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(54) Silver halide photographic emulsion.

(57) A silver halide photographic emulsion contains a dispersant and silver halide grains. At least 50% of the total projected surface area of the silver halide grains is occupied by tabular silver halide grains having an average aspect ratio of 2 or more. The mutually facing parallel major surfaces of the tabular silver halide grains are (111) faces. At least 30% of the tabular silver halide grains have dislocations in the major surface region.

The present invention relates to a light-sensitive silver halide photographic emulsion, hereinafter referred to simply as "silver halide emulsion", particularly, to a silver halide emulsion with an excellent sensitivity/grain size ratio and an improved pressure-sensitivity and to a method of preparing the same.

Tabular silver halide grains having parallel twinning planes, hereinafter referred to as "tabular grains", have merits 1 to 5 given below as photographic characteristics:

1. The tabular grains have a large specific surface area, i.e., ratio of surface area to volume, and, thus, permits adsorption of large amounts of a sensitizing dye on the surface. As a result, the tabular grains exhibit a relatively high spectral sensitivity with respect to the intrinsic sensitivity.
2. Where a photographic light-sensitive material is prepared by coating a substrate with an emulsion containing the tabular grains, followed by drying the coating, the grains are aligned in parallel on the substrate surface. It follows that the coating layer can be made thinner, leading to an improvement in sharpness.
3. If a sensitizing dye is added to the tabular grains, the light absorption coefficient of the dye is made larger than the light absorption coefficient accompanying the indirect transition of the silver halide (AgX) in the case of a roentgenographic system. As a result, the cross-over light can be markedly diminished, making it possible to prevent deterioration of the picture image quality.
4. The light scattering is low, making it possible to obtain a picture image of a high resolution.
5. The sensitivity to a blue light is low. Thus, where the tabular grains are used in a green-sensitive layer or a red-sensitive layer, it is possible to remove a yellow filter from the emulsion.

Because of these merits, the tabular grains are widely used in a light-sensitive material of high sensitivity available on the market. For example, an emulsion of tabular grains having an aspect ratio of at least 8 is disclosed in JP-A-58-113926 (Hereinafter, "JP-A-" means Unexamined Published Japanese Patent Application), JP-A-58-113927 and JP-A-58-113928.

The "aspect ratio" means a ratio of diameter to thickness of the tabular grain. The diameter of the grain means the diameter of a circle having an area equal to the projected surface area of the grain which is recognized when the emulsion is observed with a microscope or an electron microscope. Further, the thickness means the distance between two parallel planes defining the tabular silver halide grain.

U.S. Patent No. 4,439,520 discloses a color photographic light-sensitive material, in which tabular grains having a thickness of less than 0.3 µm and a diameter of 0.6 µm or more are used in at least one of a green-sensitive emulsion layer and a red-sensitive emulsion layer so as to improve the sharpness, sensitivity and graininess.

In recent years, improvement in sensitivity and miniaturization in format of the silver halide light-sensitive material are on a rapid progress. It is strongly demanded nowadays to develop a color photographic light-sensitive material of a higher sensitivity and a further improved picture image quality. Naturally, it is of high importance to develop silver halide grains having a higher sensitivity and an excellent graininess. Since the conventional tabular silver halide emulsion is incapable of sufficiently satisfying these requirements, a further improvement of performance is desired.

Further, the processing time is shortened in recent years, making it necessary to increase the silver/gelatin ratio or silver/binder ratio in the light-sensitive material. If the silver/gelatin ratio is increased, however, the pressure sensitivity of the emulsion is lowered. Thus, it is of high importance to take measures urgently for improving the pressure sensitivity of the tabular silver halide emulsion.

The present invention relates to the technique for controlling the dislocation within the major surface region of a tabular silver halide grain. The dislocation of the silver halide crystal is described in, for example:

1. C.R. Berry, J. Appl. Phys., 27, 636 (1956)
2. C.A. Berry, D.C. Skilman, J. Appl. Phys., 35 2165 (1964)
3. J.F. Hamilton, Phot. Sci. Eng., 11, 57 (1967)
4. T. Shiozawa, J. Soc. Phot. Sci. Jap., 34, 16 (1971)
5. T. Shiozawa, J. Soc. Phot. Sci. Jap., 35, 213 (1972)

The publications exemplified above teach that dislocation within the crystal can be observed by, for example, an X-ray diffraction method or a transmission electron microscopy at low temperatures, and that various dislocations can be brought about within the crystal by imparting strain to the crystal.

The influences given by the dislocation to the photographic performance are described in, for example, "G.C. Famell, R.B. Flint, and J.B. Chanter, J. Phot. Sci., 13, 25 (1965)". It is described that, in a large tabular silver bromide grain having a high aspect ratio, the site of a latent image nucleus formation is deeply related to the defect within the grain.

Each of JP-A-63-220238 and JP-A-01-201649 discloses a tabular silver halide grain having dislocation intentionally introduced therein. It is taught that the particular grain is superior to the tabular grain without dislocation in photographic characteristics such as sensitivity and reciprocity law, and that the particular grain, if used in a light-sensitive material, leads to improvements in sharpness and graininess. In these tabular silver halide grains disclosed in the prior art, however, the dislocation lines are irregularly introduced into the edge of the tabular grains. In addition, the number of dislocations differs from grain to grain.

An object of the present invention is to provide a silver halide photographic emulsion containing tabular silver halide grains exhibiting a high sensitivity, improved graininess, sharpness and covering power, and an excellent pressure-sensitivity, as well as a method of manufacturing the same.

According to the present invention, there is provided a silver halide photographic emulsion comprising a dispersant and silver halide grains, wherein at least 50% of the total projected surface area of the silver halide grains is occupied by tabular silver halide grains having an average aspect ratio of 2 or more, the mutually facing parallel major surfaces of the tabular silver halide grains are (111) faces, and at least 30% of the tabular silver halide grains have dislocations in the major surface region.

In a preferred embodiment of the present invention, the tabular silver halide grains having dislocations in the major surface region do not have the dislocation in the edge region of the major surface region.

In another preferred embodiment of the present invention, the tabular silver halide grains having dislocations in the major surface region do not have dislocations localized in only the central region of the major surface region.

In still another preferred embodiment of the present invention, at least 70% of the total projected surface area of the silver halide grains is occupied by hexagonal tabular silver halide grains having mutually facing two parallel planes as the outer surfaces, a ratio in length of the longest side to the shortest side of the hexagonal shape being 2 or less and the hexagonal tabular silver halide grains exhibit a monodispersed size distribution.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Figs. 1 and 2 are typical replica electron photomicrographs each showing the crystal structure in which micro silver chloride crystals are epitaxially grown on the major surface of the host tabular grain contained in a silver halide photographic emulsion of the present invention. The spherical latex shown in the photograph is 0.5 µm in diameter and has a shadow wing angle of about 15°.

Fig. 3A schematically shows a system in which a mixer is used for the preparation of a silver halide photographic emulsion of the present invention.

Fig. 3B is a cross sectional view showing in detail the construction of the mixer included in the system shown in Fig. 3A.

Reference numerals shown in Figs. 3A and 3B denote:

1: reaction vessel;
2: protective colloid aqueous solution;
3: propeller;
4: system for adding a halogen salt aqueous solution;
5: system for adding a silver salt aqueous solution;
6: system for adding a protective colloid;
7: mixer;
8: inlet system into the reaction vessel;
9: agitating blade;
10: reaction chamber;
11: rotary shaft.

Figs. 4, 5, 6, 7 and 8 are transmission electron photomicrographs each showing the structure of the typical silver halide crystals in emulsion 1-B, 1-C, 1-D, 1-G or 1-H prepared in Example 1 of the present invention.

Figs. 9A to 9F are views showing some examples of dislocation site distribution caused by a change in the AgI content of the host grain with respect to double parallel twinned crystal grains included in the host tabular grains contained in the silver halide photographic emulsion of the present invention.

