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㊹ Light-sensitive silver halide photographic material having superior sharpness and feasible for ultra-rapid processing.

㊼ A light-sensitive silver halide photographic material comprising a support and, provided thereon, photographic component layers containing a gelatin and including a silver halide emulsion layer and a layer containing a dye, said dye having, as an aqueous solution, at least one maximum absorption wavelength (λ_{max}) in the range of from 400 nm to 850 nm, and the amount of gelatin present on the same side of said silver halide emulsion layer being within the range from 2.0 g/m^2 to 3.5 g/m^2 and a method of processing a imagewise exposed light-sensitive silver halide photographic material as above by the use of an automatic processing machine at a speed of 20 to 60 seconds.

LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL HAVING SUPERIOR SHARPNESS AND FEASIBLE FOR ULTRA-RAPID PROCESSING

FIELD OF THE INVENTION

The present invention relates to a light-sensitive silver halide photographic material capable of being processed at a high speed. In particular, it is concerned with a light-sensitive silver halide photographic material having a high sharpness and suffering less color remaining after processing, even when applied in ultra-rapid processing.

BACKGROUND OF THE INVENTION

Recent years, consumption of light-sensitive silver halide photographic materials have been increasing steadily. This results in increase in the number for development processing, of light-sensitive silver halide photographic materials, and requires the development processing to be performed more rapidly, in other words, to be performed in an increased amount for the processing within the same time.

The above trend is also seen in the field of X-ray photographic materials as exemplified by X-ray films for medical use. Namely, diagnosis times increase with, e.g., periodical examinations encouragingly practiced, and also test items increase therewith in order to make the diagnosis more accurate, resulting in increase in the number of taking X-ray photographs.

On the other hand, it is also necessary to notice as soon as possible the outcome of the diagnosis to those who have been diagnosed.

In other words, there are strong demands for carrying out development processing more rapidly than ever to facilitate the diagnosis. Particularly in angiography, amid-operation photographing, etc., it is fundamentally necessary to view photographs in a time as short as possible.

To satisfy the above demands in the medical field, required are to promote automatization of diagnosis (as in photographing, conveyance, etc.) and at the same time to process X-ray films far more rapidly.

However, carrying out ultra-rapid processing may cause the problems such that (a) density becomes insufficient (i.e., lowering of speed, contrast and maximum density), (b) fixing can not be carried out with sufficiency, (c) washing of films becomes insufficient, and (d) films are dried with insufficiency. Also, the fixing insufficiency and washing insufficiency cause a change in color tone during preservation of films to lower image quality.

Ultra-rapid processing is sought after as stated above. The ultra-rapid processing mentioned in the present specification is meant to be the processing carried out in not less than 20 seconds and not more than 60 seconds as the total time taken after the tip of a film is inserted to an automatic processor and before the tip of the film comes out of a drying section, passing through a developing tank, a carrying path, a fixing tank, a carrying path, a washing tank, a carrying path and the drying section [in other words, the quatient (sec.) obtained by dividing the whole length (m) of a processing line by the line conveyance velocity (m/sec)]. The reason why the time for passing the carrying paths is included here is, as well known in the present industrial field, that a solution for the processing anterior thereto swells gelatin films also on the carrying paths and hence the processing steps can be deemed to substantially proceed there.

Japanese Patent Examined Publication No. 47045/1976 teaches the importance of the amount of gelatin in the rapid processing, in which, however, the processing is carried out for 60 seconds to 120 seconds as the total time including the time on the carrying paths. Such a processing time, however, can not satisfy the demands in the ultra-rapid processing recently practiced.

Another way to solve the above problems (a) to (d) is to decrease the amount of gelatin, but researches made by the inventors revealed that decreasing the amount of gelatin results in a lowering of sharpness. This was a result contradictory to the received wisdom that decreasing the amount of gelatin results in a decreased film thickness and an improved sharpness.

Thus, since decreasing the amount of gelatin for the purpose of adaptation to the rapid processing causes a serious lowering of sharpness, this must be prevented before an image having a high image quality can be obtained.

On the other hand, in order to enhance photographic effect of X-rays when X-ray photographs are taken in the medical field, it has been commonly practiced to use a light-sensitive material having silver halide emulsion layers on both sides of a support (hereinafter "both-sided light-sensitive material"), and carry out exposure to X-rays by bringing a fluorescent screen into close contact with each side thereof when taking photographs. Here, the light generated from the fluorescent screens placed on both sides of the light-sensitive material is scattered by complicated refraction and reflection at the insides and surfaces of the silver halide emulsion layers and support or on the surfaces of the fluorescent screen, etc., and, in particular, reaches the emulsion layer on the opposite side to sensitize it, thereby causing the phenomenon that the sharpness of images is extremely lowered. Such a phenomenon is generally called as a crossover phenomenon or print-through phenomenon, which is required to be prevented in order to obtain an X-ray image having a high sharpness. This phenomenon is particularly remarkable in a light-sensitive material in which the amount of gelatin has been decreased, and makes the sharpness extremely poor together with the lowering of sharpness for the reason mentioned above.

Without limitation to the both-sided light-sensitive material, the sharpness may further be lowered by the so-called halation phenomenon that the light having passed through an emulsion layer is scattered by reflection on the surface of a support and thereafter again sensitize the emulsion layer, or the so-called irradiation phenomenon that the light reflected on a certain particle sensitizes other particles adjacent thereto, which phenomenons cause further poorness in the sharpness when the amount of gelatin is decreased.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a light-sensitive silver halide photographic material that enables reduction in the amount of gelatin without causing the lowering of sharpness as mentioned above and makes it possible to carry out a high-speed processing, for example, an ultra-rapid processing carried out in a total processing time of not less than 20 seconds and not more than 60 seconds.

The above object of the present invention can be achieved by a light-sensitive silver halide photographic material in which at least one layer of any photographic component layers contains at least one kind of dye having a maximum absorption wavelength (λmax) in the range of from 400 to 850 nm as an aqueous solution, and the amount of gelatin in a photographic component layer on the side having a light-sensitive silver halide is in the range of from 2.0 to 3.5 g/m^2.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram illustrating an example of an automatic processor that can be used in Examples of the present invention; and

Fig. 2 is a graph showing the amount of silver used when an emulsion is prepared in Examples;

wherein the numeral 1 denotes a film-inserting stand; 2, a film basket; 3, an operation panel; 31, a remote control receiving portion; 4, rollers, 5, a carrying path; 6, a developing solution tank; 7, a fixing solution tank; 8, a washing tank; 9, a drying section; 91, squeegee rack; and 92, a drying rack.

DETAILED DESCRIPTION OF THE INVENTION

The light-sensitive material of the present invention comprises a support having on one side thereof at least one light-sensitive silver halide emulsion layer, and may comprise the both-sided light-sensitive material or a light-sensitive material having an emulsion layer only on one side.

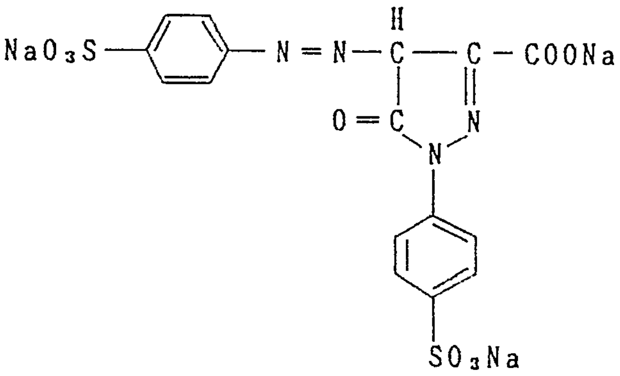
The amount of gelatin mentioned above is meant by the amount per one side.

Any dyes can be used as the dye used in the light-sensitive silver halide photographic material of the present invention and having a maximum absorption wavelength (λmax) of from 400 to 850 nm as an aqueous solution, and this dye can be used by appropriately making selection depending on the sort of light-sensitive materials, from such dyes that can absorb a desired wavelength and remove influence by said wavelength to improve the sharpness. In general, these dyes can be added alone or in combination in plurality. in a hydrophilic colloid layer by making selection so that it may have a relationship of additive complementary colors to the light emission distribution of a light source used together with the light-sensitive material. Such dyes may preferably be decolored or flowed away during the development processing of light-sensitive materials and brought into a state that no coloring can be visually detected at the time when the development is completed.

The dyes preferably used in the light-sensitive material of the present invention and decolored or flowed away during the development processing may include a number of compounds known as anti-halation dyes or anti-irradiation dyes for use in light-sensitive materials, which are exemplified by the following ones. In the following, shown are the structural formulas thereof and the maximum absorption wavelength of the aqueous solution. Provided that those usable in the present invention are by no means limited to what are exemplified below.

(Exemplary Compounds)

A

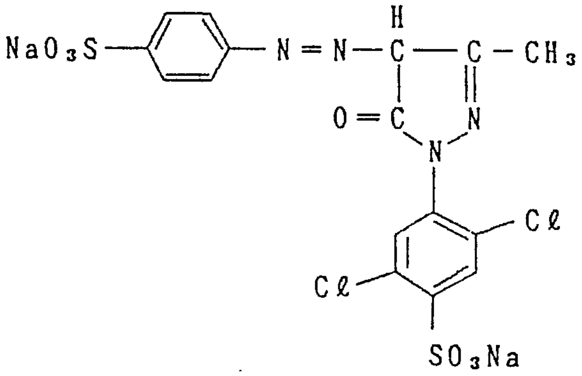


H_2O

λ_{max}(nm)

430

B



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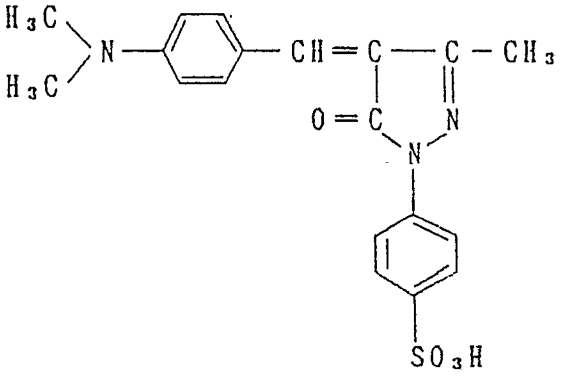
C



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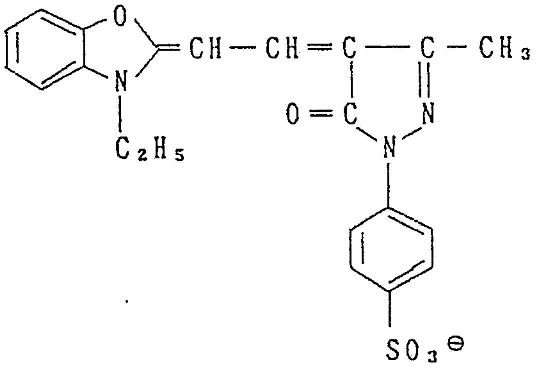
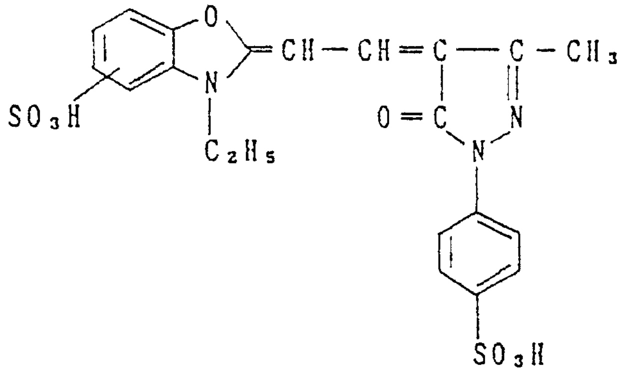
D



461

$\overset{\oplus}{N}H(C_2H_5)_3$

E



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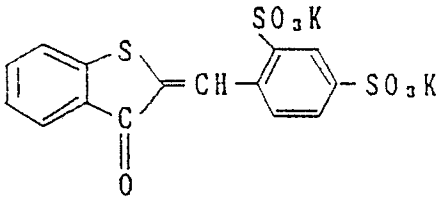
F



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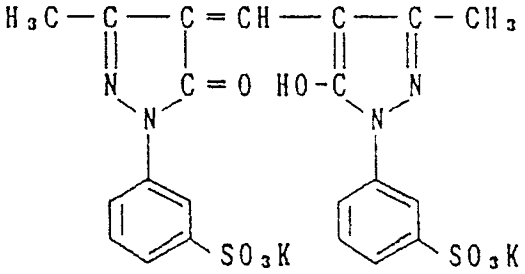
G



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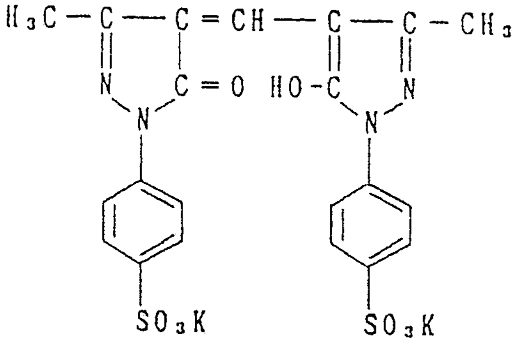
H



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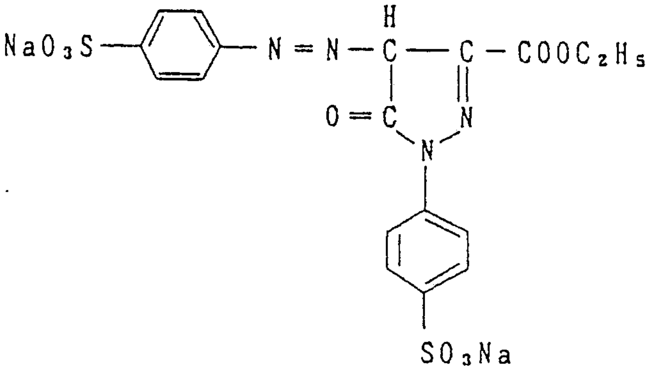
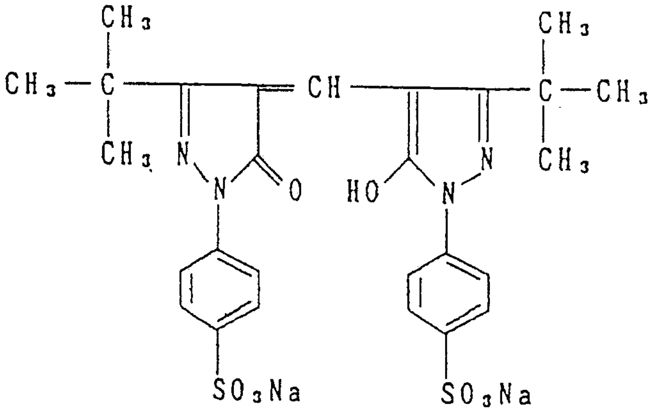
I



480

J



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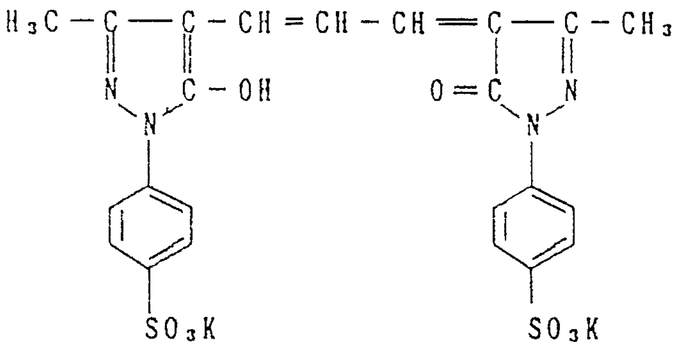
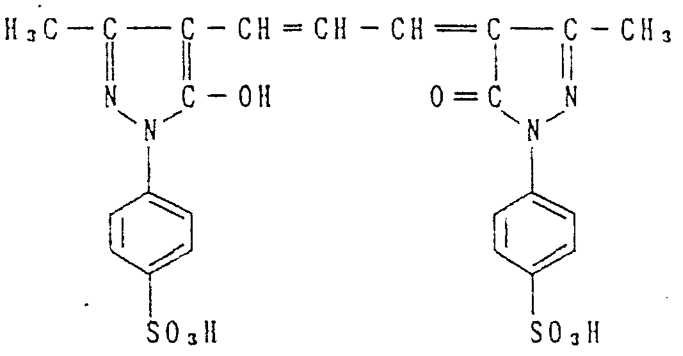
K



