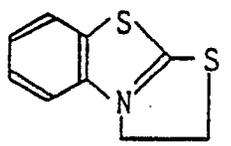
In the emulsions (light-sensitive silver halide coating solutions), the following additives were used. An amount added is indicated as an amount per mole of silver halide.

1,1-Dimethylol-1-bromo-1-nitromethane 65 mg

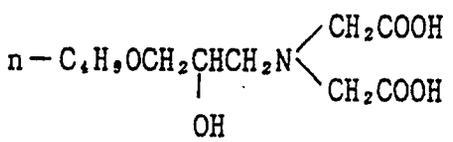


150 mg

t-Butyl-catechol	400 mg
Polyvinyl pyrrolidone (molecular weight: 10,000)	1.0 g
Styrene-maleic anhydride copolymer	2.5 g
Trimethylolpropane	10 g
Diethylene glycol	5 g
Nitrophenyl-triphenylphosphonium chloride	50 mg
Ammonium 1,3-hydroxybenzene-4-sulfonate	4 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	1.5 mg



CH_3SO_3 70 mg

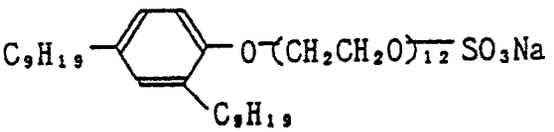
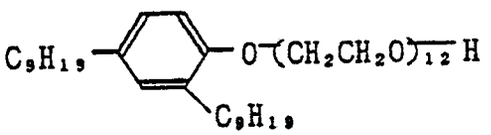


1 g

1-Phenyl-5-mercaptotetrazole 50 mg

The additives used in the protective layer solution are shown below. An amount added is indicated as an amount per liter of the coating solution.

Lime-treated inert gelatin	68 g
Acid-treated gelatin	2 g
$NaO_3S-CH(CH_2COOC_{10}H_{21})-COOC_5H_{11}$ (Coating aid)	1 g
Polymethyl methacrylate, matte agent with an average grain size per unit area of 3.5 μm	1.1 g

Silicon dioxide grains, matte agent with an average grain size per unit area of 1.2 μm	0.5 g
Ludox AM (trade name, available from Du Pont Co.) (colloidal silica)	30 g
2 % Aqueous solution of 2,4-dichloro-6-hydroxy-1,3,5-triazine sodium salt (hardener)	10 ml
40 % Aqueous solution of glyoxal (hardener)	1.5 ml
	1.0 g
	0.3 g
$C_4F_9SO_3K$	2 mg
$C_{12}H_{25}CONH(CH_2CH_2O)_5H$	0.5 g

The measurement and evaluation were conducted according to the following methods.

1. Measurement of sensitivity (Sw)

The samples were sandwiched between 2 sheets of fluorescent screen NR-160 (trade name, produced by KONICA CORPORATION) and exposed through aluminum steps under the following conditions:
Voltage in tube: 80 Kvp
Current in tube: 100 mA
Irradiation time: 50 msec

Then, the samples were developed by using an automatic processor KX-500 (trade name) and a developing solution XD-90 (trade name) at 35 °C for 30 sec, and fixed by a fixing solution XF, followed by washing and drying according to the conventional method. For the samples obtained, reciprocals of exposure dosages required for obtaining a density of base density + fog density + 1.0 were determined to obtain sensitivities.

As for sA, sB, sA' and sB', they were measured by the method as mentioned above (as the flurescent screen, NR-160 (trade name, produced by KONICA CORPORATION) was used).

2. Measurement of MTF

For the respective samples, each rectangular wave chart was photographed, and MTF was determined according to a contrast method. MTF was a value at a space frequency of 2.0/mm.

3. Evaluation of diagnostic properties

By using each sample, a chest phantom (manufactured by Kyoto Kagaku K.K.) was photographed, and development was conducted according to the same conditions as in the measurement of sensitivity. Overall evaluation was made by observation with eyes, and the results are represented by 5 ranks. In the ranks 5 to

3, there is no problem in practical use, but in the ranks 2 to 1, samples are of no practical use.
The covering power (C.P) was measured by the method as described above.
The results obtained are shown in Table 1.