In the present invention, the tabular silver halide grain is a silver halide grain having a single twinning plane or a plurality of parallel twinning planes. The "twinning plane" denotes (111) fases in the case where the ions at all the lattice points form a mirror image relationship on both sides of the (111) face. The tabular grains, when observed from above, are triangular, hexagonal or circular, the circular form resulting from roundish corner portions of the triangular or hexagonal shape. The triangular grain has parallel triangular outer surfaces. The hexagonal grain has parallel hexagonal outer surfaces. Likewise, the circular grain has parallel circular outer surfaces.

The term "average aspect ratio" of the tabular grain used in the present invention denotes the average value of the aspect ratio, i.e., the value obtained by dividing the average grain size by the thickness, with respect to tabular grains having a grain size of 0.3 μm or more. For determining the thickness of the grain, a metal is deposited from oblique direction on the grain together with a reference latex, followed by measuring the length of the shadow of the deposited metal on an electron photomicrograph. The thickness can be determined easily by calculation with the length of the shadow of the latex used as a reference.

The grain size used herein denotes the diameter of a circle having an area equal to the projected surface area of the parallel outer surfaces of the grain.

The projected surface area of the grain can be determined by measuring the area on an electron photomicrograph, followed by correction with the magnification factor of the photomicrograph.

It is desirable for the tabular grain to have a diameter of 0.3 to 0.5 μm and a thickness of 0.05 to 0.5 μm.

In the present invention, the tabular grain content of the emulsion should be preferably 50% or more, more preferably, 70% or more of the projected surface area of all the silver halide grains contained in the emulsion. Further, it is desirable for these tabular grains occupying a definite area to have an average aspect ratio of at least 2 and less than 8. Also, use of tabular grains having monodispersed grain size distribution leads to a more desirable result. The construction and preparing method of the tabular grains having monodispersed grain size distribution are described in, for example, JP-A-63-151618. It is described that 70% or more of the total projected surface area of the silver halide grains is occupied by hexagonal tabular silver halide grains having a hexagonal shape in which a ratio in length of the longest side to the shortest side is 2 or less and also having two parallel planes as outer surfaces. It is also described that the a size distribution of hexagonal silver halide grains is monodispersed. Specifically, it is described that a variation coefficient of the grain size distribution, i.e., the value obtained by dividing the standard deviation of the grain size represented by the diameter of a circle converted from the projected surface area by the average grain size, should be 20% or less.

The tabular grain contained in the emulsion of the present invention has dislocations. The dislocation of the tabular grain can be observed by a direct method using a transmission electron microscope at low temperatures, as described in, for example, "J.F. Hamilton, Phot. Sci. Eng., 11, 57 (1967)" and "T. Shiozawa, J. Soc. Phot. Sci. Japan, 35, 213 (1972)". To be more specific, silver halide grains are taken out of the emulsion under safelight carefully such that pressure high enough to generate dislocations in the grain may not be applied. The grains thus taken out of the emulsion are put on a mesh for the electron microscopic observation and observed by a transmission method under the condition that the sample is cooled so as to prevent damage done by the electron beam, e.g., print out. In order to achieve a clear observation, it is desirable to use an electron microscope of high voltage type, i.e., at least 200 kV with respect to grains having a thickness of 0.25 μm, because the electron beam passage is made more difficult with increase in the thickness of the grain. The position of the dislocation in each grain in the case of observation in a direction perpendicular to the major surface can be obtained by the photograph of the grain thus obtained.

The dislocations present in the silver halide grains contained in the emulsion of the present invention reside in the major surface region of the tabular grains.

The major surface region of the tabular grain denotes a region having a certain thickness including the outer surfaces consisting of mutually facing parallel (111) faces.

In the present invention, it is possible for the dislocations to reside within the major surface region excluding the edge region. The edge region denotes a doughnut-like region around the central region of the tabular grain, said doughnut-like region having an area corresponding to an annular area defined between a large circle equal in area to the major surface and a concentric small circle smaller in radius by 5% than the large circle. In the present invention, the dislocations are not localized in particular sites in the major surface region of the host grains such as the edge region described above and the central region. The central region noted above denotes a region of the tabular grain having a circular area corresponding to the area of a small circle whose radius is 10% of a large circle equal in area to the major surface of the grain, and having the same center point as that of the large circle.

The tabular grain is featured in that the area of the major surface is large relative to the volume of the grain. The merit of the tabular grain can be utilized to the greatest extent by introducing dislocations to the large major surface region. In the present invention, the area of the major surface in which the dislocations resides accounts for at least 10% to 100%, preferably 20% to 100%, and more preferably 30% to 100%, of the area of the total major surface.

The method for preparing the tabular grains contained in the emulsion of the present invention will be described in more detail below.

The tabular grains are prepared through processes (1) to (4) given below:

(1) Preparation of tabular grains providing substrates, hereinafter referred to as "substrate grains" or "host grains".
(2) Epitaxial growth of a large number of fine silver chloride or silver chlorobromide crystals on the major surfaces of the tabular grains acting as the substrates.
(3) Conversion of a large number of fine crystals epitaxially grown on the major surfaces of the tabular grains by the physical ripening and/or by halogen.
(4) Growth of dislocations by the silver halide shell formation.

Since the dislocations are generated at the deposition site of the fine silver chloride or silver chlorobromide, the sites of dislocations can be controlled by controlling the site of the fine epitaxial crystal formation. The site of formation of fine silver chloride epitaxially grown crystals is determined by the silver iodide content on the major surface of the tabular silver halide grain. Specifically, since fine silver chloride crystals are unlikely to grow in the high AgI content area on the major surface, it is possible to control the site of silver chloride epitaxial crystal formation by controlling the AgI content on the major surface of the substrate grain. As a result, it is possible to control the sites of dislocations. For example, dislocations can be generated within the entire major surface region of the tabular grain by making the AgI content on the major surface of the substrate grain zero or constant. For introducing dislocations selectively into a predetermined region within the major surface region of the tabular grain, the AgI content on the major surface of the predetermined region is made lower than in the other region or is made zero.

It is possible to change the growing direction on the substrate grain by changing the value of pBr during the growth. Where pBr is 2.5 or less, the growth proceeds exclusively in the lateral direction, as described in detail in "T. Sugimoto Phot. Sci. Eng. 28 137 (1984)" and "T. Sugimoto J. Imag. Sci. 33 203 (1989)". It is possible to change easily the AgI content on the major surface of the tabular grain by changing the AgI content during the substrate grain formation. Any of silver halides selected from the group consisting of silver bromide, silver iodobromide, silver chlorobromide and silver chloroiodobromide may be contained in the substrate grain. However, the substrate grain should have structure containing silver iodide in the region in which dislocations are not introduced. The method of preparing the tabular silver halide grains providing the substrate and the technique of using the particular grains are described in, for example, U.S. Patent Nos. 4,434,226, 4,439,520, 4,414,310, 4,433,048, 4,414,306 and 4,459,353.

It is desirable to prepare the substrate grains by adding fine silver halide grains to a reaction vessel holding a protective colloidal aqueous solution, in place of adding a silver salt aqueous solution and a halide aqueous solution, so as to form tabular grains. Since the method reduces increase of the tabular grain thickness during the grain formation, the structure of halogen composition on the major surface of the grains may be clear. The technique of the particular method is described in, for example, U.S. Patent 4,789,208, JP-A-01-183,644, JP-A-02-44,335, JP-A-02-43,535 and JP-A-02-68,538.

Iodine ions can be supplied for the tabular grain formation by using fine AgI grains prepared in advance, i.e., AgI grains having a grain size of 0.1 µm or less, preferably 0.06 µm or less. Alternatively, the iodine ions can be supplied by using an aqueous solution of a alkali halide. In this case, the manufacturing method disclosed in U.S. Patnet 4,789,208 can be desirably employed as a method of supplying fine AgI grains.