520

L



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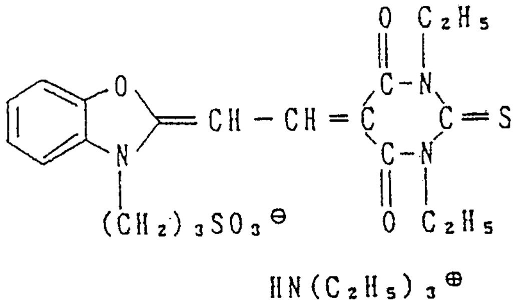
M



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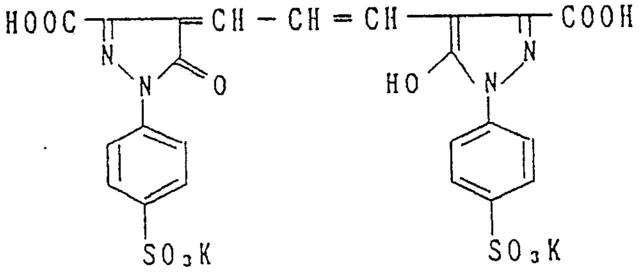
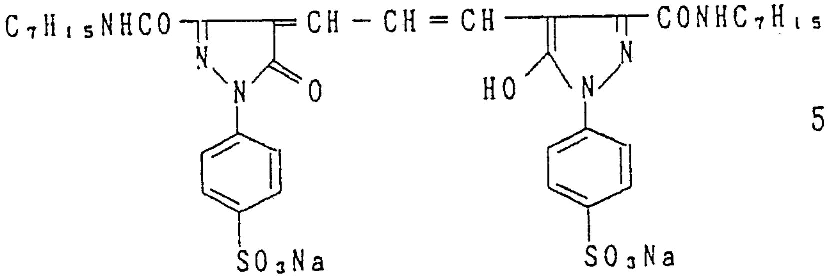
N



538

O



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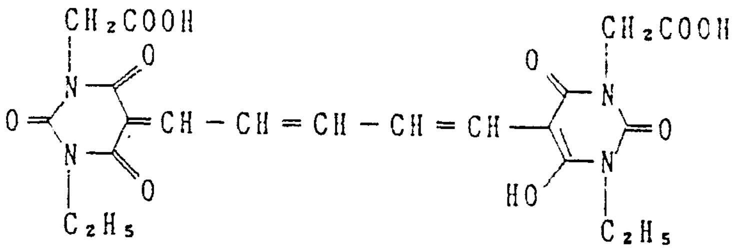
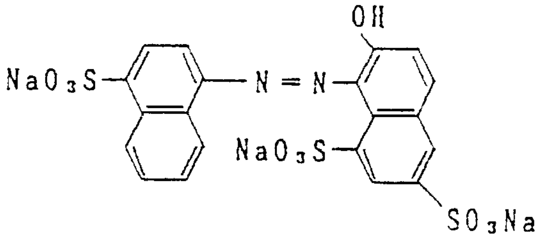
P



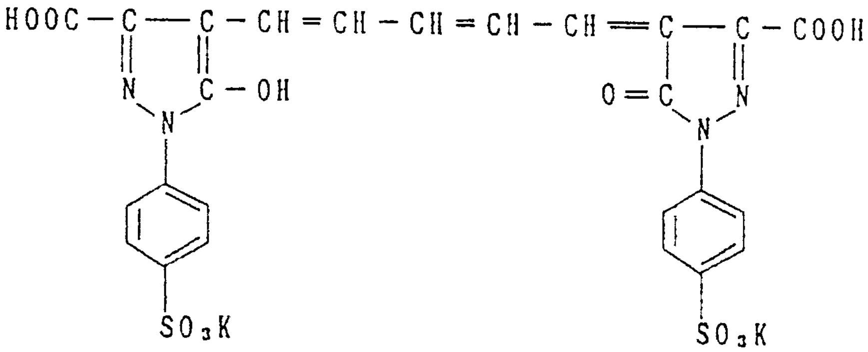
590

Q



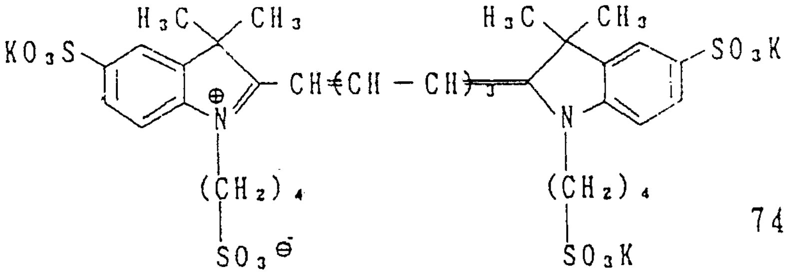
508

R



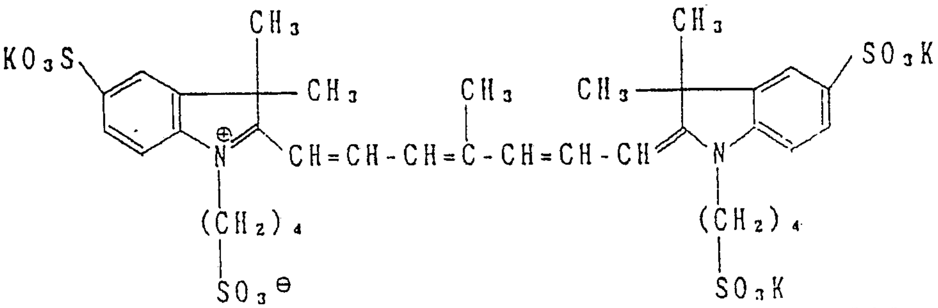
637

S



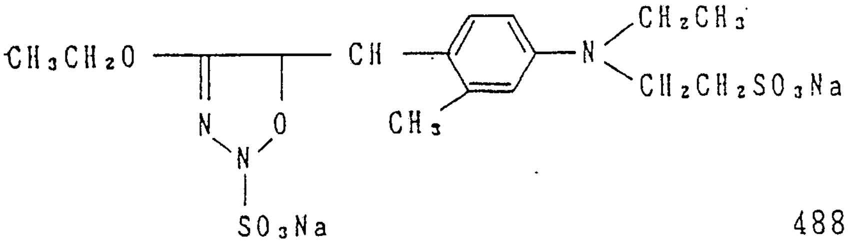
740

T



765

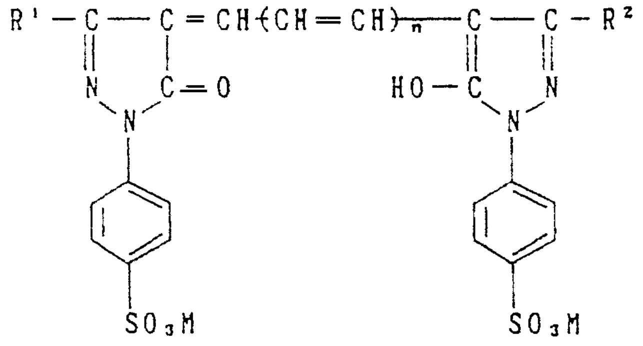
U



488

Of the above dye compounds, particularly preferred compounds may include those having the structure included in the following Formula (I).

Formula (I)



R^1 and R^2 in the formula each represent an alkyl group having 1 to 7 carbon atoms, a carboxyl group, an alkoxycarbonyl group, an alkylaminocarbonyl group, an amino group, an acylamino group or a trifluoromethyl group; M represents a hydrogen atom, an alkali metal atom or an ammonium group; and n is 0, 1 or 2.

The above dyes exemplified can be synthesized, for example, by the method described in British Patent No. 560,385, U.S. Patent No. 1,884,035 and Japanese Patent Examined Publication No. 22069/1964.

Examples of the above dyes and other usable dyes are described in West German Patent No. 616,077, British Patents No. 584,609 and No. 1,177,429, Japanese Patent Examined publications No. 7777/1951 and No. 22069/1964, Japanese Patent Publications Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publications) No. 85130/1973, No. 99620/1974, No. 114420/1974, No. 129537/1974, No. 28827/1975, No. 108115/1977 and No. 185038/1982, U.S. Patents No. 1,878,961, No. 1,884,035, No. 1,912,797, No. 2,098,891, No. 2,150,695, No. 2,274,782, No. 2,298,731, No. 2,409,612, No. 2,461,484, No. 2,527,583, No. 2,533,472, No. 2,865,752, No. 2,956,879, No. 3,094,418, No. 3,125,448, No. 3,418,187, No. 3,177,078, No. 3,247,127, No. 3,260,601, No. 3,282,699, No. 3,409,433, No. 3,540,887, No. 3,575,704, No. 3,953,905, No. 3,718,472, No. 3,865,817, No. 4,070,352 and No. 4,071,312, PB Report No. 74175, PHOTO. ABs. 1 28 ('21), etc.

The component layer to which the dye is added may be any of photographic component layers of the light-sensitive material. More specifically, the dye may be contained in at least one of light-sensitive emulsion layers, other hydrophilic colloid layers on the side on which said emulsion layers are provided by coating (as exemplified by non-light-sensitive layers such as intermediate layers, protective layers and subbing layers), etc. which consritute the light-sensitive material. It may preferably be present in a silver halide emulsion layer or a layer nearer to the support than it, or both the layers, and more preferably it is effectively added in a layer provided-by-coating facing and in contact with a transparent support. The dye may preferably be present in a higher concentration at the side near to the support. The above dye may be added preferably in an amount of from 0.2 mg/m² to 20 mg/m², more preferably from 0.8 mg/m² to 15 mg/m².

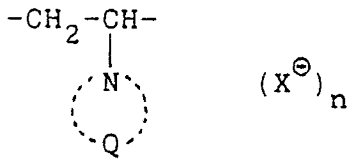
Such a dye, having a function as a filter, can be introduced in the hydrophilic colloid layers according to methods commonly used. More specifically, this dye is formed into an aqueous solution having an appropriate concentration, and added in a silver halide emulsion solution before coating in the case when emulsion layers are colored, and also in an aqueous solution of hydrophilic colloid, these solutions of which may be coated on the support directly or through other high-hydrophilic colloid layer according to various methods.

It may be added at any time in the course of preparing the light-sensitive material. Taking account of operations, it may preferably be added right before coating.

As described above, the dye may preferably be present in a higher concentration at the side near to the support, but a mordant may preferably be used to keep the dye to be fixed on the side near to the support. For example, a non-diffusible mordant can be used as the one to be combined to at least one kind of the above dyes, and preferably usable as the mordant like this are, for example, the compounds described in West German Patent No. 22 63 031, British Patents No. 1,221131 and No. 1,221,195, Japanese Patent O.P.I. publication No. 47624/1975 and No. 71332/1975, Japanese Patent Examined Publication No. 1418/1976, 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.

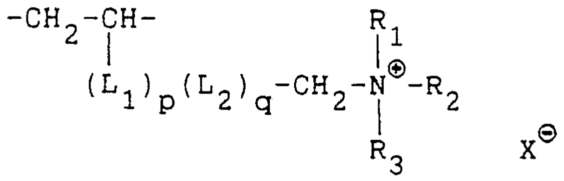
In a preferred embodiment, particularly effective are polymers represented respectively by Formulas (M-I) to (M-III) or copolymers thereof.

Formula (M-I)



In the formula, Q represents a group of atoms necessary to complete an imidazole ring nucleus together with a nitrogen atom; X, an acid group, an acid anion or a halide anion; and n, 0 or 1.

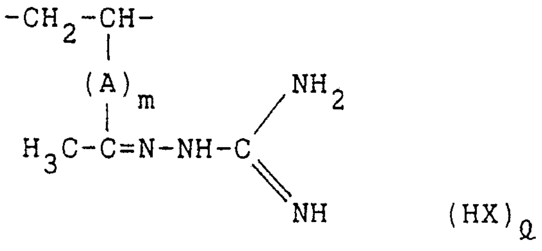
Formula (M-II)



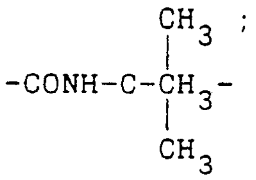
$$-CH_2-\underset{(L_1)_p(L_2)_q-CH_2-\overset{R_1}{\underset{R_3}{N^{\oplus}}}-R_2}{CH}- \qquad X^{\ominus}$$

In the formula, R_1, R_2 and R_3 each represent a C_1 to C_8 alkyl group (which alkyl group may have a substituent); L_1 represents a -CONH- group or a -O-O- group, L_2, an alkylene group or an arylene group; p and q each are 0 or 1; and X represents an acid anion or a halide anion.

Formula (M-III)



In the formula, A represents

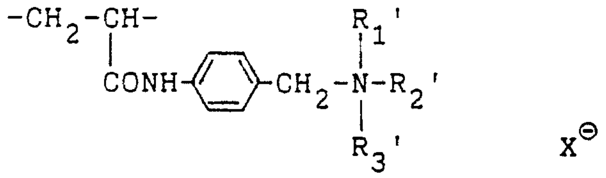


$$-CONH-C-\overset{CH_3}{\underset{CH_3}{CH_3}}- \ ;$$

X, an acid group; ℓ, an integer of 1 or 2; and m, an integer of 0 or 1.

The polymer represented by Formula (M-II) shown above or the copolymer thereof further preferably includes the one represented by Formula (M-IV) shown below.

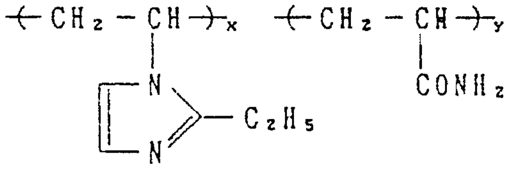
Formula (M-IV)



In the formula, R_1', R_2' and R_3' each represents a C_1 to C_8 alkyl group (which alkyl group may have a substituent); and X represents an acid anion or a halide anion.

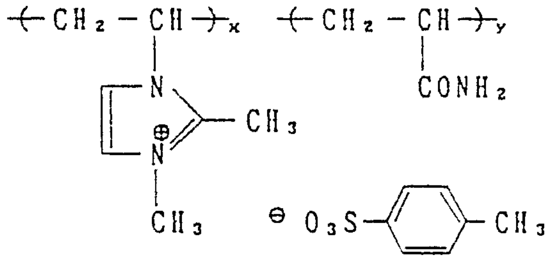
It specifically may include the following:

1.



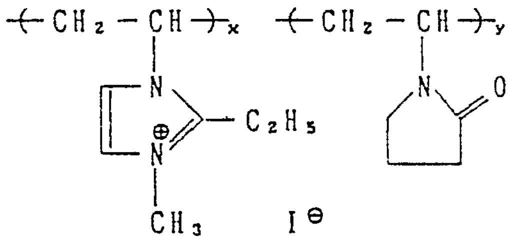
x : y = 25 : 75

2.



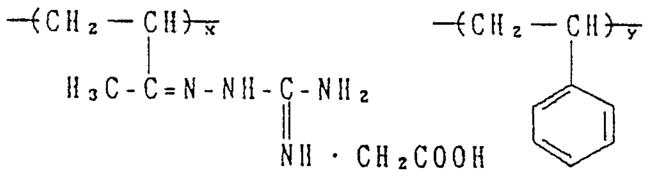
x : y = 25 : 75

3.



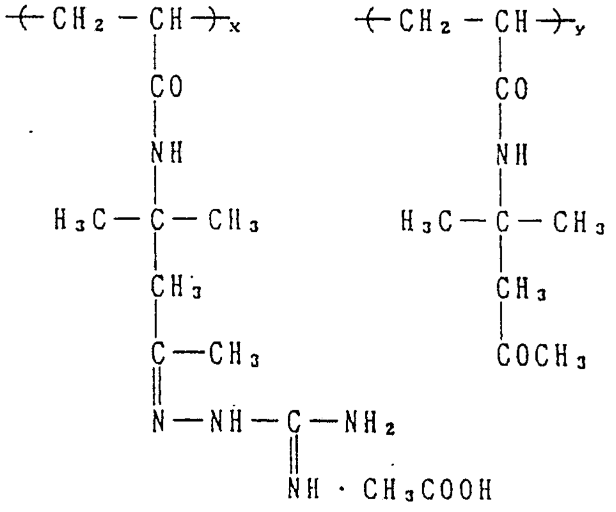
x : y = 66.7 : 33.3

4.