Table 1

Sample No.	Coating solution No. used		C.P ratio	sA/sA'	sA/sB	Dye	Amount added (mg/m^2)	Dye content	Sensitivity (Sw)	MTF	Diagnostic property	Remarks
	A surface	B surface										
1	1	1	1.00	1.00	1.00	—	—	—	100	35	2	Comparative
2	1	1	1.00	1.33	1.25	No.38	5	B	90	38	2	"
3	2	3	1.85	4.20	4.20	—	—	—	105	45	4	This invention
4	2	3	1.85	4.80	4.67	No.38	5	B	100	48	4	"
5	2	3	1.85	5.60	6.72	No.38	10	B	95	53	5	"
6	2	3	1.85	4.80	4.80	No.46	5	B	100	48	4	"
7	2	3	1.85	4.80	4.80	No. 9	5	B	100	49	4	"
8	2	3	1.85	4.80	4.80	No.45	5	B	100	48	4	"
9	2	3	1.85	5.60	5.60	No.50	5	B	100	50	5	"
10	4	5	1.71	4.10	2.53	—	—	—	100	43	4	"
11	4	5	1.71	4.80	2.88	No.38	5	B	95	47	5	"
12	4	5	1.71	5.76	3.20	No.38	10	B	95	52	4	"
13	4	5	1.71	4.80	2.88	No.37	5	B	100	48	5	"
14	4	5	1.71	4.80	2.88	No.57	5	B	95	49	5	"
15	4	5	1.71	4.80	2.88	No.46	5	B	100	50	4	"
16	4	5	1.71	4.80	2.88	No.36	5	B	100	48	5	"

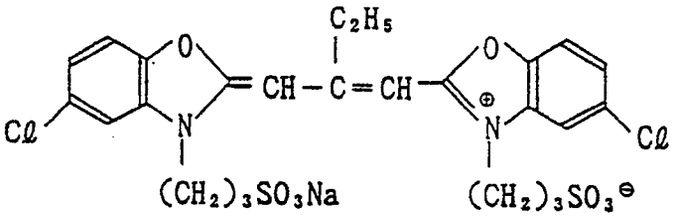
As clearly seen from Table 1, it can be understood that according to the present invention, MTF is

elevated without lowering sensitivity to greatly contribute to diagnostic properties.

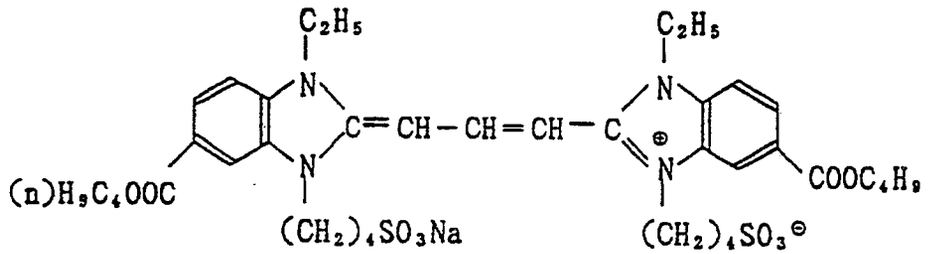
Example 2

To the above emulsions (B), (C) and (D) were added spectral sensitizing dyes A and B shown below at a weight ratio of 200:1 in a total amount of 800 mg per mole of silver halide, respectively. Subsequently, the mixtures were chemically ripened by using 3.6×10^{-3} mole of ammonium thiocyanate per mole of silver, an optimum amount of chloroauric acid and hypo. Fifteen minutes before completion of the reaction, 200 mg of potassium iodide per mole of silver was added, and then 2×10^{-2} mole of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added to effect stabilization.

Spectral sensitizing dye A



Spectral sensitizing dye B



To three kinds of the emulsions obtained, the same emulsion additives as in Example 1, water-soluble dyes shown in Table 2 and lime-treated gelatin were added to prepare emulsion coating solutions shown below. The water-soluble dye was added in the emulsion coating solution for the side of the B surface.

Coating solution 6:	a solution in which a mixing ratio of (B):(C):(D) is 25.0:35.0:40.0
Coating solution 7:	a solution in which a mixing ratio of (B):(C) is 41.7:58.3
Coating solution 8:	a solution comprising only (D)
Coating solution 9:	a solution in which a mixing ratio of (B):(C) is 50.0:50.0
Coating solution 10:	a solution in which a mixing ratio of (C):(D) is 20.0:80.0

The coating solutions obtained were coated on a support and dried in the same manner as in Example 1 to obtain Samples No. 1 to No. 16.

For the samples obtained, sensitivity and MTF were measured and diagnostic properties were evaluated in the same manner as in Example 1. The results are shown in Table 2. Sensitivity (Sw) in Table 2 was measured according to the following method.

1. Measurement of sensitivity (Sw)

The samples were sandwiched between 2 sheets of fluorescent screen KO-250 and exposed through

aluminum steps under the following conditions:
Voltage in tube: 80 Kvp
Current in tube: 100 mA
Irradiation time: 50 msec

Then, the samples were developed by using an automatic processor KX-500 and a developing solution XD-90 at 35 °C for 30 sec, and fixed by a fixing solution XF, followed by washing and drying according to a conventional method. For the samples obtained, reciprocals of exposure dosages required for obtaining a density of base density + fog density + 1.0 were determined to obtain sensitivities.

As for sA, sB, sA' and sB', they were measured by the method as mentioned above (as the flurescent screen, KO-250 (trade name, produced by KONICA CORPORATION) was used).

The results obtained are shown in Table 2.