In the present invention, it is desirable for the tabular grains acting as the substrate grains to have a mono-dispersed grain size distribution.

The construction and preparing method of the tabular grains having a mono-dispersed grain size distribution are desoribed in, for example, JP-A-63-151,618. Briefly speaking, hexagonal tabular silver halide grains, the hexagonal shape being defined such that a ratio in length of the longest side to the shortest side is 2 or less, having mutually facing two parallel outer surfaces account for at least 70% of the total projected surface area of the silver halide grains. Further, the hexagonal tabular silver halide grains should have a mono-dispersed grain size distribution such that the variation coefficient of the grain size distribution, i.e., the value obtained by dividing the standard deviation of the grain size represented by the diameter of a circle converted from the projected surface area by the average grain size, should be 20% or less.

A large number of fine silver chloride or silver chlorobromide crystals epitaxially grown are precipitated on the major surface of the tabular grains acting as host grains. Specifically, an aqueous solution of a silver salt and an aqueous solution of a halide, i.e., a chloride or a mixture of a chloride and a bromide, are added to a host emulsion put in a reaction vessel under a silver potential (a saturated calomel electrode being used as a reference electrode) of +30 mV to +300 mV, preferably +50 mV to +250 mV. The temperature of the reaction vessel should be 70 °C to 30 °C, preferably 60 °C to 35 °C, and more preferably 50 °C to 35 °C. The total amount of the silver salt (mainly silver nitrate) and the halide added to the host emulsion should be 0.1 to 30 mol %, preferably 0.5 to 20 mol %, and more preferably 1 to 10 mol %. The size and number of epitaxially grown crystals depend on the epitaxial growth condition and the halogen composition of the host grains. The size of the epitaxially grown crystal can be recognized by an electron photomicrograph of replica method. Specifically, the epitaxially grown crystals have an average size of the projected surface area of 0.15 µm or less, and 10 to 10,000 such crystals are present per µm^2 of the major surface of the tabular host grain.

Figs. 1 and 2 are typical electron photomicrographs showing the crystal structure in which fine silver chloride crystals are epitaxially grown on the major surface of the tabular host grain. Specifically, Fig. 1 shows that silver chloride crystals are epitaxially grown on a silver bromide tabular grain, with Fig. 2 showing that silver chloride crystals are grown on a tabular grain comprising the inner region of silver bromide and the outer region of silver iodobromide (AgI content being 10 mol %). As apparent from Fig. 1, the epitaxial growth is randamly generated on the entire major surface of the silver bromide tabular grains. Further, as apparent from Fig. 2, the epitaxial growth is concentrated on the silver bromide region, with no epitaxial growth being recognized in the silver iodobromide region.

The crystals epitaxially grown on the major surface of the host grain are converted by a physical ripening and/or halogen. During the physical ripening process, the fine epitaxially grown crystals are crushed to form a larger mesa-like structure. Dislocations are considered to be introduced in this step.

The physical ripening should be carried out at 40°C to 90°C, preferably 50°C to 90°C, and more preferably 60°C to 80°C.

The halogen conversion denotes that the halogen contained in the silver halide crystal is replaced by another kind of a halogen element. The halogen conversion is brought about by the addition of a halogen element capable of forming a silver halide smaller in the solubility product than the silver halide contained in the crystal. The conversion is initiated from the portion of a higher silver halide solubility. It follows that any halogen element can be used for the halogen conversion as far as the halogen is capable of forming a silver halide having a solubility smaller than that of the silver halide crystal under the epitaxial growth.

The halogen used for the halogen conversion is in the form of an iodide, a bromide or a mixture of iodide and bromide and is used in the form of an aqueous solution. It is desirable to add the halogen in the form of fine grains of silver iodide, silver iodobromide or silver bromide having a grain size of 0.1 µm or less, preferably 0.06 µm or less. It is possible to prepare in advance these fine grains in the form of a fine grain emulsion. Alternatively, it is desirable to supply silver halide fine grains from a mixer, as disclosed in U.S. Patent 4,879,208.

The amount of halogen used for the halogen conversion should be 5 to 100 mol %, preferably 10 to 50 mol %, of the amount of silver contained in the epitaxially grown crystals.

Dislocations are grown by the shell formation. After introduction of dislocations by the physical ripening and/or halogen conversion of the fine crystals epitaxially grown on the major surface of the host tabular grain, an aqueous solution of a silver salt and an aqueous solution of a halide are added for the shell formation. As a result, the dislocations are grown in accordance with the shell formation. The amount of the shell to be formed should be 50 mol % or more of the silver amount in the host grain. An optional halogen component can be used for forming the shell including, for example, silver chloride, silver bromide, silver iodobromide, silver chloroiodobromide and silver chlorobromide.

The preparing method of the substrate tabular grains described previously can be employed as it is for the shell formation. For example, it is possible to employ the preparing method and the technique of using the prepared tabular grains disclosed in U.S. Patents 4,434,226, 4,439,520, 4,414,310, 4,438,048, 4,414,306 and 4,459,353.

For the shell formation, it is possible to add fine silver halide grains, in place of adding an aqueous solution of a silver salt and an aqueous solution of a halide, to a protective colloidal aqueous solution put in a reaction vessel so as to form tabular grains. The particular technique is disclosed in U.S. Patnet 4,879,208, JP-A-01-183,644, JP-A-02-44,335, JP-A-02-43,535 and JP-A-02-68,538.

For forming a silver iodobromide shell, it is possible to supply iodine ions by using an emulsion of fine AgI grains prepared in advance (having a grain size of 0.1 µm or less, preferably 0.06 µm or less). Also, the emulsion noted above may be used together with an aqueous solution of a alkali halide. It is desirable to employ the preparing method disclosed in U.S. Patent No. 4,879,208 as a method of supplying fine AgI grains.

As described above, it is possible in the present invention to introduce dislocation into a selected region or the entire region within the major surface region of tabular silver halide grains. The distribution in the depth direction of the dislocation introduced in the present invention is considered to be apparent from the preparing method described so far. Specifically, the dislocation starts from the major surface of the host tabular grain and, by the subsequent shell formation, proceeds to reach the surface of the shell. It follows that the dislocations reside between the major surface of the host grain and the surface of the shell, which quite differs from the dislocations disclosed in JP-A-63-220238 and JP-A-01-201649. In these prior applications, the dislocations are introduced into the edge region of tabular grain and, thus, quite differs from the dislocations in the present invention in its substance and distribution. Let us describe some examples of dislocation distribution in the present invention. For the sake of brevity, the following description covers the case where the host grain is formed of silver iodobromide.

Figs. 9A to 9F show examples of distribution of sites of dislocation introduction owing to a change in the AgI content of the host grain in the double parallel twinned crystal grain of the host tabular grain used in the present invention. The shaded portions in these drawings denote a silver iodobromide phase containing silver iodide, with the white portions denoting a silver bromide phase. As described previously, the present invention makes it possible to introduce dislocations selectively into the white portion alone containing silver bromide. It is also possible to introduce dislocations into the entire major surface, as shown in Fig. 9F. The density of dislocations depends on the amount of the silver chloride or silver chlorobromide crystals epitaxially grown on the major surface. In other words, the dislocation density is increased with increase in the amount of epitaxially grown crystals.

Introduction of dislocations into tabular grains permits increasing sensitivity, improving reciprocity failure, and enhancing spectral sensitization. Also, the pressure sensitivity of the tabular grains, which originally exhibit a strong tendency toward blackening upon receipt of pressure, is markedly improved by the introduction of dislocations. In order to allow these desirable effects of dislocations to come out most effectively, it is absolutely necessary to control as desired the site of introduction (topography) and density of dislocations. The present invention is epoch-making in that the control can be achieved completely.