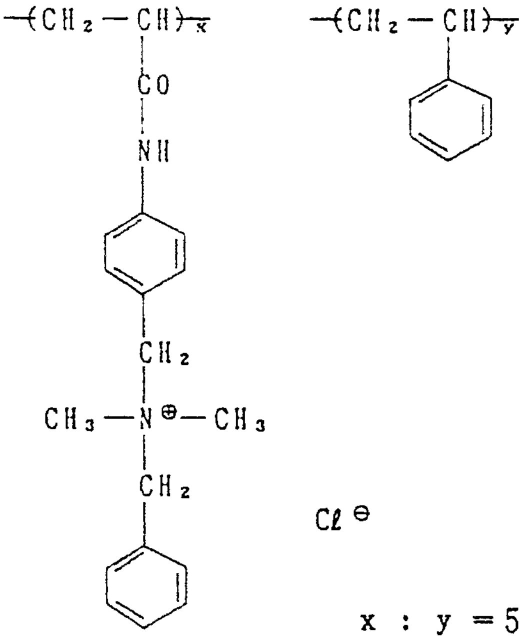
x : y = 66.7 : 33.3

5.



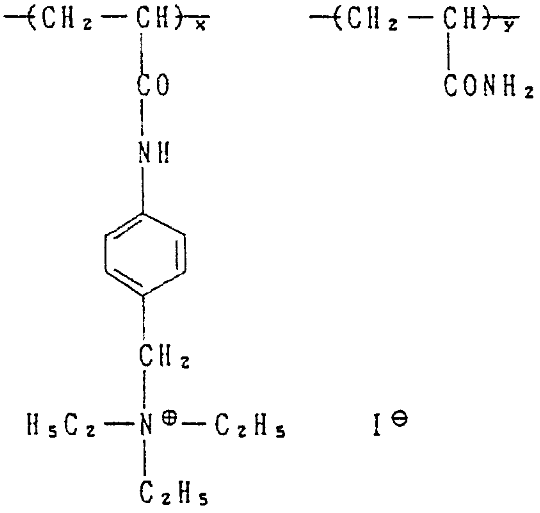
x : y = 75 : 25

6.



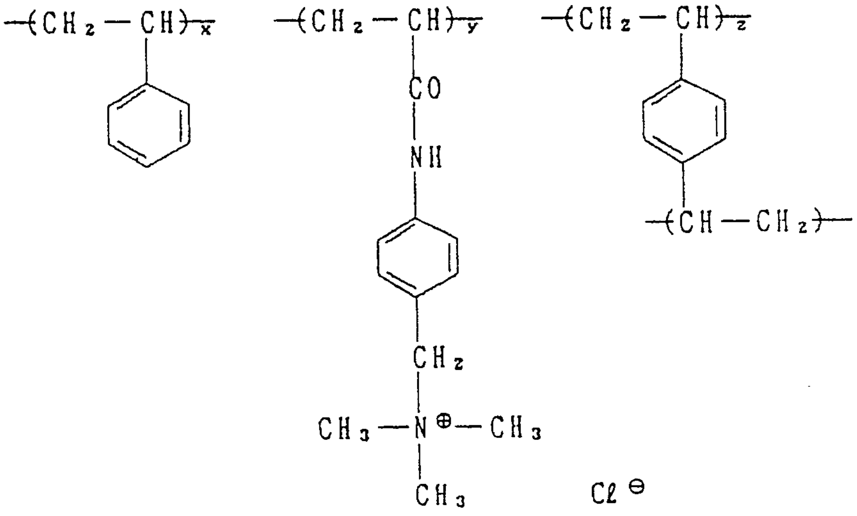
x : y = 50 : 50

7.



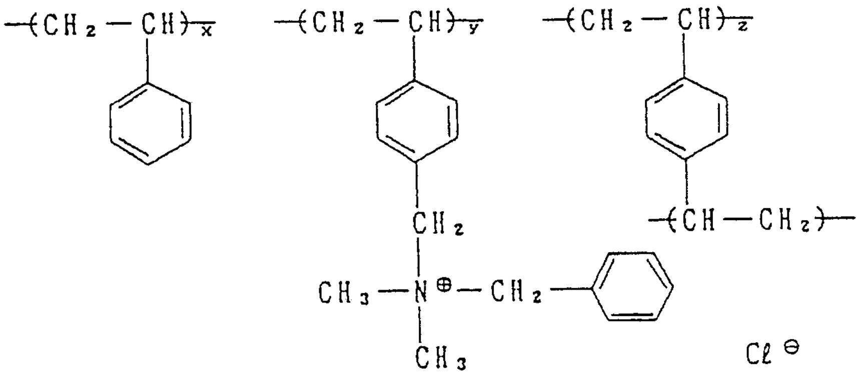
x : y = 50 : 50

8.



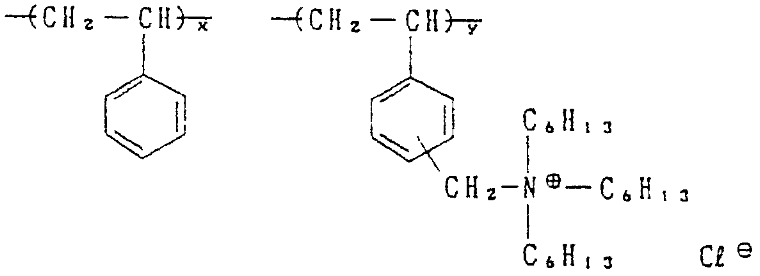
x : y : z = 48 : 48 : 4

9.



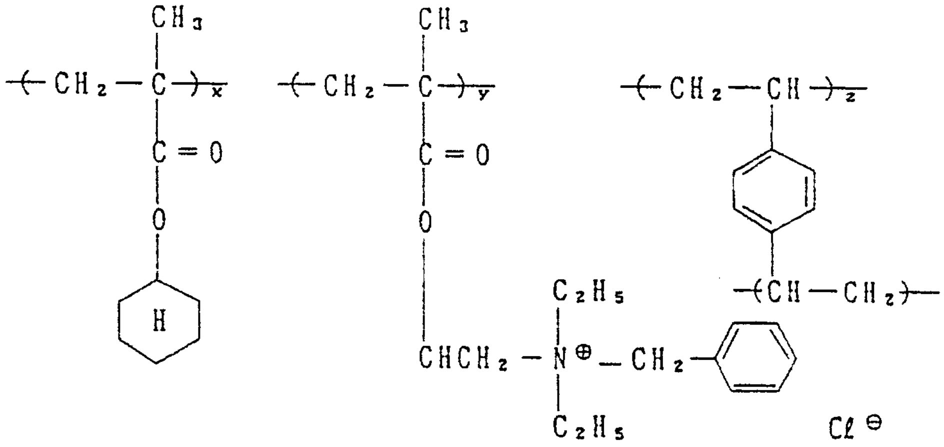
x : y : z = 49 : 49 : 2

10.



$x : y = 50 : 50$

11.



$x : y : z = 48 : 48 : 2$

These compounds can be readily synthesized according to the methods described in Japanese Patent Examined Publications No. 15820/1974 and No. 1418/1976, Japanese Patent O.P.I. Publications No. 73440/1976, No. 129034/1978, No. 74430/1979, No. 155835/1979 and No. 22766/1980, etc.

When used, these compounds are dissolved in water or a hydrophilic organic solvent as exemplified by methanol and acetone.

In working the present invention, the non-diffusible mordant may be combined to the dye according to various methods, but particularly preferably applied is a method in which they are combined in a gelatin binder. Besides, also applicable is a method in which they are combined in a suitable binder and dispersed in an aqueous gelatin solution with use of ultrasonic waves.

The ratio for combining these may vary depending on the type of the compounds, and the non-diffusible mordant is combined usually in the proportion of from 0.1 part to 10 parts based on 1 part of the water-soluble dye. As for the amount for addition as the water-soluble dye, which is brought into combination to the non-diffusible mordant, the dye can be used in an amount larger than the case when it is used alone.

In the case when the combined product of the dye and non-diffusible mordant is incorporated into the light-sensitive material, an additional component layer containing the combined product may be provided as a component layer, which may be provided at the position arbitrarily selected, but may effectively be used as a layer provided-by-coating facing and in contact with the transparent support.

The gelatin used in the present invention may be either subjected to lime treatment or treated with use of an acid. Details of the preparation method for the gelatin are described in Arther Vice. The Macromolecular Chemistry of Gelatin, Academic Press, published 1964. Hydrophilic colloids other than the gelatin that can be used includes a variety of synthetic hydrophilic polymer materials as exemplified by proteins such as gelatin derivatives, graft polymers of gelatin with other polymers, albumin, and casein: sugar derivatives such as cellulose derivatives including hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfates, sodium alginate, and starch derivatives; homopolymers or copolymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinyl pyrrolidone, polyacrylate, polymethacrylate, polyacrylamide, polyvinyl imidazole, and polyvinyl pyrazole. In the case of gelatin, the one having a jelly strength of 200 or more when measured by the PAGI method may preferably be used in light-sensitive emulsion layers.

The light-sensitive material of the present invention is suited for the high-speed processing, and can obtain excellent photographs without causing the problems previously discussed, even when applied, for example, to the ultra-rapid processing previously mentioned.

In a preferred embodiment of the present invention, the light-sensitive material of the present invention is processed using an automatic processor whose processing time is not less than 20 seconds and not more than 60 seconds.

Preferably used as grains preferred as silver halide grains used in the present invention are in the first place the flat plate-like grains disclosed in Japanese Patent O.P.I Publications No. 113927/1983 and No. 113928/1983 and at pages 252 to 253 of Japanese Patent O.P.I. Publication No. 105636/1984 and also in Japanese Patent O.P.I. Publication No. 147727/1985.

In the second place, preferred as grains of another type is, using a silver halide photographic emulsion comprising silver halide grains having a multi-layer structure, to use light-sensitive silver halide grains such that any two layers (between shell layers, or between the core and a shell layer) adjacent in the silver halide grain and each having a homogeneous iodine distribution have a difference of 10 mol % or less in average iodine content.

Further preferred is that an outermost layer has an average iodine content of 10 mol % or less and at the same time said silver halide grains are chemically sensitized.

Here, the grain having the multi-layer structure is provided at the outer side of the core with a shell having any desired halogen composition, and this shell may be comprised of only one layer, or two or more layers laminated, for example, into three layers, four layers and so on. It may preferaly be comprised of five layers or less.

Preferably used as silver halides in the core and the shell are silver bromide, silver iodobromide and silver iodide, which, however, may be a mixture with a small amount of silver chloride. Specifically, they may contain about 10 mol % or less, preferably about 5 mol % or less, of silver chloride.

The outermost layer may also preferably comprise substantially silver bromide, or substantially silver iodobromide (iodine content: 10% or less), and may also contain several % or less of chlorine atoms.

The average iodine content in the whole silver halide grain may preferably by 10 mol % or less, more preferably 6 mol % or less.

In the X-ray light-sensitive materials or the like for example, the iodine sometimes makes large the problems such as development restraint and infectious development, and hence practically preferred is to control the iodine content to a given level or less. The whole iodine content may preferably be 10 mol % or less, more preferably 7 mol % or less, and most preferably 5 mol % or less, in the whole grain.

In the case when the core comprises silver iodobromide, it may preferably be a homogeneous solid phase.

Herein, what is meant by "homogeneous" can be specifically described as follows:

Namely, it means that when a silver halide grain was subjected to powder X-ray diffraction, the half width at a peak of the face index [200] observed on silver iodobromide with use of Cu-$K^{\oplus}$ X-rays is $\Delta 2\theta$ = 0.30 (deg) or less. Here, a diffractometer was used under the conditions that $\omega\tau{\cdot}r \leqq 10$ assuming the scanning speed of a goniometer as ω (deg/min), the time constant as τ (sec), and the receiving slit width as r (mm).

As halogen composition of the core, iodine may preferably be contained in an average content of 40 mol % or less, more preferably from 0 to 20 mol %.

The adjacent two layers (any two shell layers or a shell layer and the core) may preferably have a difference of 10 mol % or more, more preferably 20 mol % or more, and particularly preferably 25 mol % or more, in silver iodide content.

The shell(s) other than the outermost shell may preferably have a silver iodide content of from 10 mol % to 100 mol %.

In the case when the silver halide grain is comprised of three or more layers and the shell layers comprises silver iodobromide, they may not necessarily be all homogeneous, but all layers may preferably comprise homogeneous silver iodobromide.

The shell(s) (or the core) having such a high iodine content may preferably exist at the position lower than the outermost surface in the case of negative silver halide emulsions. It or they may exist at the inside or on the surface in the case of positive silver halide emulsions.

The outermost shell may preferably have a silver iodide content of 10 mol % or less, more preferably from 0 to 5 mol %.

The iodine content in the core and the shell(s) of the silver halide grain used in working the present invention can also be found, for example, according to the method described in J.I. Goldstein and D.B. Williams "X-ray Diffraction in TEM/ATEM", Scanning Electron Microscopy (1977), Vol. 1 (ITT Research Institute), page 651 (March, 1977).

The silver halide grain used in working the present invention, when, for example, it is comprised of two shell layers, may preferably have a higher iodine content in the core than in the outermost layer, and when it is comprised of three layers, the grain may preferably have a higher iodine content in the shell layers other than the outermost layer, or in the core, than in the outermost layer.

The present invention can preferably be applied in respect of silver halide grains having been subjected to chemical sensitization.

The silver halide grains used in the present invention may be either of positive type or negative type.

In the case of the negative type, the chemical sensitization may preferably be applied in such a degree that may come to 60% or more of an optimum sensitization degree when taking a sensitivity point of "fog + 0.1" in the optical density.

In the case of the positive type, the chemical sensitization may preferably be applied to the inside of the grain in such a degree that may come to 60 % or more of an optimum sensitization degree when taking a sensitivity point of "fog - 0.1" in the optical density.

Average grain size of the silver halide grains used in the present invention is indicated as an average value obtained when the length of diameter calculated as a sphere having an equal volume is assumed as grain size.

The grain size can be obtained by using a centrifugal separation type Stolkes diameter measuring device, or can also be measured by an electron microscope.

The present invention may include an embodiment in which the silver halide emulsion grains used in silver halide emulsion layers may preferably have an average grain size of from 0.20 to 2.50 µm, more preferably from 0.30 to 1.30 µm, and most preferably from 0.30 to 1.10 µm.

The silver halide grains may have any grain size distribution, which may be monodisperse ones. Here, what is meant by "monodisperse" is a dispersion system in which 95 % of the grains is included in the size within ± 60 %, preferably within ± 40 %, of the number average grain size. Here, the number average grain size indicates the number average diameter of diameters of projected areas of silver halide grains.

The silver halide grains in a photographic emulsion may have a regular crystal form suoh as a cube, an octahedron, a tetradecahedron and a dodecahedron, or may have an irregular crystal form such as a sphere and a plate, or also may have a composite form of these crystal forms. They may also comprise a mixture of various crystal forms.

Also available are joined silver halide crystals obtained by combining oxide crystals such as PbO to silver halide crystals such as silver chloride, silver halide crystals obtained by causing epitaxial growth (for example, silver chloride, silver iodobromide, silver iodide or the like is brought to epitaxially grow on silver bromide), crystals comprising regular hexahedral silver chloride overlapped with orientation on hexagonal or regular octahedral silver iodide.

There may also be used an emulsion such that silver halide grains in the form of an ultra-flat plate, comprising a grain having a diameter 5 times or more its thickness, comprises 50 % or more of the whole projection areas. Details thereof are described in Japanese Patent O.P.I. Publications No. 127921 1983 and No. 113927 1983.

In a preferred embodiment, at least from about 60 to 70 % by weight is comprised of regular silver halide grains.

In preparing the monodisperse emulsion and/or the emulsion having the regular silver halide grains, silver ions and halide ions may preferably be fed in the manner that the growth rate is brought to continuously or stepwise increase by degrees at the critical growth rate, or within the tolerance limits thereof, at which the silver halide necessary and sufficient for the growth of only the existing grains is fed without the dissolving-away of the existing crystal grains along the growth of crystal grains and, on the contrary, without causing generation or growth of any new grains. The manner by which the growth rate is brought to increase by degrees is described in Japanese Patent Examined Publications No. 36890/1973 and No. 16364/1977, and Japanese Patent O.P.I. Publication No. 142329/1980.

In other words, the silver ions and halide ions are effectively fed at the rate such that the growth rate of silver halide grains may come to comprise 30 to 100 % of the critical growth rate.

It is also possible to use in combination the internal latent image type silver halide grains and surface latent image type silver halide grains, which are described in Japanese Patent Examined Publication No. 2086/1966.