Table 2

Sample No.	Coating solution No. used A surface	Coating solution No. used B surface	C.P ratio	sA/sA'	sA/sB	Dye	Amount added (mg/m^2)	Dye content	Sensitivity (Sw)	MTF	Diagnostic property	Remarks
1	6	6	1.00	1.05	1.00	—	—	—	100	50	2	Comparative
2	6	6	1.00	1.43	1.25	No.11	5	B	90	55	2	"
3	7	8	2.08	4.86	5.67	—	—	—	100	60	4	This invention
4	7	8	2.08	5.67	6.80	No.11	5	B	100	63	4	"
5	7	8	2.08	6.80	8.50	No.11	10	B	95	68	5	"
6	7	8	2.08	5.67	6.80	No.13	5	B	100	63	4	"
7	7	8	2.08	5.67	6.80	No.19	5	B	100	63	4	"
8	7	8	2.08	6.30	6.80	No.16	5	B	95	65	4	"
9	7	8	2.08	5.67	6.80	No.12	5	B	100	64	4	"
10	9	10	1.98	4.21	4.57	—	—	—	100	60	3	"
11	9	10	1.98	4.85	5.33	No.11	5	B	100	63	4	"
12	9	10	1.98	5.33	6.40	No.11	10	B	95	65	5	"
13	9	10	1.98	5.00	5.33	No.18	5	B	100	63	4	"
14	9	10	1.98	4.57	5.33	No.17	5	B	100	64	4	"
15	9	10	1.98	4.57	5.00	No.14	5	B	100	65	4	"
16	9	10	1.98	5.33	5.71	No.56	5	B	95	64	4	"

As clearly seen from Table 2, also in a system subjected to ortho sensitization, the effect of the present invention was exhibited markedly similarly as in Example 1.

According to the present invention, sharpness could be improved without lowering sensitivity. The effect of the present invention thus obtained was significant in a light-sensitive silver halide photographic material for medical use for improving diagnostic properties.

Claims

1. A light-sensitive silver halide photographic material comprising:
a support;
a first light-sensitive unit comprising a first light-sensitive layer and a first non-light-sensitive layer; and
a second light-sensitive unit comprising a second light-sensitive layer and a second non-light-sensitive layer,
said first light-sensitive unit being provided on one side of said support and said second light-sensitive unit being provided on the other side of said support,
wherein a sensitivity of said first light-sensitive unit when exposure is effected only from said one side (sA), a sensitivity of said second light-sensitive unit when exposure is effected only from said other side (sB) and a sensitivity of said first light-sensitive unit when exposure is effected only from said other side (sA') satisfy the following equations:

$$(I) \qquad sA/sA' > 4.0$$

$$(II) \qquad sA/sB = 1.5 \text{ to } 20$$

2. The material of Claim 1 wherein said sA/sA' is 4.5 or more.

3. The material of Claim 2 wherein said sA/sA' is 5.0 or more.

4. The material of Claim 1 wherein said sA/sB is 2.5 to 10.

5. The material of Claim 2 wherein the ratio is 1 : 1.5 to 5.0.

6. The material of Claim 5 wherein the ratio is 1 : 1.5 to 2.0.

7. The material of Claim 1 wherein at least one of the light-sensitive silver halide photographic emulsion layer and the hydrophilic colloidal layer at the B surface side contains at least one water-soluble dye.

8. The material of Claim 1 wherein silver halide grains with a small grain size are used at the B surface side.

9. The material of Claim 1 wherein a constitution rate of fine silver halide grains used at the B surface side is made larger.

10. The material of Claim 1 wherein silver halide grains with a small grain size is used at the B surface side and a water-soluble dye is added to at least one of the above silver halide emulsion layer and the hydrophilic colloidal layer.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 4462

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,Y	EP-A-0 345 483 (3M) * page 6, line 54 - page 7, line 13 *	1-10	G 03 C 5/16 G 03 C 7/30
X,Y	EP-A-0 126 644 (KONISHIROKU) * page 6, line 21 - page 8, line 13 * * page 11, lines 17 - 19 * * page 13, lines 8 - 16 *	1-10	
X,Y	DE-B-1 017 464 (SCHLEUSSNER FOTOWERKE) * claim 1 *	1-10	
X,Y	DE-C-1 000 687 (AGFA) * column 1, lines 46 - 52 *	1-10	
Y	EP-A-0 065 877 (3M) * claim 1 *	1-10	
Y	RESEARCH DISCLOSURE. no. 184, August 1979, HAVANT GB pages 433 - 441; J.W.Carpenter: "Radiographic films/materials" * page 433, left-hand column *"Types of Emulsion s" *	1-10	
Y	INGENIEURSBLAD. vol. 39, no. 8, 16 April 1970, ANTWERPEN BE pages 252 - 261; R.Bollen: "Fotografische aspekten van de medische radiologie" * page 256, right-hand column, lines 32 - 39 *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	22 February 91	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document