Figs. 9A to 9F show no more than examples. Of course, the present invention permits introducing dislocations selectively in various other sites, though such cases are omitted for the sake of brevity.

The dislocation in the present invention can be recognized easily by observing a transmission image of silver halide tabular grains using a transmission electron microscope. For example, the dislocations can be observed by a direct method using a transmission type electron microscope under low temperature, which is described in "J.F. Hamilton, Photographic Science and Engineering, Vol. 11, 1967, p.p. 57" or "T. Shiozawa, Japan Photographic Associate, Vol. 35, No. 4, 1972, p.p. 213". To be more specific, silver halide grains taken out under a safelight such that emulsion grains may not print out are put on a mesh for observation with an electron microscope. Observation by a transmission method is performed, with the sample cooled with a liquid nitrogen or liquid helium so as to prevent damage such as print out done by an electron beam.

The higher accelerating voltage of the electron microscope leads to the clearer transmission image. It is desirable to set the accelerating voltage at 200 KV where the grain has a thickness of 0.25 µm or less, and at 1000 KV where the thickness of the grain exceeds the value given above. The damage done to the grain by the exposure of the electron beam is increased with increase in the accelerating voltage. Naturally, where the accelerating voltage is set at a high level, it is desirable to cool the sample with a liquid helium rather than with a liquid nitrogen. The magnification, which depends on the grain size and is changeable, is 20,000 to 40,000.

In the present invention, the size of the tabular silver halide grains is not particularly restricted. However, it is desirable for the grain to have a thickness of 0.6 µm, preferably 0.5 µm or less, and an average grain size of 0.3 to 4 µm, preferably 0.6 to 3 µm.

The silver halide photographic emulsion of the present invention can be spectrally sensitized with, for example, methane dyes. Examples of the dye are a cyanine dye, a merocyanine dye, a composite cyanine dye, a composite merocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye, and a hemioxonol dye. In these dyes, any nucleus normally used as a basic heterocyclic nucleus in cyanine dyes can be applied. Examples of the nucleus are a pyrroline nucleus, an oxazoline nucleus, a thiozoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, and a pyridine nucleus; a nucleus obtained by condensation of an alicyclic hydrocarbon ring to each of the above nuclei; and a nucleus obtained by condensation of an aromatic hydrocarbon ring to each of the above nuclei, e.g., an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxadole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, and a quinoline nucleus. These nuclei can have a substituent group on a carbon atom.

As the merocyanine dye or composite merocyanine dye, a 5- or 6-membered heterocyclic nucleus, e.g., a pyrazoline-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus and a thiobarbituric acid nucleus can be used as a nucleus having a ketomethylene structure.

The sensitizing dye described above is added after or before chemical ripening. Most preferably, the sensitizing dye is added to the silver halide grains used in the present invention during or before chemical ripening, e.g., in the step of forming grains or during physical ripening step.

The silver halide emulsion of the present invention is generally subjected to chemical sensitization. The chemical sensitization includes, for example, a sulfur sensitization method using a sulfur-containing compound capable of reaction with active gelatin, e.g., a thiosulfate, a thiourea, a mercapto compound and a rhodanine compound; a reduction sensitization method using a reducing substance, e.g., stannous salt, an amine, a hydrazine derivative, formamidine-sulfinic acid and a silane compound; and a noble metal sensitization method using a noble metal compound, e.g., gold complex salt, and complex salts of group VIII metals in the Periodic Table such as Pt, Ir and Pd. These methods can be employed singly or in combination.

It is possible to add various compounds to the photographic emulsion of the present invention in order to prevent fogging during the manufacturing process and preservation, or during the photographic processing of the light-sensitive material or to stabilize the photographic performance. Specifically, it is possible to add various compounds known as anti-foggants and stabilizers including, for example, azoles such as benzothiazolium salt, nitroindazoles, triazoles, benzotriazoles, benzimidazoles (particularly, nitro- or halogen-substituted compound); hetero ring mercapto compounds such as mercapto thiazoles, mercapto benzothiazoles, mercapto benzimidazoles, mercapto thiadiazoles, mercapto tetrazoles (particularly, 1-phenyl-5-mercapto tetrazole) and mercapto pyrimidines; hetero ring mercapto compounds noted above, which have hydrophilic groups such as carboxyl group and sulfonic group; thioketo compounds such as oxazolinethione; azaindenes such as tetrazaindenes (particularly, 4-hydroxy-substituted (1,3,3a,7) tetrazaindens); benzene thiosulfonic acids; and benzene sulfinic acids.

In general, these anti-foggants or stabilizers are normally added after the chemical sensitization. Preferably, these compounds should be added during the chemical ripening or after initiation of the chemical ripening.

The emulsion of the present invention can be used for a photographic light sensitive material whether the material comprises a single emulsion layer or a plurality of emulsion layers.

The emulsion of the present invention can be used for a silver halide multi-layered color photographic light sensitive material. In this case, the light-sensitive material is of a multilayered structure comprising emulsion layers superposed one upon the other. These emulsion layers contain binders and silver halide grains for individually recording blue, green and red light beams, and each emulsion layer has at least two layers, i.e., a high sensitive layer and a low sensitive layer.

The silver halide emulsion of the present invention, which can be used for the color photographic light-sensitive material described above, can also be applied to other light-sensitive materials whether the light sensitive material may include a single emulsion layer or a plurality of emulsion layers. For example, the emulsion can also be used for a light-sensitive material for X-ray photography, a black and white photography, a reprophotography, or a photographic paper.

It is possible to use various additives in the silver halide emulsion of the present invention including, for example, a binder, a chemical sensitizer, a spectral sensitizer, a stabilizer, a gelatin hardening agent, a surfactant, an antistatic agent, a polymer latex, a matting agent, a color coupler, an ultraviolet absorber, a discoloration inhibitor, and a dye. These additives, the support of a light-sensitive material using the emulsions of the present invention, the coating method, the exposure method and the developing method are not particularly restricted in the present invention. Useful in the present invention are the descriptions in, for example, "Research Disclosure" (hereinafter referred to as "R.D."), Vol. 176, Item 17643 (R.D.-17643); Vol. 187, Item 18716 (R.D.-18716); and Vol. 225, Item 22534 (R.D.-22534). Listed below are these descriptions:

Additive	R.D. No.17643	R.D. No.18716	R.D. No.22534
1. Chemical sensitizers	page 23	page 648 right col.	page 24
2. Sensitivity increasing agents		do	
3. Spectral sensitizers, super sensitizers	pages 23-24	page 648, right col. to p. 649, right col.	p.24-28
4. Brighteners	page 24		
5. Antifoggants and stabilizers	pages 24-25	page 649, right col.	pp. 24 and 31
6. Light absorbent, filter dye, ultra-violet absorbents	pages 25-26	p.649, right col. to p.659, left column	
7. Stain preventing agents	page 25, right col.	p.650, left col. to right column	
8. Dye image stabilizers	page 25		page 32
9. Hardening agents	page 26	page 651, left col.	page 28
10. Binders	page 26	do	
11. Plasticizers, lubricants	page 27	page 650, right col.	
12. Coating aids, surfactants	pp.26-27	do	
13. Antistatic agents	page 27	do	
14. Color couplers	page 25	page 649	page 31

Where the silver halide photographic emulsion of the present invention is applied to the color light-sensitive material, it is possible to use various color couplers. The color coupler used in the present invention should desirably have a ballast or, when polymerized, should exhibit a diffusion resistance. A diequivalent coupler substituted by a coupling releasing radical permits decreasing the silver coating amount and, thus, is preferred to a tetraequivalent coupler in which the coupling active site is provided by a hydrogen atom. It is also possible to use a coupler in which the colored dye exhibits a suitable diffusion capability, a colorless compound forming coupler, a DIR coupler which releases a development restrainer or a coupler which releases a development accelerator in accordance with the coupling reaction.

Preferred examples of a yellow coupler used in the present invention are acylaceto-amide couplers of an oil protect type.