In working the present invention, the silver halide grains used in the silver halide emulsion can be prepared, for example, by applying the methods described in publications such as T.H. James, The Theory of The Photographic Process, Fourth Ed., published by Macmillan Co. (1977); P. Glfkides, Chimie et Physigue Photographigue, published by Paul Montel Co. (1967); G.F. Duffin, Photogaphic Emulsion Chemistry, published by The Focal Press (1966); and V.L. Zelikman et al, Making And Coating Photographic Emulsion, published by The Focal Press (1964).

In forming the silver halide grains, it is possible to use a silver halide solvent as exemplified by ammonia, potassium rhodanide, ammonium rhodanide, thioether compounds disclosed, for example, in U.S. Patents No. 3,271,157, No. 3,574,628, No. 3,704,130, No. 4,297,439 and No. 4,276,374, thion compounds disclosed, for example, in Japanese Patent O.P.I. Publications No. 144319/1978, No. 82408/1978 and No. 77737/1980, and amine compounds disclosed, for example, in Japanese Patent O.P.I. Publication No. 100717/1979. Particularly preferred is ammonia.

It is also possible to make use by mixing two or more kinds of silver halide emulsions separately formed.

These silver halide grains or the silver halide emulsion may preferably contain at least one of salts (soluble salts) of iridium, thallium, palladium, rhodium, zinc, nickel, cobalt, uranium, thorium, strontium, tungsten or platinum. They may preferably be contained in an amount of from 10^{-5} to 10^{-1} mol per 1 mol Ag. Particularly preferred is to contain at least one of salts of thallium, palladium or iridium. These may be used alone or as a mixture, and may be added at any position (or time). This enables expectation for the effect of improving flash exposure characteristics, preventing pressure desensitization, preventing the fading of latent image, achieving sensitization, or the like effect.

To remove the soluble salts from the emulsion after formation of precipitates or after physical ripening, there may be used the noodle washing method carried out by setting gelatin to a gel, or may be used a sedimentation method (or flocculation method) utilizing inorganic salts, anionic surface active agents, anionic polymers as exemplified by polystyrenesulfonic acid, or gelatin derivatives as exemplified by acylated gelatin and carbamoylated gelatin. The step of removing the soluble salts may be omitted.

The silver halide emulsion may be or may not be chemically sensitized, but may preferably be chemically sensitized. To effect chemical sensitization, there can be used, for example, the method described in H. Fieser, Die Glundlagen der Photographischen Prozesse mit Silverhalogeniden, Akademische Verlagaesellschaft, 1968, pp. 675-734.

More specifically, there can be used alone or in combination the sulfur sensitization employing a compound containing sulfur and capable of reacting with active gelatin silver, as exemplified by thiosulfates, thioureas, mercapto compounds and rhodanines; the reduction sensitization employing reducible substances as exemplified by silver-tin salts, amines, hydrazine derivatives, formamidinesulfinic acid and silane compounds; and the noble metal sensitization employing noble metal compounds as exemplified by gold complex salts as well as complex salts of metals belonging to Group VIII of the periodic table, such as Pt, Ir and Pd.

Specific examples of these are described in U.S. Patents No. 1,574,944, No. 3,410,689, No. 2,278,947, No. 2,728,668, No. 3,656,955, etc. in respect of the sulfur sensitization, U.S. Patents No. 2,983,609 No. 2,419,974, No. 4,054,458, etc. in respect of the reduction sensitization, and U.S. Patents No. 2,599,083 and No. 2,448,060, British Patent No. 618,061, etc. in respect of the noble metal sensitization.

Sensitizing dyes may be used alone, or may be used in combination of any of them, and the sensitizing dyes are often used in combination particularly for the purpose of supersensitization.

Typical examples thereof are described in U.S. Patents No. 2,688,545, No. 2,977,229, No. 3,397,060, No. 3,322,052, No. 3,617,293, No. 3,666,450, No. 3,272,898, No. 3,679,428, No. 3,703,377, No. 3,769,301, No. 3,814,609, No. 3,837,862 and No. 4,026,707, British Patents No. 1,344,281 and No. 1,207,503, Japanese Patent Examined Publications No.4536/1970 and No. 12375/1978, and Japanese Patent O.P.I. Publications No. 110618/1977 and No. 109925/1977.

Together with the sensitizing dyes, the emulsion may also contain a dye having in itself no spectrally sensitizing action, or a substance that may not substantially absorb visible light and shows supersensitization.

For example, there may be contained an aminostilbene compound substituted with a nitrogen-containing heterocyclic ring group, as exemplified by those described in U.S. Patents No. 2.933.290 and No. 3.635.721, an aromatic organic acid formaldehyde condensate as exemplified by those described in U.S. Patent No. 3.743.510 cadmium salts, or azaindene compounds. A particularly effective is the combination described in U.S. Patents No. 3.615.615, No. 3.615.641, No. 3.617.295 and No. 3.635.721.

The photographic emulsion used in the present invention may be incorporated with various compounds for the purpose of preventing fog from being generated in the course of preparation of light-sensitive materials, during preservation or in the course of photographic processing, or stabilizing photographic performances. More specifically, there can be added a number of compounds known as antifoggants or stabilizers including thiazoles as exemplified by benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (in particular, 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines; thioketo compounds as exemplified by oxazolinethion, azaindenes as exemplified by triazaindenes, tetrazaindenes (in particular, 4-hydroxy substituted (1.3.3a.7)tetrazaindenes) and pentaazaindenes; benzenethiosulfonic acid, benzenethiosulfinic acid, and benzenethiosulfonic acid amide.

Details are available by making reference to E.J. Birr, Stabilization of Photographic Silver Halide Emulsions, Focal Press, 1974.

Usable compounds include, for example, thiazolium salts described in U.S. Patents No. 2,131,038, No. 2,694,716, etc.; azaindenes described in U.S. Patents No. 2,886,437, etc.; urazoles described in U.S. Patent No. 3,287,135, etc.; sulfocatechols described in U.S. Patent No. 3,236,632, etc.; oximes described in British Patent No. 623,448, etc.; mercaptotetrazoles described in U.S. Patents No. 2,403,927, No. 3,266,897, No. 3,397,987, etc., nitron;nitroindazoles; polyvalent metal salts described in U.S. Patent No. 2,839,403; thiuronium salts described in U.S. Patent No. 3,220,839, etc.; and salts of palladium, platinum or gold, described in U.S. Patents No. 2,566,263, No. 2,597,715, etc.

The photographic emulsion layers of the light-sensitive photographic material of the present invention may contain, for example, polyalkylene oxides or ether, ester or amine derivatives thereof, thioether compounds, thiomorpholines, quaternary ammonium chloride compounds, urethane derivatives, urea derivatives, imidazole derivatives or 3-pyrazolidones, for the purpose of increasing speed, increasing contrast and accelerating development.

In the light-sensitive photographic material of the present invention, the photographic emulsion layers and other hydrophilic colloid layers may contain inorganic or organic hardening agents. For example, there can be used alone or in combination, chromium salts (such as chromium alum and chromium acetate), aldehydes (such as formaldehyde, glyoxale and glutaldehyde), N-methylol compounds (such as dimethylol urea and methyloldimethyl hydantoin), dioxane derivatives (such as 2,3-dihydroxydioxane), active vinyl compounds (such as 1,3,5-triacryloyl-hexahydro-2-triazine and 1,3-vinylsulfonyl-2-propanol), active halide compounds (such as 2,4-dichloro-6-hydroxy-3-triazine), mucohalogen acids (such as mucochloric acid and mucophenoxychloric acid), etc.

Taking account of graininess and dryness, the light-sensitive silver halide photographic material of the present invention may preferably be hardened by adding a hardening agent so that the time by which silver halide grains are released from a support when immersed in an aqueous solution of 50.0°C, containing 1.5 % by weight of sodium hydroxide, may come to be not less than 10 minutes, more preferably not less than 15 minutes.

In instances in which the light-sensitive silver halide photographic material of the present invention is processed, for example, by using a roller carrier type automatic processor, where, in many instances, processing is carried out in such a state that from developing processing up to drying have been completed, the light-sensitive photographic material may preferably contain water in the range of from 6.0 to 15.0 g/m^2, particularly in the range of from 9.0 to 14.0 g/m^2, in order to make better the dryness and other performances. The water content in the light-sensitive silver halide photographic material, mentioned in the present specification, refers to what has been obtained by the following measuring method under the conditions of 25°C and a relative humidity of 75 %. Namely, a sample having been subjected to exposure by the degree only necessary for obtaining maximum density was subjected to development using an automatic processor KX-500 (processing speed change-over switch: 90 seconds/hour; its construction is schematically illustrated in Fig. 1) manufactured by Konica Corporation, using a developing solution obtained by adding in SAKURA XD-90 produced by Konica Corporation a given amount of a starter XD-90S (available from the same company), which was used at 35°C, also using as a fixing solution SAKURA NEW XF (available from the same company) at 32°C, and using city water of 18°C as washing water so that it is fed in an amount of 3 liter per minute. The drying rack (denoted by the numeral 92 in Fig. 1) of the automatic processor was dismounted, 101 sheets of samples which are same with the sample for which the water content was measured were continuously processed at intervals of one sheet per 12 seconds, and thereafter the sample of one hundred first sheet which was used as a sample for measuring the water content was pulled out when it came out of the squeegee rack (denoted by the numeral 91 in Fig. 1) to measure its weight after 15 seconds. (At this this time, a measure is taken so that no electric source for the drying system may be turned on.)

The weight measured here is assumed as W_w (g).

Next, the above sample was sufficiently dried, and thereafter left for more than 1 hour under the conditions of 25 °C and 55 % RH to measure its weight. The found is assumed as W_d. The water content is calculated from the following equation:

Water content $(g/m^2 = W_w - W_d \times (10{,}000\ cm^2/20\ cm \times 20\ cm)$

The weight must be measured at a place where the wind velocity is 0.5 m/sec or less.

In the light-sensitive photographic material of the present invention, the photographic emulsion layers and other hydrophilic colloid layers may contain a dispersion of a water-insoluble or sparingly soluble synthetic polymer for the purpose of improving dimension stability or the like purposes. For example, there can be used alone or in combination, alkyl (meth)acrylates, alkoxyalkyl (meth)acrylates, glycidyl (meth)-acrylate, (meth)acrylamide, vinyl esters (as exemplified by vinyl acetate), acrylonitrile, olefins, styrene, etc., or polymers having as monomer components any combination with the above and acrylic acid, methacrylic acid, α,β-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulfoalkyl (meth)acrylates, styrenesulfonic acid or the like. In the foregoing, the term "(meth)acrylate" is abbriviation for both the acrylate and methacrylate.

The light-sensitive silver halide photographic material of the present invention may preferably be provided with a protective layer. This protective layer is a layer comprised of a hydrophilic colloid, and the hydrophilic colloid to be used includes those previously described. The protective layer may comprise a single layer or overlapped layers.

A matting agent and/or a smoothening agent may be added in the emulsion layers or protective layer-(s), preferably in the protective layer(s), of the light-sensitive silver halide photographic material of the present invention. Usable as the matting agent are those known in the art, but more preferably are polymer matting agents or silica matting agents, whose average particle diameter may preferably be in the range of from 0.3 µm to 12 µm, particularly preferably from 3 µm to 9 µm.

In working the present invention, as specific examples of the polymer matting agents to be used, used are water-dispersible vinyl polymers such as polymethyl methacrylate, and cellulose acetate propionate, starch, or the like. Particularly preferred are matting agents comprising water-dispersible vinyl polymers including homopolymers of acrylic acid esters such as methyl methacrylate, glycidyl acrylate and glycidyl methacrylate, or copolymers of these acrylic acid esters or with other vinyl monomers. Among these, particularly preferred are spherical matting agents comprising polymethyl methacrylate having an average particle diameter of from 3 µm to 9 µm.

As for the position at which the matting agent is added, it may be added to the protective layer above an emulsion layer, or, for example, to the protective layer on the reverse side, but the above polymer matting agent may more preferably be added to the protective layer on the side of the emulsion layer, so that it may not occur that the light-sensitive materials slip when light-sensitive photographic materials containing the polymer matting agent are processed using a roller carrier type automatic processor.

The smoothening agent facilitates prevention of sticking troubles, like the matting agent, and in addition it is effective for improving friction properties concerned with the adaptability to cameras particularly when projection or cinematographing of motion picture films is performed. Specific examples thereof are waxes such as liquid paraffin and esters of higher fatty acids, fluorinated hydrocarbons or derivatives thereof, silicones such as polyalkylpolysiloxanes, polyarylpolysiloxanes, polyalkylarylpolysiloxanes, or alkylene oxide addition derivatives thereof, etc., which are preferred for use.

In the light-sensitive material of the present invention, it is preferred to use a plasticizer to prevent fog at the time of coating or drying, or prevent fog, desensitization or the like caused when folded under a low moisture condition. The plasticizer that can be used are exemplified by those described in Japanese Patent O.P.I. Publication No. 63715/1973, Japanese Patent Examined Publications No. 4939/1968 and No. 8745/1972, U.S. Patents No. 306,470, No. 2,960,404, No. 3,412,159 and No. 3,791,857, etc., but preferred is to incorporate at least one kind of polyhydric alcohol compounds melting at 40 °C and having at least two hydroxyl groups. Preferred as such compounds are alcohols having 2 to 12 hydroxyl groups, having 2 to 20 carbon atoms, and in which the hydroxyl groups are not conjugated with a conjugating chain, in other words, for which any oxidized form can not be written. Further preferred are those having a melting point of not less than 50 °C and not more than 300 °C. Examples of the compounds include those described in

Japanese Patent O.P.I. Publication No. 147449/1987.

In working the present invention, a surface active agent can be used in the light-sensitive material for various purposes, and may include, for example, nonionic surface active agents such as saponin (steroid type); alkylene oxide derivatives as exemplified by polyethylene glycol, a polyethylene glycol polypropylene glycol condensate, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol sorbitan acid esters, polyethylene glycol alkylamines or amides and polyoxyethylene oxide addition products of silicone; glycidol derivatives as exemplified by alkenyl succinic acid polyglycerides and alkylphenol polyglycerides; fatty acid esters of polyhydric alcohols; and alkyl esters of sugars. Also usable are anionic surface active agents having an acidic group such as a carboxyl group, a sulfo group, a phospho group, a sulfuric acid ester group or a phosphoric acid ester group, as exemplified by alkylcarboxylates, alkylsulfonates, alkylbenzenesulfonates, alkylnaphthalenesulonates, alkylsulfuric acid esters, alkylphosphoric acid esters, N-acyl-N-alkyltaurines, sulfosuccinic acid esters, sulfoalkylpolyoxyethylene alkyl phenyl ethers and polyoxyethylene alkylphosphoric acid esters. There may be further included amphoteric surface active agents such as amino acids, aminoalkylsulfonic acids, aminoalkylsulfuric acids, alkylbetaines and amine oxides. Also included are cationic surface active agents such as alkylamine salts, aliphatic or aromatic quaternary ammonium salts, heterocyclic quaternary ammonium salts as exemplified by pyridinium and imidazolium, and phosphonium or sulfonium salts containing an aliphatic or heterocyclic ring. Further usable are fluorine containing surface active agents, and fluorine-containing surface active agents having a polyoxyethylene group.

The surface active agents of alkylene oxide type may include those disclosed in Japanese Patent Examined Publication No. 9610/1976, DT 26 48 746, Japanese Patent O.P.I. Publications No. 129623/1978, No. 89624/1979, No. 98235/1978, No. 203435/1983, No. 208743/1983, No. 80848/1985 and No. 94126/1985, etc. Examples in which the surface active agents of alkylene oxide type and other compounds are used in combination may include those disclosed in Japanese Patent O.P.I. Publications No. 89626/191979, No. 70837/1980, No. 11341/1982, No. 109947/1982, No. 74554/1984, No. 76741/1985, No. 76742/1985, No. 76743/1985, No. 80839/1985, No. 80846/1985, No 80847/1985, No. 131293/1975, No. 29715/1978, etc.

The anionic surface active agents may include those disclosed in Japanese Patent O.P.I. Publication No. 21922/1978, GB 1,503,218, Japanese Patent Examined Publication No. 1617/1981, and also sulfuric acid ester salts of higher alcohols, higher alkylsulfonates, alkylybenzenesulfonates, dialkylsulfosuccinates, acylmethyltauride, N-acylglucocinate, fatty acid monoglyceride sulfate, and α-sulfonic acid.