Typical examples are oxygen atom releasing type yellow couplers or nitrogen atom releasing type yellow couplers. α-pivaloyl acetanilide couplers are excellent in stability of the colored dye, particularly, the light stability. On the other hand, α-benzoyl acetanilide couplers exhibit a high color density.

Examples of a magenta coupler used in the present invention are oil protect type pyrazoloazole couplers such as indazolone or cyanoacetyl compounds, preferably, 5-pyrazolone and pyrazolotriazole compounds. When it comes to the 5-pyrazolone couplers, couplers in which an arylamino group or amylamino group is substituted for the 3-position are preferred in terms of the hue and color density of the colored dye.

Imidazo [1, 2-b] pyrazoles described in U.S. Patent 4,500,630 are preferred examples because the compounds are low in yellow sub-absorption of the colored dye and are satisfactory in light stability. Particularly preferred is pyrazolo [1, 5-b] [1, 2, 4] triazole described in U.S. Patent 4,540,650.

Examples of a cyan coupler used in the present invention are oil protect type naphthol and phenol couplers including the naphthol couplers described in U.S. Patent 2,474,293. Typical examples are preferably diequivalent naphthol couplers of an oxygen atom releasing type described in U.S. Patents 4,052,212, 4,146,396, 4,228,233 and 4,296,200.

Cyan couplers in which a sulfonamide group or an amide group is substituted for the 5-position of naphthol are described in Japanese Patent Applications Nos. 59-93606; 59-264277 and 59-268135. These cyan couplers are excellent in stability of the colored image and, thus, can be used effectively in the present invention.

Couplers in which the colored dye exhibits a suitable diffusibility can also be used in the present invention together so as to improve the graininess. Examples of magenta couplers of this type are described in U.S. Patent No. 4,366,237 and British Patent No. 2,125,570. Also, examples of yellow, magenta or cyan couplers of this type are described in European Patent No. 96,570 and West German Patent Disclosure Gazette (OLS) No. 3,234,533.

The emulsion of the present invention may also contain a so-called "DIR" coupler which releases the development restrainer in accordance with progress of the development.

The DIR couplers which can be effectively combined with the emulsion of the present invention include, for example, a developing solution deactivation type described in JP-A-57-151944, a timing type described in U.S. Patent No. 4,248,962 and JP-A-57-154234, and a reaction type described in Japanese Patent Application No. 59-39653. Particularly preferred are developing solution deactivation type DIR couplers described in, for example, JP-A-57-151944, JP-A-58-217932, Japanese Patent Applications Nos. 59-75474; 59-82214; and 59-90438, and reaction type DIR couplers described in, for example, Japanese Patent Application No. 59-39653.

Compounds which release imagewise nucleating agents or development accelerators, or precursors thereof, (hereinafter referred to as "development accelerators or the like") in the development can also be used in the light sensitive material prepared by using the emulsion of the present invention. Typical examples of such a compound are described in British Patents Nos. 2,097,140 and 2,131,188. Such a compound acts as a coupler which performs a coupling reaction with the oxide of an aromatic primary amine developing reagent so as to release a development accelerator or the like, i.e., acts as a DAR coupler.

Examples of a high-boiling organic solvent used for the color coupler dispersion are phthalic esters (e.g., dibutylphthalate, dicyclohexylphthalate, di-2-ethylhexylphthalate, and decylphthalate), phosphates or phosphonates (e.g., triphenylphosphate, tricresylphosphate, 2-ethylhexyl diphenylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, tributoxyethylphosphate, trichloropropylphosphate, and di-2-ethylhexylphenylphosphonate), benzoates (e.g., 2-ethylhexylbenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., diethyldodecaneamide, and N-tetradecylpyrrolidone), alcohol or phenol (e.g., isostearylalcohol and 2,4-ditert-amylphenol), aliphatic carboxylates (e.g., dioctylazelate, glyceroltributylate, isostearyllactate and trioctylcitrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), and hydrocarbons (e.g., paraffin, dodecylbenzene and diisopropylnaphthalene). An organic solvent having a boiling point of about 30° C or more, and preferably, 50° C to about 160° C can be used as a co-solvent. Typical examples of the co-solvent are ethyl acetate, butyl acetate, ethyl propionate, methylethylketone, cyclohexanone, 2-ethoxyethylacetate and dimethylformamide.

Examples of a gelatin hardening agent used in the emulsion of the present invention include, for example, an active halogen compound (e.g., 2,4-dichlor-6-hydroxy-1,3,5-triazine and a sodium salt thereof), an active vinyl compound (e.g., 1,3-bisvinylsulfonyl-2-propanol and 1,2-bis (vinylsulfonylacetoamide) ethane), and a vinyl polymer having a vinylsulfonyl group attached to the side chain. These compounds serve to promptly harden a hydrophilic colloid such as gelatin so as to provide stable photographic characteristics and, thus, are preferably used in the present invention. Additional compounds exhibiting an excellent hardening rate are N-carbamoylpyridinium salts (e.g., 1-morpholinocarbonyl-3-pyridinio) methanesulfonate) and haloamidinium salts (e.g., 1-(1-chloro-1-pyridinomethylene) pyrrolidinium-2-naphthalene-sulfonate).

In general, a washing or stabilizing is applied after the development, bleach fixing or fixing to the color photographic light sensitive material using the silver halide photographic emulsion of the present invention.

In the washing, a counter current washing is employed in general using a plurality of water vessels to save the amount of water used. A multi-stage counter current stabilizing described in JP-A-57-8543 can be employed in place of the washing as a typical example of the stabilizing.

An alkaline aqueous solution which preferably contains an aromatic primary amine-based color developing agent as a main component is used as a color developer in the developing of the light sensitive material using the emulsion of the present invention. Aminophenolic compounds are useful as the color developing agent. Also, p-phenylene-diamine compounds are preferably used as the color developing agent. Typical examples of the color developing agent include, for example, 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-Nethyl-N-ß-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-β-methane sulfonamide ethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, a sulfate thereof, a hydrochloride thereof, and a p-toluenesulfonate thereof. These compounds can be used in a combination of two or more thereof in accordance with applications.

In order to perform reversal development, black-and-white development is performed first in general and, then, color development is performed. As a black-and-white developer, well-known black-and-white developing agents, e.g., dihydroxybenzenes such as hydroquinone, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, and aminophenols such as N-methyl-p-aminophenol can be used singly or in a combination of two or more thereof.

The pH of the color developer and the black-and-white developer is generally 9 to 12. Although a replenishment amount of the developer depends on a color photographic light-sensitive material to be processed for development, it is generally 3 liters or less per m^2 of the light-sensitive material. The replenishment amount can be decreased to be 500 mℓ or less by decreasing a bromide ion concentration in a replenishing solution.

The photographic emulsion layer is generally subjected to bleaching after color development. The bleaching can be performed either simultaneously with fixing (bleach-fixing) or independently thereof. In addition, in order to increase a processing speed, bleach-fixing can be performed after bleaching. Further, an iron (III) complex salt of aminopolycarboxylic acid is particularly useful both in the bleaching solution and in the bleach-fixing solution. The pH of the bleaching solution or bleach-fixing solution containing an iron (III) salt of aminopolycarboxylic acid is generally 5.5 to 8. For promoting the treatment, however, it is possible to use a solution having a lower pH value.

A bleaching accelerator can be used in the bleaching solution, the bleach-fixing solution, and their prebath, if necessary. Compounds having a mercapto group or disulfide group exhibit prominent accelerating effects. Examples of effective bleaching accelerators are disclosed in U.S. Patent No. 3,893,858, West German Patent No. 1,290,812 and JP-A-53-95,630. It is also desirable to use the compounds disclosed in U.S. Patent No. 4,552,834. Alternatively, these bleaching accelerators may be added to the light-sensitive material.

The silver halide color photographic light-sensitive material of the present invention is normally subjected to washing and/or stabilizing after desilvering. An amount of water used in the washing can be arbitrarily determined over a broad range depending on the properties of the light-sensitive material (e.g., a property determined by used substance such as a coupler), the application of the material, the temperature of the water, the number of water tanks (the number of stages), a replenishing scheme representing a counter or forward current, and other conditions. The relationship between the amount of water and the number of water tanks in a multi-stage counter-current scheme can be obtained by a method described in "Journal of the Society of Motion Picture and Television Engineers", Vol. 64, pp. 248 - 253 (May, 1955).

Described below are some Examples of the present invention.

Example 1

Emulsion 1-A (Emulsion containing tabular silver bromide host grains)

Added to 1 liter of 0.8 wt % gelatin solution containing 0.08 M of potassium bromide were 150 cc of a solution containing 2.00 M silver nitrate and 150 cc of a solution containing 2.00 M of potassium bromide by a double jet method while stirring the gelatin solution, which was maintained at 30° C. The gelatin solution was then heated to 75° C. Also, 30 g of gelatin was further added to the solution.

After the first stage addition noted above, 90 cc of a solution containing 1.0 M of silver nitrate was added to the solution.

Further, the resultant solution was subjected to ripening for 30 minutes after addition of the silver nitrate solution. The grains thus formed (hereinafter referred to as "seed crystals") were washed by the ordinary flocculation method and, then, adjusted to exhibit pH of 5.0 and pAg of 7.5 at 40° C.

One tenth of the seed crystals were dissolved in 1 liter of a solution containing 3% by weight of gelatin and maintained at 75° C at pBr of 2.55. Then, 150 g of silver nitrate was added over a period of 60 minutes at an accelerated flow rate such that the flow rate at the end was 19 times as high as that at the beginning.

During the silver nitrate addition, pBr was maintained at 2.55.

The resultant emulsion was cooled to 35°C and washed by the ordinary flocculation method. After adjusted to exhibit pH of 6.5 and pAg of 8.6 at 40°C, the emulsion was preserved at a cool and dark place.

In emulsion 1-A thus prepared, 80% of the silver halide grains was occupied by hexagonal tabular grains, and the variation coefficient of the grain size distribution was found to be 18%. Further, the grains were found to have an average circle-equivalent size of the projected surface area of 1.8 µm and an average thickness of 0.16 µm.

Emulsion 1-B (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

1300 mℓ of water was added to 500 g of emulsion 1-A containing 90 g of $AgNO_3$. Then, 160 mℓ of a solution containing 0.34 M of silver nitrate and 160 mℓ of an aqueous solution containing 0.8 M of NaCℓ were added to the diluted emulsion, which exhibited a potential of +190 mV at 40°C with respect to a saturated calomel electrode, over a period of 8 minutes. As a result, a large number of fine silver chloride crystals were epitaxially grown on the major surfaces of the tabular host grains except the edge portions of the tabular grains, as shown in Fig. 1. Then, the reaction system was heated to 75°C to carry out a physical ripening for 12 minutes, followed by adding 30 mℓ of an aqueous solution containing 2.5 M of KBr. Then, 160 mℓ of an aqueous solution containing 0.34 M of silver nitrate and 160 mℓ of an aqueous solution containing 0.34 M of KBr were added over a period of 8 minutes.

The resultant emulsion was cooled to 35°C and washed by the ordinary flocculation method. After 50 g of bone gelatin addition, the washed emulsion was adjusted to exhibit pH of 6.5 and pAg of 8.5 at 40°C, and preserved at a cool and dark place.

Emulsion 1-C (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

Emulsion 1-C was prepared substantially as in preparation of emulsion 1-B, except that 20 mℓ of a solution containing 0.06 M of KI was added to the reaction system after temperature elevation of the system to 75°C.

Emulsion 1-D (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

Emulsion 1-D was prepared substantially as in preparation of emulsion 1-B, except that 100 mℓ of a solution containing 0.06 M of KI was added to the reaction system after temperature elevation of the system to 75°C.

Emulsion 1-E (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

Emulsion 1-E was prepared substantially as in preparation of emulsion 1-B, except that 0.0036 mol (in terms of silver) of an emulsion containing fine AgI grains having an average grain size of 0.03 µm was added to the reaction system after temperature elevation of the system to 75°C.

Emulsion 1-F (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

Emulsion 1-F was prepared by using a system as shown in Fig. 3A. In this case, the emulsion was prepared substantially as in preparation of emulsion 1-B, except that the AgI grains were added to the reaction system immediately after the system was heated to 75°C within the reaction vessel 1 shown in Fig. 3A.

The AgI grains were prepared within the mixer 7 disposed in the vicinity of the reaction vessel 1, as follows, and introduced into the reaction vessel 1 through the inlet system 8. Specifically, 30 mℓ of a solution containing 0.12 M of silver nitrate, 30 mℓ of a solution containing 0.12 M of KI and 65 mℓ of an aqueous solution containing 1% by weight of gelatin were introduced at constant flow rates into the mixer 7 over a period of 5 minutes through the addition systems 5, 4 and 6, respectively. The residence time of these solutions within the mixer 7 was 36 seconds and the agitating blades 9 were rotated at 3000 rpm. The resultant AgI fine grains were observed with a direct method using transmission electron microscope (magnification of 20,000), and found to be 0.01 µm in average grain size. The temperature of the mixer 7 was maintained at 25° C, and the fine grains formed were continuously supplied to the reaction vessel 1 through the inlet system 8.

Emulsion 1-G (Emulsion containing tabular grains which do not have dislocations; comparative example):

Emulsion 1-G was prepared exactly as in preparation of emulsion 1-B, except that 160 mℓ of a solution containing 0.34 M of silver nitrate and an aqueous solution containing 0.8 M of KBr were added over a period of 8 minutes under a potential of +190 mV at 40° C.

Emulsion 1-H (Emulsion containing tabular grains having dislocations in the edge region alone; comparative example):

Added to 500 g of emulsion 1-A were 1300 mℓ of water and an aqueous solution containing 2.5 M of KBr, followed by adding at 40° C by a double jet method 100 mℓ of an aqueous solution containing 0.09 M of silver nitrate and 100 mℓ of a solution containing 0.09 M of KI over a period of 10 minutes. The reaction system was heated to 75° C and, then, physically ripened for 12 minutes. Further, 160 mℓ of an aqueous solution containing 0.34 M of silver nitrate and 160 mℓ of an aqueous solution containing 0.34 M of KBr were added to the system over a period of 8 minutes. Further, the subsequent steps equal to those for emulsion 1-B were followed so as to prepare emulsion 1-H.

Observation of Dislocations introduced into Tabular Grains

Dislocations in each of emulsions 1-B to 1-H were directly observed by a transmission electron microscope JEM2000FX II manufactured by Nihon Denshi K.K. under an accelerating voltage of 200 KV and a temperature of -120° C. Figs. 4 to 8 are resultant electron photomicrographs showing emulsions 1-B, 1-C, 1-D, 1-G and 1-H, respectively.

Figs. 4 to 6 clearly show that dislocations are present over the entire major surface region. It is also seen that the dislocations introduced into emulsion 1-C, which was prepared by using a KI solution, were greater than that introduced into emulsion 1-B. Further, distribution of the dislocation density among the grains was narrower in emulsions 1-E and 1-F than in emulsions 1-C and 1-D prepared by using a KI solution, indicating that dislocations were more uniformly introduced into emulsions 1-E and 1-F. On the other hand, Figs. 7 and 8 show that dislocations were not recognized at all in emulsion 1-G, and that dislocations were concentrated in the edge region alone of the tabular grain in emulsion 1-H.