The fluorine-containing surface active agents may include, for example, the compounds disclosed in Japanese Patent Examined Publications No. 9303/1972, No. 43130/1973, No. 25087/1977 and No. 1230/1982, Japanese Patent O.P.I. Publications No. 46733/1974, No. 16525/1975, No. 34233/1975, No. 32322/1976, No. 14224/1979, No. 111330/1979, No. 557762/1980, No. 19042/1981, No. 41093/1981, No. 34856/1981, No. 11341/1982, No. 29691/1982, No. 64228/1982, No. 146248/1982, No. 114944/1981, No. 114945/1981, No. 196544/1983, No. 200235/1983, No. 109548/1985 and No. 136534/1982, U.S. Patents No. 3,589,906, No. 3,775,126 and No. 4,292,402, RD 16630, etc., and the compounds exemplified in Japanese Patent O.P.I. Publication No. 164738/1985.

In the light-sensitive photographic material of the present invention, other various additives can be optionally used. For example, they include dyes, development accelerators, brightening agents, color-fog preventive agents and ultraviolet absorbents. Specifically, there can be used those described in Research Disclosure No. 176, pages 22-31, (RD-17643, 1978).

The light-sensitive silver halide photographic material of the present invention can besides be optionally provided with antihalation layers, intermediate layers, filter layers and so forth.

In the light-sensitive photographic material of the present invention, the photographic emulsion layers and other layers can be embodied by being coated on one side or both sides of a flexible support commonly used in light-sensitive photographic materials. Useful as the flexible support are films comprising semisynthetic or synthetic polymers such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, and polycarbonate, or paper coated or laminated with a baryta layer, or α-olefin polymers as exemplified by polyethylene, polypropylene and an ethylene/butene copolymer. The supports may be colored using dyes or pigments. They may be blackened for the purpose of interception of light. In general, the surfaces of these supports are applied with subbing treatment to improve the adhesion to photographic emulsion layers. The subbing may preferably be carried out using the technique described in Japanese Patent O.P.I. Publication No 148944/1987. The surfaces of the supports may be applied with corona radiation, ultraviolet irradiation, flame treating, or the like before or after the subbing treatment. In detail, used are those described in the paragraph of "Supports" at page 25 of Research Disclosure, Vol. 176.

In the light-sensitive photographic material of the present invention, the photographic emulsion layers and other hydrophilic colloid layers can be coated on the support or on other layers according to various coating methods. In coating, usable are dip coating, roller coating, curtain coating, extrusion coating, or the like. In detail, there can be used the methods described in the paragraph of "Coating Procedures" at pages 27-28 of Research Disclosure, Vol 176.

The light-sensitive silver halide photographic material of the present invention can be used specifically in X-ray light-sensitive materials, lithographic light-sensitive materials, black and white photographing light-sensitive materials, color negative light-sensitive materials, color reversal light-sensitive materials, color photographic paper, colloid transfer processes, silver salt diffusion transfer processes, silver dye bleaching methods, print-out light-sensitive materials, light-sensitive materials for use in heat development, and so forth.

Exposure for obtaining a photographic image may be carried out by using conventional methods. Namely, there can be used any of various kinds of light sources containing ultraviolet light, including natural light (sunlight), a tungsten lamp, a fluorescent lamp, a mercury lamp, a xenon arc lamp, a carbon arc lamp, a xenon flash lamp, a cathode ray tube flying spot, a light-emitting diode, laser beams (for example, of a gas laser, a YAG laser, a dye laser and a semiconductor laser) . Also, exposure may be carried out by use of light emitted from phosphors excited by electron rays, X-rays, γ-rays, α-rays etc. Exposure may be carried out in the exposure time of 1 1000 second to 1 second used in ordinary cameras, as well as in exposure time shorter than 1 1000 second, for example, exposure time of 1 10^4 to 1 10^6 second using a xenon flash lamp or a cathode ray tube, or exposure longer than 1 second may also be used. If necessary, spectral composition of light used in exposure can be controlled by using a color filter.

Any of the various methods and various processing solutions as disclosed in Research Disclosure No. 176, pp.28-30 (RD-17643) can be used in the photographic processing of the light-sensitive material of the present invention. This photographic processing may be either photographic processing for the formation of silver images (i.e., black and white photographic processing) or photographic processing for the formation of color images (i.e., color photographic processing). The processing temperature may be selected in the range between 18° C to 50° C in usual cases, but may be made lower than 18° C or higher than 50° C.

Other various development methods as exemplified by heat development can be used as occasion demands.

A developing solution to be used when, for example, carrying out a black and white processing may contain known developing agents. There can be used as the developing agents, solely or in combination, dihydroxybenzenes as exemplified by hydroquinone, 3-pyrazolidones as exemplified by 1-phenyl-3-pyrazolidone, aminophenols as exemplified by N-methyl-n-aminophenol, etc. In general, besides these, the developing solution may contain a preservative, an alkali agent, a pH buffering agent, an antifoggant, etc., and may further contain, if necessary, a dissolution auxiliary, a color toning agent, a development accelerator, a surface active agent, an antifoaming agent, a hard water-softening agent, a hardening agent, a viscosity-imparting agent, etc.

As a special developing processing system, there may be employed a method in which a development agent is incorporated in a light-sensitive material, for example, in emulsion layers, and the light-sensitive material is processed in an aqueous alkali solution to carry out the development. Of the development agent, a hydrophobic development agent can be incorporated in the emulsion layers according to various methods as disclosed in Research Disclosure No. 169 (RD-16928), U.S. Patent No. 2,739,890, British Patent No. 813,253 and West German Patent No. 15 47 763. Such a developing processing may be combined with a silver salt stabilizing processing carried out by using thiocyanate.

As a fixing solution, those having the formulation generally employed can be used. As a fixing agent, there can be used thiosulfate and thiocyanate, as well as organic sulfur compounds known to be effective as fixing agents. The fixing solution may contain a water soluble aluminum salt as a hardening agent.

The photographic emulsion of the present invention may contain a color image-forming coupler, i.e., a compound capable of forming a dye by reacting with an oxidized product of an aromatic primary amine (for example, phenylenediamine derivative or aminophenol derivative) developing agent. For example, as a magenta coupler, there may be included 5-pyrazolone couplers, pyrazolone benzimidazole couplers, cyanoacetylcumarone couplers and open-chain acylacetonitrile couplers; as a yellow coupler, acylacetamide couplers as exemplified by benzoylacetanilides and pivaloylacetanirides, and as a cyan couplers, naphthol couplers and phenol couplers.

These couplers are preferably non-diffusible couplers having a hydrophobic group called a ballast group. The couplers may be either of four equivalent type or two equivalent type with respect to silver ion. There may be also included colored couplers having the color correcting effect or couplers capable of releasing a development restrainer as the development proceeds (the socalled DIR couplers).

Besides the DIR couplers, there may be included colorless DIR coupling compounds that may form a colorless product by the coupling reaction and release a development restrainer.

The light-sensitive silver halide photographic material of the present invention may contain a color-fog preventive agent including hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives, ascorbic acid derivatives, etc.

The light-sensitive silver halide photographic material of the present invention may contain an ultraviolet absorbent in the hydrophilic colloid layer. For example, there can be used benzotriazole compounds substituted with an aryl group as exemplified by those disclosed in U.S. Patent No. 3,533,794, 4-thiazolidone compounds as exemplified by those disclosed in No. 3,314,794 and No. 3,352,651, benzophenone compounds as exemplified by those disclosed in Japanese Patent O.P.I. Publication No. 2784/1971, cinnamic acid ester compounds as exemplified by those disclosed in U.S. Patents No. 3,705,805 and No. 3,705,375, butadiene compounds as exemplified by those disclosed in U.S. Patent No. 4,045,229, or benzooxydole compounds as exemplified by those disclosed in U.S. Patent No. 3,700,455. Those disclosed in U.S. Patent No. 3,499,762 and Japanese Patent O.P.I. Publication No. 48534/1979 can be further used. Couplers having ultraviolet absorbing properties as exemplified by cyan dye-forming couplers of α-naphthol type, or polymers having ultraviolet absorbing properties may be also used. These ultraviolet absorbents may be mordanted in a particular layer.

In working the present invention, a variety of anti-color-fading agents can be used in combination, and any color image stabilizers can be used alone or in combination of two or more of them. The anti-color-fading agents may include hydroquinone derivatives, gallic acid derivatives, p-alkoxyphenols, p-oxyphenol derivatives and bisphenols.

In general, a color developing solution may comprise an alkaline aqueous solution containing a color development agent. The color development solution that can be used may include various primary aromatic amine developing agents such as phenylenediamines as exemplified by 4-amino-N,N-diethylamine, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamide ethylaniline and 4-amino-3-methyl-N-ethyl-N-β-methoxyethylaniline.

Besides these, there may also be used those disclosed in L.F.A. Mason, Photographic Processing Chemistry, Focal Press (1966), pp.226-229, U.S. Patents No. 2,193,015 and No. 2,592,364, Japanese Patent O.P.I. Publication No. 64933/1973, etc.

The color developing solution may further contain a pH buffering agent such as sulfite of alkali metals, carbonate, borate and phosphate, a development restrainer or antifoggant such as bromide, iodide and organic antifoggants, and so forth. If necessary, it may also contain a hard water softening agent, a preservative such as hydrozylamine, an organic solvent such as benzyl alcohol and diethylene glycol, a development accelerator such as polyethylene glycol, quaternary ammonium salts and amines, a color dye-forming coupler, a competing coupler, a fogging agent such as sodium boron hydride, an auxiliary development agent such as 1-phenyl-3-pyrazolidone, a viscosity imparting agent, a polycarboxylic acid type chelating agent and an antioxidant.

After the color development, the photographic emulsion layers are usually subjected to bleaching processing. The bleaching processing may be carried out simultaneously with fixing processing, or may be carried out separately. As a bleaching agent, there may be used polyvalent metal compounds such as iron (III), cobalt (IV), chrome (VI) and copper (II), peracids, quinones and nitroso compounds.

For example, there can be used ferricyanide, dichromate, organic complex salts of iron (II) or cobalt light, as exemplified by complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, nitrilotriacetic acid and 1,3-diamino-2-propanoltetraacetic acid, or of organic acids such as citric acid, tartaric acid and malic acid; persulfate; permanganate; and nitrsophenol. Of these, particularly useful are potassium ferricyanide, sodium ethylenediaminetetraacetic acid iron (III) and ammonium ethylenediaminetetraacetic acid iron (III). Ethylenediaminetetraacetic acid iron (III) complex salts are useful in both an independent bleaching solution and a combined bleach-fixing solution.

The embodiments of the present invention can be applied in the entirely same manner also in light-sensitive silver halide photographic materials in which a high-contrast agent is used.

The high-contrast agent includes tetrazolium compounds disclosed in Japanese Patent O.P.I. Publications No. 18317/1977, No. 17719/1978, No. 17720/1978 and No. 149946/1986, and specific acylhydrazine compounds as seen in U.S. Patents No 4,166,742, No. 4, 168,977, No. 4,221,857, No 4,224,401, No 4,243,739, No. 4,272,606 and No. 4,311,781. These high-contrast agents may be added in light-sensitive silver halide emulsion layers, or may be added in other hydrophilic colloid layers existing at the same side as said silver halide emulsion layers with respect to the support. Light-sensitive silver halide photographic materials in which the tetrazolium compound is used as the high-contrast agent or the acylhydrazine compound may particularly preferably processed using a PQ type or MQ type developing solution (pH 10.0

to 12.9) containing a sulfite in a relatively high concentration.

Also, particularly when the high-contrast agent is used, the dye of λmax of 400 to 850 nm may be coated as a backing layer on the side opposite to a hydrophilic colloid layer containing the high-contrast agent, thus bringing about more effectiveness. In that occasion, the dye may be added only in the backing layer, or may be coated on both the backing layer side and the side containing the high-contrast agent with respect to the support.

EXAMPLES

Examples of the present invention will be described below in detail. As a matter of course, the present invention is by no means limited by Examples described below.

Example 1

Emulsion E-1 was obtained according to the procedures shown below. First, while making control to 60 °C, pAg = 8.0 and pH = 2.0, obtained was a monodisperse cubic emulsion comprising a silver iodobromide emulsion having an average grain size of 0.28 µm and containing 2.0 mol % of silver iodide. An electron microscope photograph showed that, in this emulsion, twin crystal grains were generated in the rate of 1 % or less in number. This emulsion, serving as a seed crystal emulsion, was added and dispersed in a solution containing protective gelatin maintained at 40 °C and ammonia that may be optionally added, followed by adjustment of pH by use of glacial acetic acid.

Using the resulting solution as a mother solution, an aqueous 3.2 N ammoniacal silver ion solution and an aqueous halide solution containing iodine were added therein according to a double jet method while controlling the flow rate, and layers (shell layers) having various silver iodide contents were successively formed on cores. Here, in the case when a layer (shell layer) having a silver iodide content of 30 mol % is formed, the emulsion was prepared by controlling the pAg to 7.3 and the pH to 9.7. Also, to form a layer (shell layer) having a silver iodide content of 0 mol %, the emulsion was prepared by controlling the pAg to 9.0, or more than 9.0. More specifically, as shown in Fig. 2, a layer (shell layer) was formed with a silver iodide content of 20 mol % or more until the proportion of the silver used in preparation reaches 7 %, and thereafter a layer (shell layer) with a silver iodide content of 20 mol % or less was formed by preparing the emulsion according to the pattern as shown in Fig. 2. The emulsion thus obtained was a monodisperse silver iodide emulsion having an average grain size of 1.25 µm, and having the proportion of silver iodide to the whole silver halides, of 2 % in all.

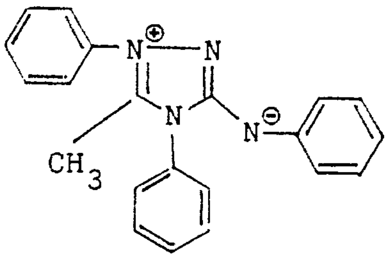
Next, the same procedures as in E-1 were repeated to obtain emulsion E-2 having an average grain size of 0.90 micron and emulsion E-3 having an average grain size of 0.65 micron. Both E-2 and E-3 were monodisperse emulsions containing silver iodide in the proportion of 2 mol %.

These resulting three kinds of emulsions were subjected to a usual flocculation method to remove excess salts. More specifically, they were maintained at 40 °C, and a formalin condensate of sodium naphthalene sulfonate and an aqueous solution of magnesium sulfate were added thereto to effect flocculation. After supernatants were removed, pure water of 40 °C was further added, and an aqueous solution of magnesium sulfate was again added to effect flocculation, thus removing supernatants. Thereafter, to each emulsion, 2.0 x 10^{-3} mol/mol AgX of ammonium thiocyanate was added, and chloroaurate and hypo were further added in appropriate amounts to effect chemical ripening. Lime-treated gelatin was thereafter added to prepare emulsions so as to give the amount of gelatin as shown in Table 1. Thereafter, the respective emulsions were mixed in the proportion of E-1: 25 wt.%, E-2: 40 wt.% and E-3: 35 wt.%, to which the additives shown below were added, and exemplary compounds of the dyes previously described were further added in the manner as shown in Table 1, thus making emulsion coating solutions. Next, a protective layer coating solution having the composition shown below was prepared, and then finished by appropriately adding a hardening agent comprising 2 % of an aqueous solution of sodium 2,4-dichloro-6-hydroxy-1,3,5-triazine so as to give the value of melting time as shown in Table 1.

The melting time is expressed as the time by which silver halide grains are released from a support when immersed in an aqueous solution of 50 °C, of 1.5 % by weight of sodium hydroxide in a state that no stirring was made.

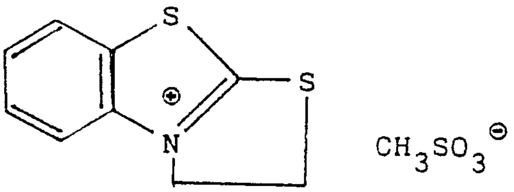
The additives used in the emulsions (silver halide coating solutions) are as follows. The amount for addition is expressed as the amount per mol of silver halide.