Preparation of Emulsion-Coated Sample

A mixture of spectral sensitizing dyes A and B shown in Table A below, which were mixed at a weight ratio of 200 : 1, was added in an amount of 800 mg/mol of the silver halide to each of emulsions 1-B to 1-H maintained at 60° C. Ten minutes later, 0.6 g of styrene-maleic anhydride copolymer was added, followed by further adding 2 minutes later ammonium thiocyanate in an amount of 1.9×10^{-3} mol/mol of silver and suitable amounts of chloroauric acid and hypo so as to initiate chemical ripening. Further, 3×10^{-2} mol of 4-hydroxy-6-methyl-1,3,3a,7-tetrazainden was added and, one minute later, the temperature of the system was lowered so as to finish the chemical ripening and, thus, to prepare a photographic emulsion coating liquid.

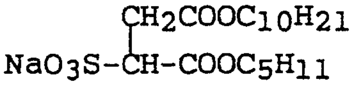
Both surfaces of a polyethyleneterephthalate film base were simultaneously coated with the coating liquid thus prepared using two slide hopper type coaters at a speed of 60 m/min such that the photographic emulsion layer would contain 1.8 g/m^2 of silver and 2.0 g/m^2 of gelatin on each surface of the support member and that the protective layer would contain 1.0 g/m^2 of gelatin. The coating was dried for 140 seconds so as to obtain samples.

The additives given below were used for preparing the silver halide photographic emulsion coating liquid. The amount of additive indicated below is the amount per mol of silver halide.

1,1-dimethylol-1-bromo-1-nitromethane	... 70 mg
Additive-1	... 150 mg
t-butyl catechol	... 400 mg
Polyvinylpyrrolidone (molecular weight 10,000)	... 1.0 g
Styrene-maleic anhydride copolymer	... 2.5 g
Trimethylolpropane	... 10 g
Diethylene glycol	... 5 g
Nitrophenyl-triphenylphosphonium chloride	... 50 mg
Ammonium 1,3-hydroxybenzene-4-sulfonate	... 4 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	... 1.5 g

Additive-2	... 70 mg
Additive-3	... 1 g

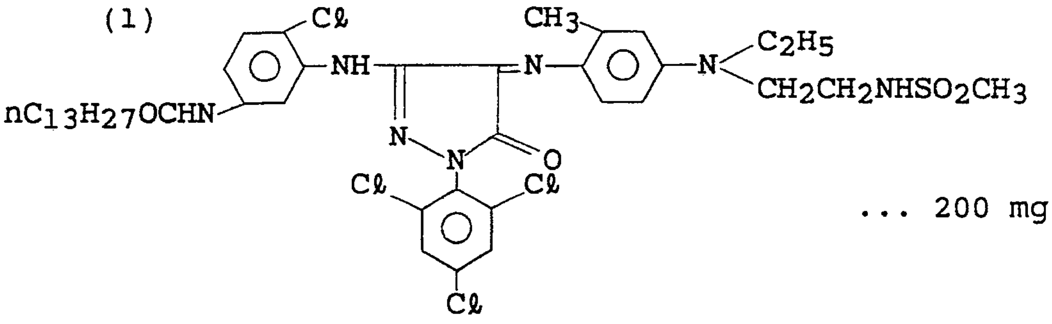
The additives used in the protective layer liquid were as follows. The amount of the additive indicated below is the amount per liter of the coating liquid.

Lime-treated inert gelatin	... 68 g
Acid-treated gelatin	... 2 g
 $NaO_3S\text{-}\overset{\displaystyle CH_2COOC_{10}H_{21}}{\overset{\vert}{C}H}\text{-}COOC_5H_{11}$ (Coating Aid)	... 1g
Polymethymethacrylate (matting agent having an area average grain size of 3.5 μ)	... 1.1 g
Silicon dioxide particle (matting agent having an area average grain size of 1.2 μ)	... 0.5 g
Rudox AM (colloidal silica manufactured by Du Pont)	... 30 g
2% aqueous solution of sodium 2,4-dichloro-6-hydroxy-1,3,5-triazinate (hardening agent)	... 10 mℓ
35% formalin (hardening agent)	... 2 mℓ
40% aqueous solution of glyoxal (hardening agent)	... 1.5 mℓ
Additive-4	... 1.0 g
Additive-5	... 0.4 g
Additive-6	... 0.3 g
Additive-7 (mixture of compounds in which n is 2 to 5)	... 2.5 g
Additive-8	... 0.5 g
Additive-9	... 3 mg
Additive-10	... 2 mg
Additive-11	... 3 g

The additives 1-11 indicated above are listed in Table B below.

In addition to the additives noted above, compounds (1) and (2) given below were added to the coating liquid in amounts given below per mol of silver halide:

(1)



... 200 mg

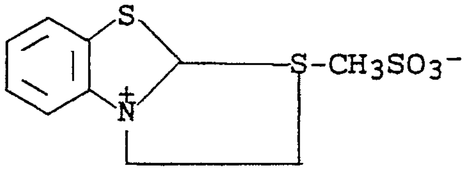
(2) Tricresylphosphate ... 0.6 g

To be more specific, compound (1) was dissolved in an oil of compound (2) in accordance with the method described in item (3) in Example 1 of JP-A-61-285445 so as to prepare a hydrophilic colloidal solution. The colloidal solution thus prepared was added in the amounts of compounds (1) and (2) given above. The samples obtained above were subjected to exposure and the following color development, and, then, evaluated for photographic properties.

Development wish Automatic Developing Machine

The developing solution and the fixing solution used were as follows:

[Developing Solution]

Potassium sulfite	... 70 g
Trisodium hydroxyethyl ethylenediamine triacetate	... 8 g
1,4-dihydroxybenzene	... 28 g
Boric acid	... 10 g
5-methylbenzotriazole	... 0.04 g
1-phenyl-5-mercaptotetrazol	... 0.01 g
Sodium metabisulfite	... 5 g
Acetic acid (90%)	... 13 g
Triethylene glycol	... 15 g
1-phenyl-3-pyrazolidone	... 1.2 g
5-nitroindazol	... 0.2 g
	... 0.001 g
Glutaraldehyde	... 4.0 g

Disodium ethylenediamine tetraacetate	... 2.0 g
Potassium bromide	... 4.0 g
5-nitrobenzoimidazole	... 1.0 g

These components were dissolved in water to prepare one liter of aqueous solution, and potassium hydroxide was added to the solution to adjust pH at 10.50.

[Fixing Solution]

Sodium thiosulfate (pentahydrate)	... 45 g
Disodium ethylenediamine tetraacetate	... 0.5 g
Ammonium thiosulfate	... 150 g
Anhydrous sodium sulfite	... 8 g
Potassium acetate	... 16 g
Aluminum sulfate (containing 10 to 18 crystal water molecules)	... 27 g
Sulfuric acid (50 wt %)	... 6 g
Citric acid	... 1 g
Boric acid	... 7 g
Glacial acetic acid	... 5 g

These components were dissolved in water to prepare one liter of an aqueous solution, and pH of the aqueous solution was controlled at 4.0 by adding glacial acetic acid to the solution.

The concentrate of the developing solution obtained above was charged in parts A, B, C of a polyethylene container, said parts A, B, C being joined together to form the container.

The concentrate of the fixing solution obtained above was also charged in a polyethylene container. Each of a developing tank and a fixing tank of an automatic developing machine was filled with these developing solutions and fixing solutions in amounts given below by using a measuring pump included in the automatic developing machine:

Developing Solution I	
Solution A	55 mℓ
Solution B	10 mℓ
Solution C	10 mℓ
Water	125 mℓ
pH	10.50

Fixing Solution	
Concentrate	80 mℓ
Water	120 mℓ
pH	4.65

A water-washing tank was filled with tap water, and sunk at the bottom of the tank were four bags each prepared by wrapping in a nonwoven fabric 50 g of a silver releasing agent containing 1.0% by weight of AgO_2 in a soluble glass of $Na_2O/B_2O_5/SiO_2$.