1,1-Dimethylol-1-bromo-1-nitromethane	70 mg

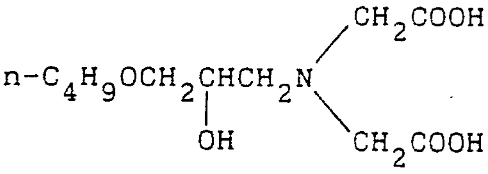


150 mg

t-Butyl-catechol	400 mg
Polyvinyl pyrrolidone (molecular weight: 10,000)	1.0 g
A 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



70 mg

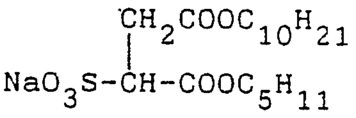


$$n\text{-}C_4H_9OCH_2\underset{\displaystyle OH}{CH}CH_2N(CH_2COOH)_2$$

1 g

The additives used in the protective layer coating solution were as follows. The amount for addition is expressed as the amount per liter.

Lime-treated inert gelatin	68 g
Acid-treated gelatin	2 g



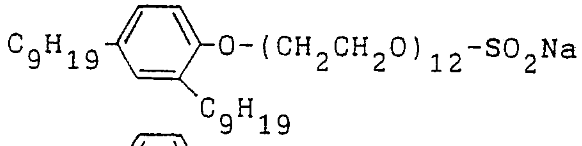
$$NaO_3S\text{-}\overset{\displaystyle CH_2COOC_{10}H_{21}}{CH}\text{-}COOC_5H_{11}$$

(coating aid)

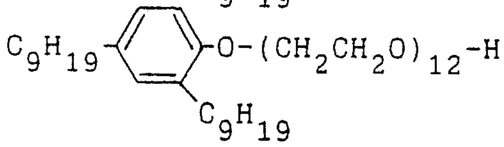
1 g

Polymethyl methacrylate, a matting agent having the area average particle diameter of 4.5 µm	1.1 g
Silicon dioxide particles, a matting agent having the area average particle diameter of 1.2 µm	0.5 g
Ledox (available from Du Pont)	30 g

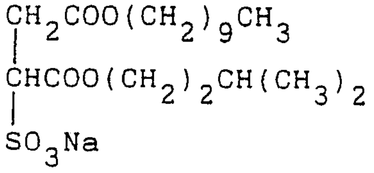
(Colloidal silica)



1.0 g

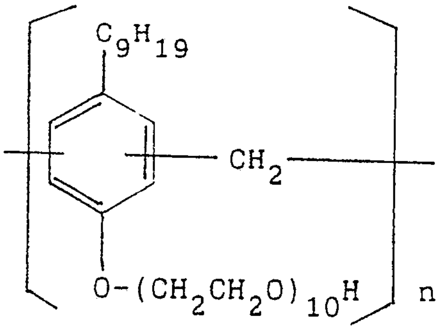


0.4 g



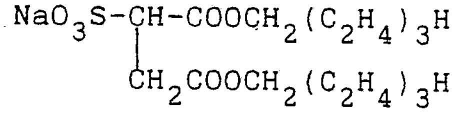
$$CH_2COO(CH_2)_9CH_3 \mid CHCOO(CH_2)_2CH(CH_3)_2 \mid SO_3Na$$

0.3 g



2.5 g

(n is 2 to 5, a mixture)



$$NaO_3S\text{-}CH\text{-}COOCH_2(C_2H_4)_3H \mid CH_2COOCH_2(C_2H_4)_3H$$

0.5 g

$C_9F_{19}\text{-}O\text{-}(CH_2CH_2O)_{10}\text{-}CH_2CH_2\text{-}OH$ 3 mg

$C_4F_9SO_3K$ 2 mg

On polyethylene terephthalate film bases of 176 μm thick which were coated, as a subbing solution, with a water-based copolymer dispersion obtained by diluting a copolymer comprising three monomers of 50 wt.% of glycidyl methacrylate,10 wt.% of methyl methacrylate and 40 wt.% of butyl methacrylate so as to give its concentration of 10 wt.%, the respective emulsion coating solutions and protective layer coating solution obtained in the above were coated simultaneously on both sides in overlapped layers with use of two slide hopper type coaters under a coating rate of 75 m/min so as to give the amount of gelatin as shown in Table 1, followed by drying to obtain Samples No. 1 to No. 20. The emulsions were so coated that the amount of coated silver may be 5.5 g/m^2.

On the samples thus obtained, speed was measured in the following manner: Samples were held between two pieces of optical wedges whose density gradients were mirror-symmetrically adjusted, and exposed to light simultaneously from both sides with use of a light source having a color temperature of 5,400° K, for 1/12.5 second in equal amount.

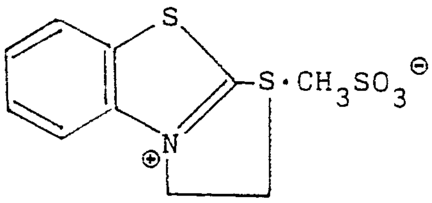
Subsequently, processing was carried out according to the following procedures, using a roller carrier type automatic processor whose total processing time can be arbitrarily made variable, and in a total processing time of 45 seconds.

	Temperature	Time
Inserting		1.2 second
Developing + carrying	35°C	14.6 seconds
Fixing + carrying	33°C	8.2 seconds
Washing + carrying	25°C	7.2 seconds
Squeegeeing	40°C	5.7 seconds
Drying	45°C	8.1 seconds
Total:	-	45.0 seconds

The developing solution and fixing solution used had the following make-up. Processing was carried out at temperatures of 34° C for the developing and 33° C for the fixing,

(Developing solution)

Potassium sulfite	70 g
Trisodium hydroxyethyl ethylenediaminetetraacetate	8 g
1,4-Dihydroxybenzene	27 g
Boric acid	10 g
5-Methylbenzotriazole	0.035 g
1-Phenyl-5-mercaptotetrazole	0.015 g
Sodium methabisulfate	5.0 g
Acetic acid (90 %)	12.5 g
Triethylene glycol	16.0 g
1-Phenyl-3-pyrazolidone	1.3 g
S-nitroindazole	0.2 g



0.001 g

Glutaldehyde	3.00 g
Disodium ethylenediaminetetraacetate	2.0 g
Potassium bromide	4.0 g
5-Nitrobenzimidazole	0.8 g

Made up to 1 liter of an aqueous solution, which was adjusted to pH 10.40 with potassium hydroxide.

(Fixing solution)

Sodium thiosulfate pentahydrate	45 g
Disodium ethylenediaminetetraacetate	0.5 g
Ammonium thiosulfate	140 g

Sodium sulfurous anhydride	7.5 g
Potassium acetate	15 g
Aluminum sulfate deca- to octadecahydrate	28 g
Sulfuric acid (50 wt.%)	6.0 g
Citric acid	1.0 g
Boric acid	7.0 g
Glacial acetic acid	5.2 g

Made up to 1 liter of an aqueous solution, which was adjusted to pH 4.0 by adding glacial acetic acid.

A reciprocal of the exposure at base density + fog density + 1.0 was found from the characteristic curve showing the resulting log-E (a logarithm of the exposure) and D (optical density) to determine the relative speed.

Subsequently, the sharpness of images was visually evaluated to indicate it by a five rank system of from 1 (poor) to 5 (excellent). There is no problem when it is 3 to 5, but, when it is 1 or 2, such samples are of no practical use.

The water content was also measured according to the procedures previously described.

The drying performance was also evaluated in the following manner: The above 45 second automatic processing was carried out, and overall evaluation on hand feeling, blocking to other samples, etc. was made on the samples having passed the drying section, and indicated by a five rank system of from 1 (poor) to 5 (excellent). There is no problem when it is 3 to 5, but, when it is 1 or 2, such samples are of no practical use.

Results obtained in the above are shown together in Table 1.

As will be clear from Table 1, the samples according to the present invention retain the sharpness and at the same time have a superior sharpness, as well as good drying performance and the suitability to the ultra-rapid processing.

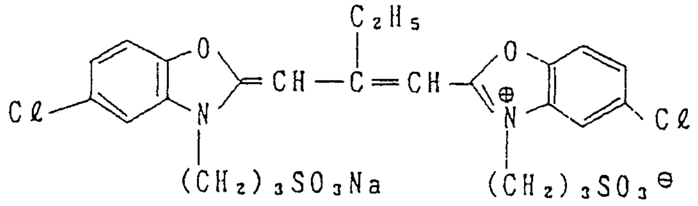
Table 1

Sample No.	Amount of gelatin (g/m^2); per one side)			Dye added		Speed	Sharpness	Drying performance	Invention or not	Melting time (min)	Water content (g/m^2)
	Emulsion layer	Protective layer	Total amount	Kind	Amount (mg/m^2)						
1	2.70	1.15	3.85	-	-	100	3	1	No	10	20.3
2	2.70	1.15	3.85	G	4.0	80	4	1	No	10	20.3
3	2.70	1.15	3.85	H	4.0	75	4	1	No	10	20.3
4	2.30	1.15	3.45	-	-	120	2	3	No	10	14.8
5	2.30	1.15	3.45	G	4.0	110	3	3	Yes	10	14.8
6	2.30	1.15	3.45	H	4.0	110	3	3	Yes	10	14.8
7	2.05	1.15	3.20	-	-	130	2	4	No	10	12.6
8	2.05	1.15	3.20	G	4.0	120	3	4	Yes	10	12.6
9	2.05	1.15	3.20	H	1.0	130	3	4	Yes	10	12.6
10	2.05	1.15	3.20	H	2.0	125	3	4	Yes	10	12.6
11	2.05	1.15	3.20	H	3.0	120	3	4	Yes	10	12.6
12	2.05	1.15	3.20	H	8.0	110	4	4	Yes	10	12.6
13	2.05	1.15	3.20	H	15.0	100	5	4	Yes	10	12.6
14	2.05	1.15	3.20	H	19.0	85	5	4	Yes	10	12.6
15	1.80	1.00	2.80	-	-	145	2	5	No	10	11.0
16	1.80	1.00	2.80	G	4.0	135	3	5	Yes	10	11.0
17	1.80	1.00	2.80	H	4.0	135	3	5	Yes	10	11.0
18	0.90	0.90	1.90	-	-	170	1	5	No	10	5.3
19	0.90	0.90	1.90	G	4.0	155	2	5	No	10	5.3
20	0.90	0.90	1.90	H	4.0	155	2	5	No	10	5.3

Example 2

Prepared in the same manner as in Example 1 were monodisperse silver iodobromide emulsions each having an average grain size of 0.58 micron (Emulsion E-4) and an average grain size of 0.4 micron (Emulsion E-5). Emulsions E-1, used in Example 1, E-4 and E-5 were mixed in the mixing proportion of E-1 : E-4 : E-5 = 30 wt.% : 30 wt.% : 40 wt.%, to which the sensitizing dye shown below was added in an amount of 600 mg per mol of silver halide, thereafter the amount of gelatin was so adjusted as to give the amount as shown in Table 2, and the exemplary compounds previously shown were added in the kind and amount as shown in Table 2. Other additives were thereafter further added in the same manner as in Example 1 (but using 15 g of trimethylolpropane) to make emulsion coating solutions. A protective layer coating solution was also prepared in the same manner as in Example 1. Provided that in the present Example polymethyl methacrylate particles having an average particle diameter of 5.5 µm were used, and, in the hardening agent, 35 % of formalin and 40 % of an aqueous glyoxal solution were used in place of the aqueous solution of sodium 2,4-dichloro-6-hydroxy-1,3,5-triazine, making adjustment to give the value of melting time as shown in Table 2.

Sensitizing dye



The resulting coating solutions were coated and dried under the same conditions as in Example 1 to make Samples No. 21 to No. 41.

A solution obtained by adding a dye as a non-light-sensitive layer coating solution in the kind and amount as shown in Table 2, subsequently adding gelatin to give the amount of gelatin as shown in Table 2, and further adding as a mordant agent the exemplary compound No. 5 and a coating aid, and an emulsion coating solution (no dye is added) and a protective layer coating solution which were prepared in the same manner as in the above, were coated simultaneously on both sides of a support in overlapped layers in the order of a non-light-sensitive layer, an emulsion layer and a protective laver from the support. Drying was thereafter carried out to obtain Sample No. 42.

On the resulting samples, speed was determined, sharpness and drying performance were evaluated and water content was measured in the same manner as in Example 1.

Results obtained in the above are shown together in Table 2.

As will be clear from Table 2, according to one of preferred embodiments of the present invention, it is seen how the invention is effective also in the system sensitized with a dye. The same effect is seen to be obtained also in accordance with one of other preferred embodiments of the present invention.

Similar evaluation was made on samples having the same constitution as the samples of the present Example but prepared to have the melting time of 13 minutes (a 20 % increase as the water content) and the melting time of 30 minutes (a 7 % decrease as the water content), respectively, by adjusting the amount of the hardening agent. As a result, there was obtained the same effect with the effect seen from Table 2.

Table 2

Sample No.	Amount of gelatin: Nonsensitive layer	Amount of gelatin (g/m^2; per one side)			Dye added		Speed	Sharpness	Drying performance	Invention or not	Melting time (min)	Water content (g/m^2)
		Emulsion layer	Protective layer	Total amount	Kind	Amount (mg/m^2)						
21	-	2.70	1.15	3.85	-	-	100	3	1	No	20	18.9
22	-	2.70	1.15	3.85	K	3.5	80	4	1	No	20	18.9
23	-	2.70	1.15	3.85	N	3.5	75	4	1	No	20	18.9
24	-	2.30	1.15	3.45	-	-	120	2	3	No	20	13.8
25	-	2.30	1.15	3.45	K	3.5	100	3	3	Yes	20	13.8
26	-	2.30	1.15	3.45	N	3.5	95	3	3	Yes	20	13.8
27	-	2.05	1.15	3.20	-	-	135	2	4	No	20	11.0
28	-	2.05	1.15	3.20	K	4.0	110	3	4	Yes	20	11.0
29	-	2.05	1.15	3.20	N	4.0	105	3	4	Yes	20	11.0
30	-	2.05	1.15	3.20	K + H	1.0 each	130	3	4	Yes	20	11.0
31	-	2.05	1.15	3.20	K + H	2.0 each	125	3	4	Yes	20	11.0
32	-	2.05	1.15	3.20	K + H	3.0 each	120	4	4	Yes	20	11.0
33	-	2.05	1.15	3.20	K + H	4.0 each	110	4	4	Yes	20	11.0
34	-	2.05	1.15	3.20	K + H	5.0 each	100	5	4	Yes	20	11.0
35	-	2.05	1.15	3.20	K + H	10.0 each	75	5	4	Yes	20	11.0
36	-	1.70	1.00	2.70	-	-	150	1	5	No	20	9.3
37	-	1.70	1.00	2.70	K	5.0	130	3	5	Yes	20	9.3
38	-	1.70	1.00	2.70	N	5.0	130	3	5	Yes	20	9.3
39	-	1.00	0.90	1.90	-	-	180	1	5	No	20	4.5
40	-	1.00	0.90	1.90	K	6.0	150	2	5	No	20	4.5
41	-	1.00	0.90	1.90	N	6.0	150	2	5	No	20	4.5
42	0.40	1.65	1.15	3.20	K + H	2.5 each	125	4	4	Yes	20	4.5

Example 3

Emulsions E-4 and E-5 used in Example 2 were mixed to give the mixing proportion of E-4 : E-5 = 75 wt.% : 25 wt.%, followed by addition of the sensitizing dye used in Example 2, in an amount of 700 mg per mol of silver halide, adjustment of the amount of gelatin and the kind and amount of the above exemplary compounds serving as dyes, in the manner as shown in Table 3, and also similar addition of other additives (but using 5 g of trimethylolpropane), to make emulsion coating solutions. Also, protective layers were formed in the same manner as in Example 1 but by making a protective layer coating solution prepared by using polymethyl methacrylate having an average particle diameter of 7.5 microns as a matting agent and using as a hardening agent the same compound as in Example 1, so as to give the melting time as shown in Table 3. The resulting two coating solutions were coated simultaneously on one side of supports in two layers. Drying was carried out to obtain Samples No. 43 to No. 61. The resulting samples had the amount of coated silver, of 3.7 g/m^2.

Subsequently, on the resulting samples, speed was determined, sharpness and drying performance were evaluated and water content was measured in the same manner as in Example 1.

Results obtained in the above are shown together in Table 3.

As will be clear from Table 3, according to the present invention, the effect of the invention is seen to be great also in the light-sensitive material provided with the light-sensitive silver halide emulsion layer only on one side of the support.

The same effect as in Example 3 was obtained also in the sample in which the exemplary compound serving as a dye was not added in the emulsion layer and the exemplary compound was added in the non-light-sensitive photographic component layer provided on the reverse side.

Table 3

Sample No.	Amount of gelatin (g/m^2); per one side)			Dye added		Speed	Sharpness	Drying performance	Invention or not	Melting time (min)	Water content (g/m^2)
	Emulsion layer	Protective layer	Total amount	Kind	Amount (mg/m^2)						
43	2.70	1.15	3.85	-	-	100	3	1	No	15	17.3
44	2.70	1.15	3.85	K	3.5	75	4	1	No	15	17.3
45	2.70	1.15	3.85	N	3.5	75	4	1	No	15	17.3
46	2.30	1.15	3.45	-	-	115	2	3	No	15	12.7
47	2.30	1.15	3.45	K	3.5	100	3	3	Yes	15	12.7
48	2.30	1.15	3.45	N	3.5	100	3	3	Yes	15	12.7
49	2.05	1.15	3.20	-	-	140	2	4	No	15	10.0
50	2.05	1.15	3.20	K	4.5	115	3	4	Yes	15	10.0
51	2.05	1.15	3.20	N	4.5	115	3	4	Yes	15	10.0
52	2.05	1.15	3.20	K+H	1.5 each	130	3	4	Yes	15	10.0
53	2.05	1.15	3.20	K+H	3.0 each	110	4	4	Yes	15	10.0
54	2.05	1.15	3.20	K+H	6.0 each	95	5	4	Yes	15	10.0
55	2.05	1.15	3.20	K+H	10.0 each	85	5	4	Yes	15	10.0
56	1.70	1.00	2.70	-	-	160	1	5	No	15	8.5
57	1.70	1.00	2.70	K	5.5	135	3	5	Yes	15	8.5
58	1.70	1.00	2.70	N	5.5	135	3	5	Yes	15	8.5
59	1.05	0.90	1.95	-	-	180	1	5	No	15	3.8
60	1.05	0.90	1.95	K	6.0	150	2	5	No	15	3.8
61	1.05	0.90	1.95	N	6.0	150	2	5	No	15	3.8

Example 4

Light-sensitive silver halide photographic materials were made in the following manner:

(Preparation of emulsion)

A silver chlorobromide containing 2 mol % of silver bromide was prepared in the following manner.

An aqueous solution containing 23.9 mg of potassium pentabromorhodate per 60 g of silver nitrate together with sodium chloride and potassium bromide and an aqueous silver nitrate solution were simultaneously mixed into an aqueous gelatin solution with stirring, over a period of 25 minutes at 40 °C to make a silver chlorobromide emulsion having an average grain size of about 0.17 µm.

In this emulsion 200 mg of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene was added as a stabilizing agent, followed by washing with water and desalting.

After 20 mg of 6-methyl-4-hydroxy1,3,3a,7-tetrazaindene was added thereto, sulfur sensitization was applied. After the sulfur sensitization, 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene was added as a stabilizing agent, followed by making-up to 260 ml with water to prepare the emulsion.

(Preparation of latex (α) for use in addition of emulsion)

In a solution obtained by adding 0.25 kg of KMDS (dextran sulfuric acid ester sodium salt) available from Meito Sangyo Co., Ltd. and 0.05 kg of ammonium persulfate in 40 ml of water, a mixed solution comprising 4.51 kg of n-butyl acrylate, 5.49 kg of styrene and 0.1 kg of acrylic acid was added over a period of 1 hour at a liquid temperature of 81 °C with stirring and under a nitrogen atmosphere, followed by addition of 0.005 kg of ammonium persulfate, and cooling after further stirring for 1.5 hour, and then the pH was adjusted to 6 with ammonia water. The resulting latex solution was filtered using GF D Filter available from Whotman Co., and made up to 50.5 kg with water, thus making a latex solution (α) for use in addition of emulsion, having an average grain size of about 0.25 microns and monodispersed.

In the above emulsion, additives shown below were added to prepare a silver halide emulsion coating solution.

(Preparation of emulsion coating solution)

In the above emulsion, 9 mg of compound (a) was added as a fungiside. Thereafter, the pH was adjusted to 6.5 with use of a 0.5 N sodium hydroxide solution, and the following compound (I-1) was added as a high contrast agent in an amount of 4 x 10^{-3} mol per mol of silver. Further successively added were 5 ml of an aqueous 20 % saponin solution, 180 mg of sodium dodecylbenzenesulfonate, 80 mg of 5-methylbenztriazole, 43 ml of the above latex solution (α) for use in addition of emulsion, 60 mg of compound (b) shown below and as a thickening agent 280 mg of a water-soluble polymer of a styrene/maleic acid copolymer, all per mol of silver halide, followed by making-up to 475 ml with water to prepare emulsion coating solution E1.

Similarly also prepared was emulsion coating solution E2 by adding as a high-contrast agent 4 x 10^{-4} mol of acylhydrazine compound (I-2) in place of tetrazolium compound (I-1).

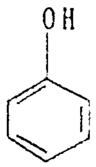
Next, an emulsion protective layer coating solution was prepared in the following manner.

(Preparation of emulsion protective layer coating solution P-1)

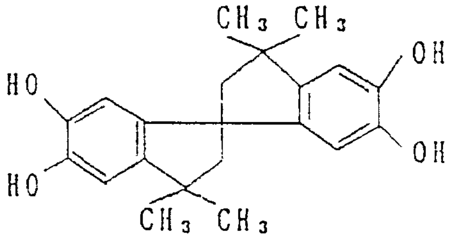
In 1 kg of gelatin, 10 lit. of pure water was added to make dissolution at 40 °C after swell. and then successively added were 2.9 lit. of an aqueous 1 % solution of the following compound (c) as a coating aid, 65 g of exemplary compound (C) as the dye having a maximum absorption wavelength (λmax) of 400 to 850 nm according to the present invention, 20 g of amorphous silica of 8 microns in average particle diameter and 10 g of amorphous silica of 3 microns in average particle diameter as matting agent, and 62 g of the following compound (d). The mixture was further adjusted to pH 5.4 using a citric acid solution. followed by making-up to 17 lit. using water. thus preparing emulsion protective layer coating solution P-1.

In entirely the same manner. emulsion protective layer coating solution P-2 was also prepared by using exemplary compound (U) as the dye in place of exemplary compound (C).

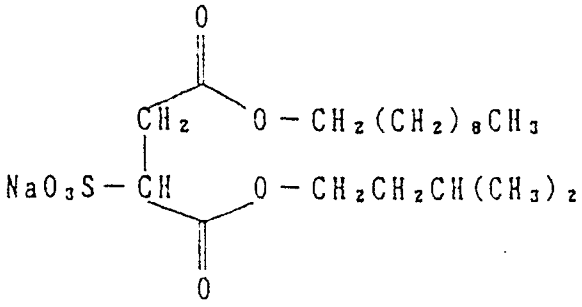
Compound (a)



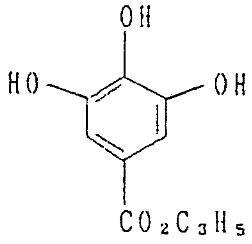
Compound (b)



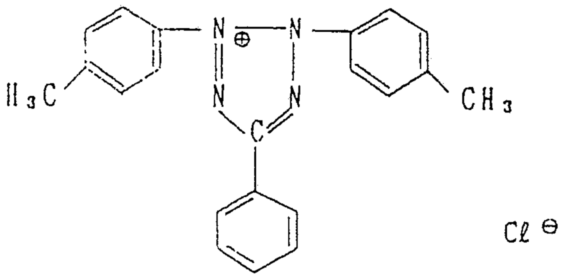
Compound (c)



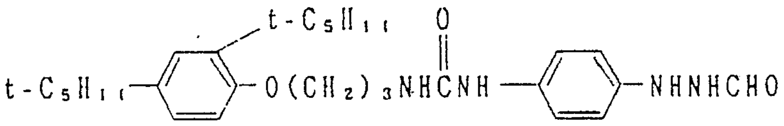
Compound (d)



Compound (I-1)



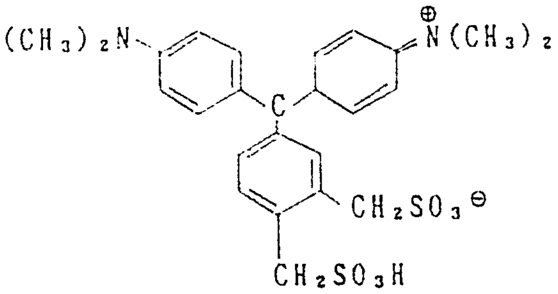
Compound (I-2)



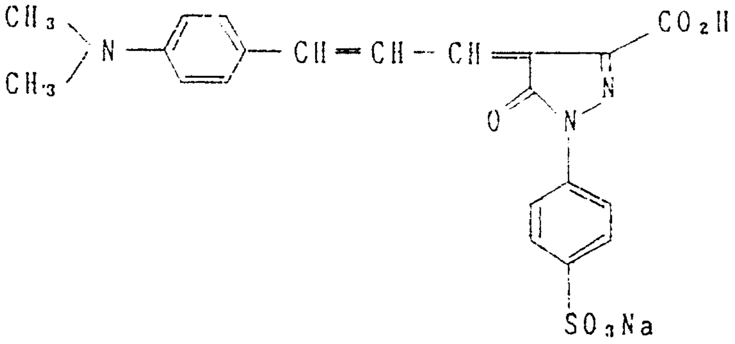
(Preparation of backing coating solution B-1)

After dissolution of 36 kg of gelatin by swelling in water and heating, added in the form of aqueous solutions were 1.6 kg of the following compound (e-1) as a dye, 310 g of compound (e-2), 1.9 kg of compound (e-3) and 2.9 kg of the above exemplary compound (C) according to the present invention. next added were 11 lit. of an aqueous 20 % solution of saponin and 5 kg of the following compound (e-4) as a property adjusting agent, and further added were 63 g of the following compound (e-5) as a methanol solution and 270 g of the following compound (e-6). To the resulting solution, 800 g of a water-soluble polymer of a styrene/maleic acid copolymer was added as a thickening agent to make adjustment of viscosity, and further the pH was adjusted to 5.4 using an aqueous citric acid solution. Finally, 144 g of glyoxal was added, followed by making-up to 960 lit. with water to prepare backing coating solution B-1.

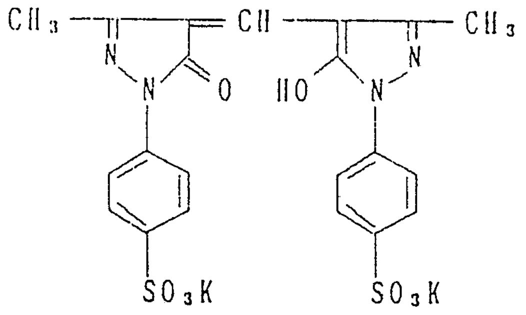
Compound (e-1)



Compound (e-2)

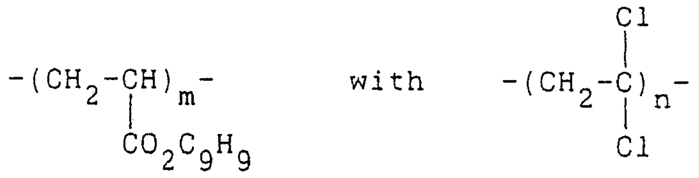


Compound (e-3)



Compound (e-4)

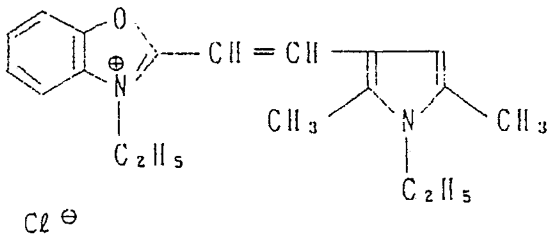
A copolymer latex of;



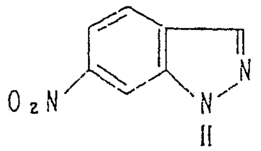
$-(CH_2-\underset{CO_2C_9H_9}{CH})_m-$ with $-(CH_2-\underset{Cl}{\overset{Cl}{C}})_n-$

wherein m:n = 1:1

Compound (e-5)



Compound (e-6)



Subsequently, for use in protective layer coating for the backing layer, protective layer coating solution P-3 was prepared in the following manner.

(Preparation of protective layer coating solution)

After dissolution of 50 kg of gelatin by swelling in water and heating, added was 340 g of sodium 2-sulfonate-succinic acid bis (2-ethylhexyl)ester, also added were 1.7 kg of polymethyl methacrylate (average particle diameter: about 0.4 microns) as a matting agent and 3.4 kg of sodium chloride, and further added were 1.1 kg of glyoxal and 540 g of mucochloric acid, followed by making-up to 1.000 lit. with water to prepare protective layer coating solution P-3.

(Preparation of samples for evaluation)

The above respective coating solutions were coated on both sides and for each side of polyethylene terephthalate films (thickness: 100 microns) each applied with the subbing layer of Example 1, thus preparing the samples for evaluation as shown in Table 4. In that occasion, on the one side of each support provided by coating with the subbing layer, a backing lower layer was coated by use of coating solution B-1 to have a gelatin dry weight of 2 g m^2, and at the same time a backing protective layer was coated thereon by use of protective layer coating solution P-3 to have a gelatin dry weight of 1 g m^2, followed by drying. Subsequently, an emulsion layer was coated on the other side of each support to have the gelatin dry weight as shown in Table 4, and, while adding formalin as a hardening agent, an emulsion protective layer was coated thereon simultaneously with the emulsion layer by use of protective layer coating solution P-1 to have the gelatin dry weight as shown in Table 4, followed by drying to make Samples 62 to 79 for evaluation.

The combination of the emulsion coating solution with the emulsion protective layer coating solution corresponds to the combination shown in Table 4, of the high-contrast agent with the dye.

(Evaluation on photographic performances)

Using the same automatic processor and under the same processing conditions as in Example 1, processing was carried out by only the 45 second processing. Provided that prepared were processing solutions of two kinds of make-up for developing solutions (B) and (C) as shown below, which were properly used for each high-contrast agent as shown in Table 4. The fixing solution used had the following make-up.

Exposure to light was carried out by using a non-electrode discharge tube manufactured by Fusion Co., U.S.A., and by making irradiation only on the emulsion face side through an optical wedge. The speed was expressed by a relative value of density 2.5 and a reciprocal value of the exposure to be given, assuming that of Sample 62 as 100. The sharpness was visually evaluated. The manner for the ranking follows Example 1. The drying performance was evaluated by the feel, and the manner for the ranking also follows Example 1.

Developing solution (B):

(Make-up (1)

Pure water (ion exchanged water)	150 ml
Disodium ethylenediaminetetraacetate	2 g
Diethylene glycol	50 g
Potassium sulfite (an aqueous 55 % w v solution)	100 ml
Potassium carbonate	50 g
Hydroquinone	15 g
5-Methylbenzotriazole	200 mg
1-Phenyl-5-mercaptotetrazole	30 mg
Potassium hydroxide, in the amount by which the pH of a solution used is brought to 10.4	
Potassium bromide	4.5 g

(Make-up 2)

Pure water (ion exchanged water	3 mg
Diethylene glycol	50 g
Disodium ethylenediaminetetraacetate	25 mg
Acetic acid (an aqueous 90 % solutions)	0.3 ml
5-Nitroindazole	110 mg
1-Phenyl-3-pyrazolidone	500 mg

When the developing solutions were used, they were used by dissolving in 500 ml of water the above solutions of make-up 1 and make-up 2 in this order, finishing them to 1 lit.

Developing solution (C):

(Make-up 1)

Hydroquinone	45.0 g
N-methyl-p-aminophenol 1 2 sulfate	0.8 g
Sodium hydroxide	18.0 g
Potassium hydroxide	55.0 g
5-sulfosalicylic acid	45.0 g
Boric acid	25.0 g
Potassium sulfite	110.0 g
Disodium ethylenediaminetetraacetate	1.0 g
Potassium bromide	6.0 g
5-Methylbenzotriazole	0.6 g
n-Butyl-diethanolamine	15.0 g

Made up to 1 lit. by adding water. (pH = 11.6)

Fixing solution formulation:

(Make-up 1)

Ammonium thiosulfate (an aqueous 72.5 % w/v solution)	230 ml
Sodium sulfite	9.5 g
Sodium acetate trihydrate	15.9 g
Boric acid	6.7 g
Sodium citrate dihydrate	2 g
Acetic acid (an aqueous 90 % w w solution)	8.1 ml

(Make-up 2)

Pure water (ion exchanged water)	17 ml
Sulfuric acid (an aqueous 50 % w/w solution)	5.8 g
Aluminum sulfate (an aqueous solution having a content of 8.1 % w/w in terms of Al_2O_3	26.5 g

When the fixing solutions were used, they were used by dissolving in 500 ml of water the above solutions of make-up 1 and make-up 2 in this order, finishing them to 1 lit.

The resulting fixing solutions had the pH of about 4.3.

Table 4

Sample No.	Amount of gelatin (g/m^2; per one side)			Dye added (Exemplary compound)		High-contrast agent		Kind of developing solution	Speed	Sharpness	Drying performance	Invention or not
	Emulsion layer	Protective layer	Total amount	Kind	Amount (mg/m^2)	Kind	Amount (mol/Ag 1 mol)					
62	2.85	1.0	3.85	-	-	I-1	4×10^{-3}	(B)	100	2	2	No
63	2.85	1.0	3.85	C	65	I-1	4×10^{-3}	(B)	92	4	2	No
64	2.85	1.0	3.85	U	65	I-1	4×10^{-3}	(B)	93	4	2	No
65	2.85	1.0	3.85	-	-	I-2	4×10^{-4}	(C)	105	2	2	No
66	2.85	1.0	3.85	C	65	I-2	4×10^{-4}	(C)	83	4	2	No
67	2.85	1.0	3.85	U	65	I-2	4×10^{-4}	(C)	84	4	2	No
68	2.5	1.0	3.5	-	-	I-1	4×10^{-3}	(B)	102	2	4	No
69	2.5	1.0	3.5	C	65	I-1	4×10^{-3}	(B)	90	5	4	Yes
70	2.5	1.0	3.5	U	65	I-1	4×10^{-3}	(B)	89	5	4	Yes
71	2.5	1.0	3.5	-	-	I-2	4×10^{-4}	(C)	93	2	4	No
72	2.5	1.0	3.5	C	65	I-2	4×10^{-4}	(C)	81	5	4	Yes
73	2.5	1.0	3.5	U	65	I-2	4×10^{-4}	(C)	80	5	4	Yes
74	1.5	0.5	2.0	-	-	I-1	4×10^{-3}	(B)	105	2	5	No
75	1.5	0.5	2.0	C	32.5	I-1	4×10^{-3}	(B)	96	4	5	Yes
76	1.5	0.5	2.0	U	32.5	I-1	4×10^{-3}	(B)	94	4	5	Yes
77	1.5	0.5	2.0	-	-	I-2	4×10^{-4}	(C)	94	2	5	No
78	1.5	0.5	2.0	C	32.5	I-2	4×10^{-4}	(C)	81	4	5	Yes
79	1.5	0.5	2.0	U	32.5	I-2	4×10^{-4}	(C)	83	4	5	Yes

As will be clear from Table 4, the present invention is seen to achieve good sharpness and drying performance in the rapid processing even in the case of the light-sensitive silver halide photographic material in which the high-contrast agent is used.

As described above, the present invention makes it possible to reduce the amount of gelatin while retaining a high sharpness, and can provide light-sensitive materials that can be suitably applied in the ultra-rapid processing of the total processing time ranging from 20 seconds to 60 seconds.

Claims

1. A light-sensitive silver halide photographic material comprising a support and, provided thereon, photographic component layers containing a gelatin and including a silver halide emulsion layer and a layer containing a dye, said dye having, as an aqueous solution, at least one maximum absorption wavelength (λ_{max}) in the range of from 400 nm to 850 nm, and the amount of gelatin present on the same side of said silver halide emulsion layer being within the range from 2.0 g/m^2 to 3.5 g/m^2.

2. The light-sensitive silver halide photographic material of claim 1, wherein said silver halide emulsion layer is provided on both sides of said support.

3. The light-sensitive silver halide photographic material of claim 1, wherein said layer containing said dye is said silver halide emulsion layer or any other hydrophilic colloidal layer provided closer to said support than said silver halide emulsion layer.

4. The light-sensitive silver halide photographic material of claim 1, wherein said dye is present in said layer in an amount of from 0.2 mg/m^2 to 20 mg/m^2.

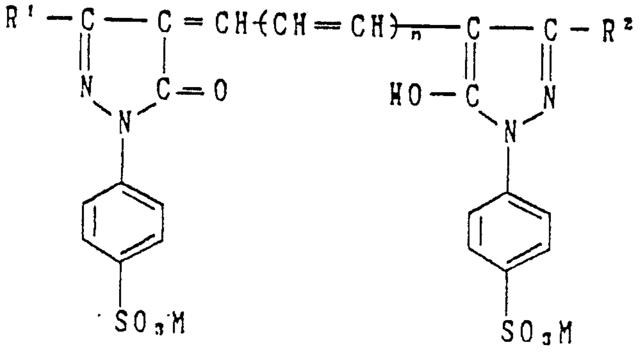
5. The light-sensitive silver halide photographic material of claim 4, wherein said dye is present in said layer in an amount of from 0.8 mg/m^2 to 15 mg/m^2.

6. The light-sensitive silver halide photographic material of claim 1, wherein said dye is a diffusible dye capable of eluting from the layer during development process. present in an amount of from 0.2 mg/m^2 to 20 mg/m^2.

7. The light-sensitive silver halide photographic material of claim 1, wherein said photographic component layer contains a mordant.

8. The light-sensitive silver halide photographic material of claim 1, wherein said support is a transparent support.

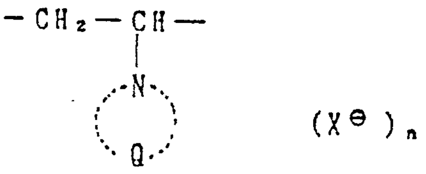
9. The light-sensitive silver halide photographic material of claim 1, wherein said dye is selected from the compound represented by general formula [I];



[I]

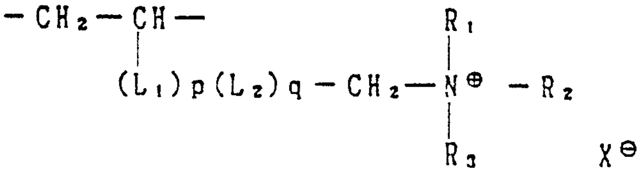
wherein R^1 and R^2 independently represent an alkyl group having 1 to 7 carbon atoms, a carboxyl group, an alkoxycarbonyl group, an alkylaminocarbonyl group, an amino group, an acylamino group, or a trifluoromethyl group; M represents a hydrogen atom, an alkalimetal atom or an ammonium group; and n is an integer of 0, 1 or 2.

10. The light-sensitive silver halide photographic material of claim 7, wherein said mordant is a polymer or a copolymer compound having therein a repeating unit represented by forllowing formula [M-I] , [M-II] or [M-III];



[M-I]

wherein Q is a group of atoms necessary to complete an imidazole ring nucleus together with the nitrogen atom of the formula; X is an acid group, an acid anion or a halide anion; and n is 0 or 1,

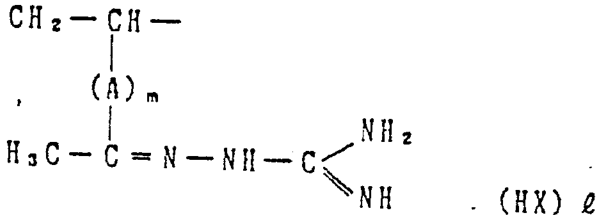


$$-CH_2-\underset{(L_1)_p(L_2)_q-CH_2-\overset{R_1}{\underset{R_3}{N^{\oplus}}}-R_2 \quad X^{\ominus}}{CH}-$$

[M-II]

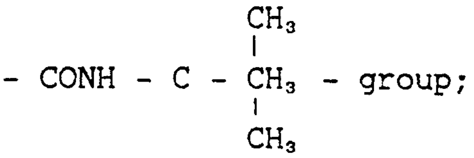
wherein R^1, R^2 and R^3 independently represent an alkyl qroup having 1 to 8 carbon atoms, which may have a substituent; L_1 is a - CONH - group or a - $\overset{O}{\overset{\parallel}{C}}$ - 0 - group;

L_2 is an alkylene group or an arylene group; p and q are respectively 0 or 1; and X is an acid group or a halide anion;



[M-III]

wherein A represents a



$$-CONH-C-\overset{CH_3}{\underset{CH_3}{CH_3}}-\text{group;}$$

X is an acid group; l is an integer of 1 or 2; and m is an integer of 0 or 1.

11. A method of processing a light-sensitive silver halide photographic material comprising a step of processing an imagewise exposed light-sensitive silver halide photographic material by the use of an automatic developing apparatus, wherein the total time of processing in said automatic developing machine is not less than 20 seconds and less 60 seconds, and said light-sensitive silver halide photographic material comprises a support and, provided thereon, at least one photographic component layer containing a gelatin and including a silver halide emulsion layer, said photographic component layer containing a dye of which at least one maximum absorption wavelength (λ_{max}) as an aqueous solution is in the range of from 400 nm to 850 nm, and the amount of gelatin present on the same side of said silver halide emulsion layer being within the range from 2.0 g/m^2 to 3.5 g/m^2.

FIG. I

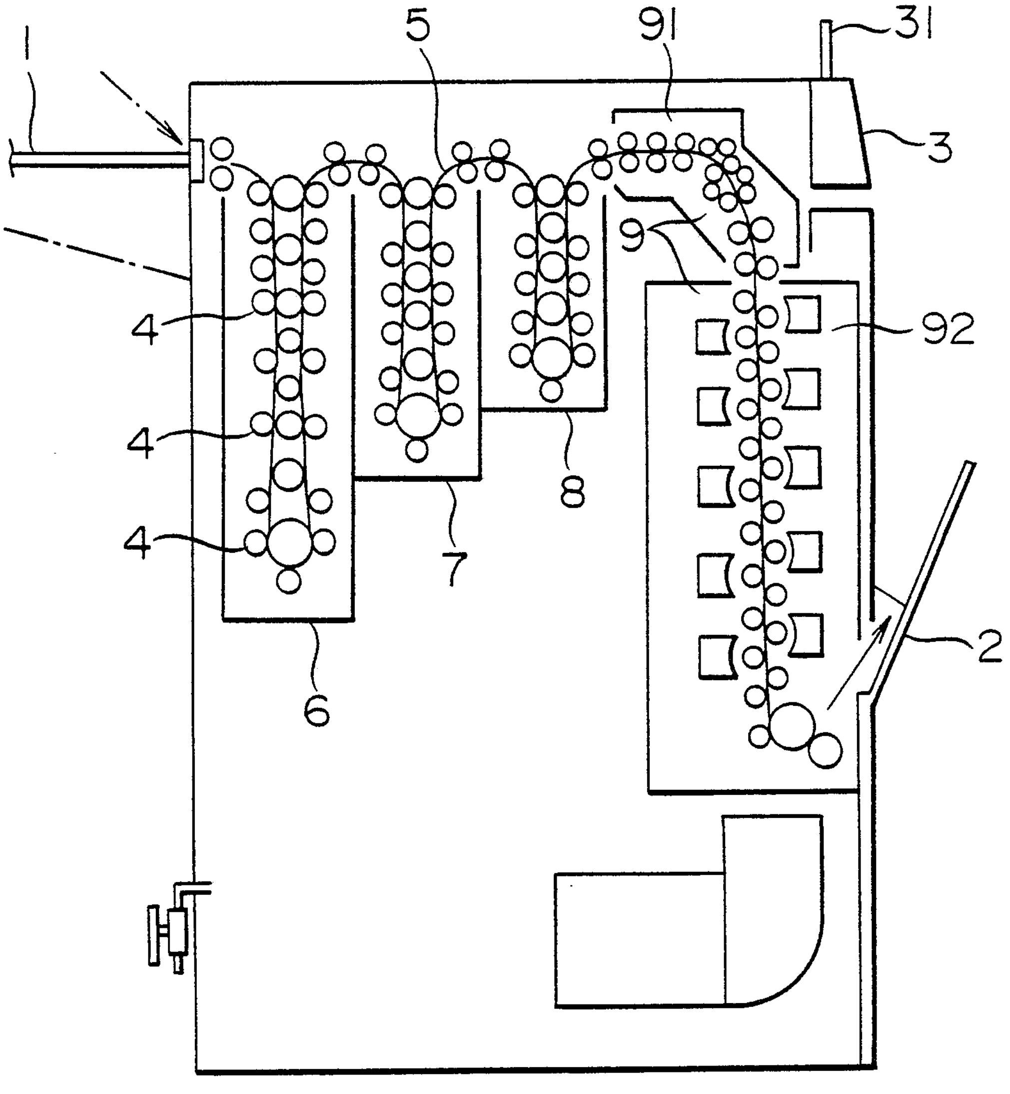
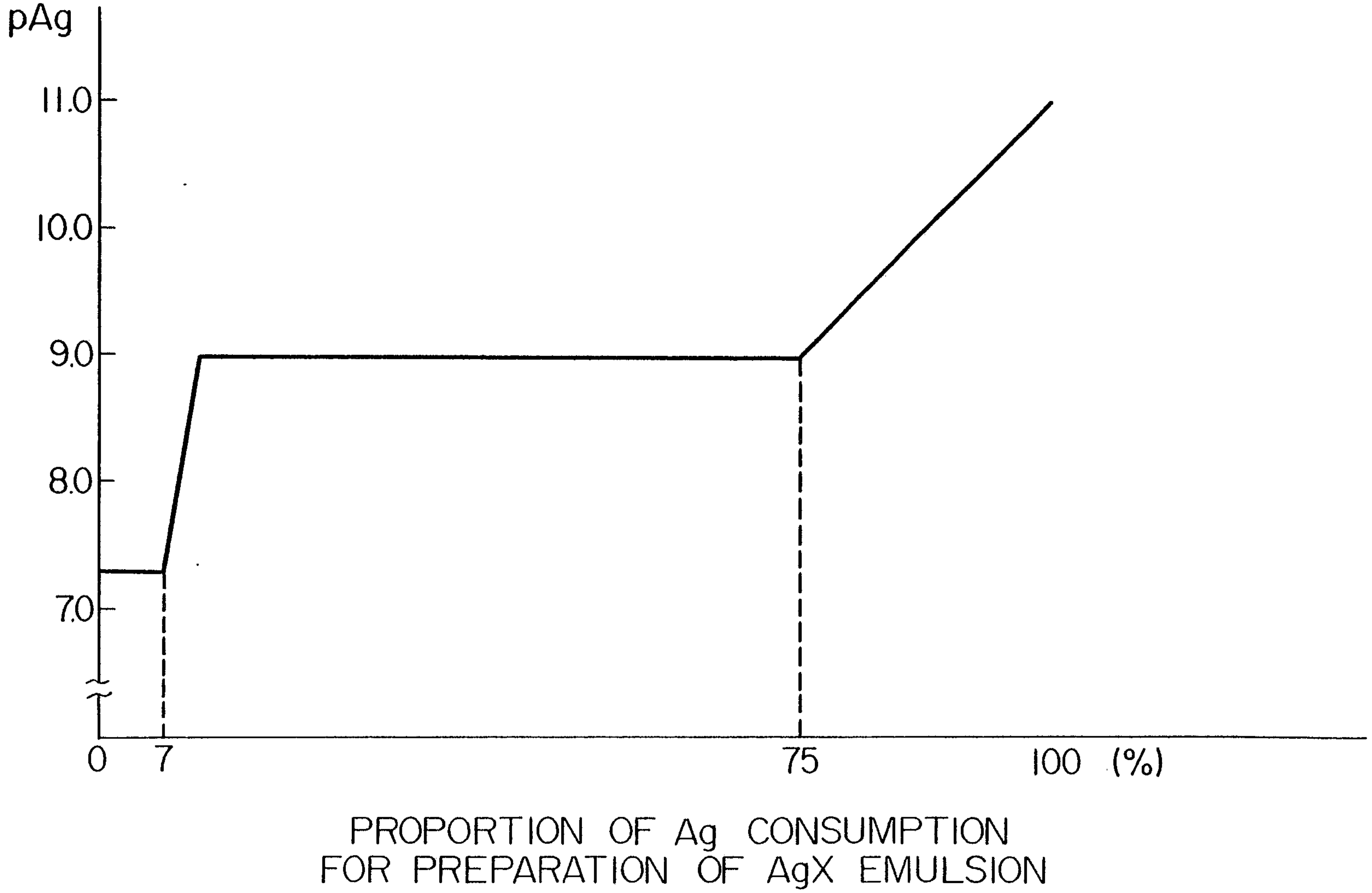


FIG. 2


pAg
11.0
10.0
9.0
8.0
7.0
0
7
75
100 (%)
PROPORTION OF Ag CONSUMPTION
FOR PREPARATION OF AgX EMULSION