Construction of the Automatic Developing Machine

The automatic developing machine used was of the following construction.

	Liquid level in the Tank (liters)	Processing temp. (°C)	Processsing pass length (mm)	Processing time (seconds)
Development	15*	35	466	10.1
Fixing	15	32	328	7.1
Water-wash	13	17 (flowing water)	268	5.0
Squeezing				5.0
Drying		58	299	6.5
Total				33.7

* Ratio of liquid surface area to tank volume was 35 cm^2/liter.

Evaluation for Photographic Properties

The samples were interposed between fluorescent intensifying screens KO-250 manufactured by Konica K.K. and, then, exposed to an X-ray through Penetrometer B-type (trademark of an aluminum step manufactured by Konica Medical K.K.) for 0.05 second. The X-ray was emitted under a tube voltage of 130 KVP and a current of 220 mA. Then, the processings described above were performed.

Measured was a relative sensitivity in which the inverse of the X-ray dose giving a blackening degree of fog +1.0 to the sample coated with emulsion 1-B was set at 100. Also measured was gradation represented by inclination of the straight line joining concentration points of fog +0.25 and fog +2.0. The results are summarized in Table 1 below.

Evaluation for Stress Characteristics of Samples

The emulsion-coated film samples were folded at 25° C and relative humidity of 40% by 180° along an iron rod having a diameter of 6 mm. Immediately after the folding, a wedge light exposure was applied for 10^{-2} second. After the light exposure, the samples were subjected to the development, fixing, washing and drying using the processing solutions and the automatic developing machine described previously.

The blackening caused by the folding, which was left in the film after the processing, was represented by ΔFog/Dm, i.e., a ratio of change in fogging to the maximum density. The results are summarized in Table 1 below.

Table 1

Emulsion	Relative sensitivity	Gradation	Pressure mark ΔFog/Dm (%)
1-B (present invention)	130	2.7	1
1-C (present invention)	140	2.8	0
1-D (present invention)	140	2.7	0
I-E (present invention)	140	2.7	0
I-F (present invention)	140	2.8	0
1-G (comparative example)	100	2.8	5
1-H (comparative example)	120	2.7	2

As seen from Table 1, the emulsion of the present invention is high in sensitivity and gradation, and permits markedly improving the pressure mark.

Example 2

Emulsion 2-A (Emulsion containing tabular silver iodobromide host grains)

One tenth of the seed crystals obtained from emulsion 1-A was dissolved in 1 liter of a solution containing 3% by weight of gelatin and held at 75° C and pBr 2.55. Then, an aqueous solution containing 75 g of silver nitrate and an aqueous solution of potassium bromide were added by a double jet method over a period of 30 minutes so as to control pAg while maintaining pBr at 2.55. The aqueous solution of silver nitrate was added with an accelerated flow rate such that the flow rate at the end was 10 times as high as that at the beginning. Further, an aqueous solution containing 75 g of silver nitrate and an aqueous solution of KBr containing 10 mol % of KI were added by a double jet method at 75° C so as to maintain pBr at 2.55.

The resultant emulsion was cooled to 35° C and, then, washed by the ordinary flocculation method. The emulsion was adjusted to exhibit pH 6.5 and pAg 7.8 at 40° C.

Emulsion 2-B (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

1300 mℓ of water was added to 500 g of emulsion 2-A containing 90 g of $AgNO_3$. Then, 120 mℓ of a solution containing 0.34 M of silver nitrate and 120 mℓ of a solution containing 0.8 M of NaCℓ were added over a period of 6 minutes at 40° C and a potential of +190 mV with respect to a saturated calomel electrode. The resultant tabular grains were observed by a replica photograph of an electron microscope. Epitaxial growth of fine silver chloride crystals was not recognized at all in the edge portion (silver iodobromide portion) on the major surfaces of the host tabular grains. However, a large number of epitaxial growth of fine silver chloride crystals was recognized in the other portion (silver bromide portion) on the major surfaces of the tabular grains.

In the next step, the reaction system was heated to 75° C and physically ripened for 12 minutes, followed by adding 30 mℓ of an aqueous solution containing 2.5 M of KBr and further adding at 75° C 160 mℓ of an aqueous solution containing 0.34 M of silver nitrate over a period of 8 minutes.

The resultant emulsion was cooled to 35° C and washed by the ordinary flocculation method. Then, 50 g of bone gelatin was added so as to adjust the emulsion at pH 6.5 and pAg 8.5 at 40° C.

Emulsion 2-C (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

Emulsion 2-C was prepared substantially as in preparation of emulsion 2-B, except that 15 ml of a solution containing 0.06 M of KI was added immediately after the temperature elevation to 75 °C.

Emulsion 2-D (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

Emulsion 2-D was prepared substantially as in preparation of emulsion 2-B, except that 50 mℓ of a solution containing 0.06 M of KI was added immediately after the temperature elevation to 75 °C.

Emulsion 2-E (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

Emulsion 2-E was prepared substantially as in preparation of emulsion 2-B, except that an emulsion containing fine AgI grains having an average grain size of 0.03 µm, the silver amount being 0.0036 mol, was added immediately after the temperature elevation to 75 °C.

Emulsion 2-F (Emulsion containing tabular grains having dislocations on the major surface (within the major surface region); present invention):

Emulsion 2-F was prepared substantially as in preparation of emulsion 2-B using the system shown in Fig. 3A, except that fine AgI grains were added to the reaction vessel 1 immediately after the reaction system was heated to 75 °C.

The fine AgI grains, were prepared within the mixer 7 disposed in the vicinity of the reaction vessel 1, as follows, and introduced into the reaction vessel 1 through the inlet system 8. Specifically, 30 mℓ of a solution containing 0.12 M of silver nitrate, 30 mℓ of a solution containing 0.12 M of KI, and 65 mℓ of an aqueous solution containing 1% by weight of gelatin were supplied at constant flow rates into the mixer 7 through addition systems 5, 4, and 6, respectively, over a period of 5 minutes. The residence time within the mixer 7 was 36 seconds, and the agitating blades 9 were rotated at 3000 rpm. The resultant fine AgI fine grains were observed by a direct method using transmission electron microscope (magnification of 20,000). The average size of the grains was found to be 0.01 µm. The temperature within the mixer 7 was maintained at 25 °C, and the formed fine grains were continuously supplied to the reaction vessel 1 through the inlet system 8.

Emulsion 2-G (Emulsion containing tabular grains which do not have dislocations; comparative example):

Emulsion 2-G was prepared exactly as in preparation of emulsion 1-B, except that 160 mℓ of a solution containing 0.34 M of silver nitrate and an aqueous solution containing 0.8 M of KBr were added over a period of 8 minutes at 40 °C and a potential of +190 mV.

Emulsion 2-H (Emulsion containing tabular grains having dislocations in the edge region alone; comparative example):

1300 mℓ of water and 30 mℓ of an aqueous solution containing 2.5 M of KBr were added to 500 g of emulsion 2-A. Then, 100 mℓ of an aqueous solution containing 0.09 M of silver nitrate and 100 mℓ of a solution containing 0.09 M of KI were further added at 40 °C by a double jet method over a period of 10 minutes. After heated to 75 °C, the reaction system was subjected to a physical ripening for 12 minutes, followed by adding 160 mℓ of an aqueous solution containing 0.34 M of silver nitrate and 160 mℓ of an aqueous solution containing 0.34 M of KBr over a period of 8 minutes. Further, the subsequent steps equal to those for emulsion 2-B were followed so as to prepare emulsion 2-H.

Observation of Dislocations introduced into Tabular Grains

Dislocations were directly observed by a transmission electron microscope JEM2000FX II manufactured by Nihon Denshi K.K. under an accelerating voltage of 200 KV and a temperature of -120 °C with respect to emulsions 2-B to 2-H. In the tabular grains contained in emulsions 2-B and 2-F, dislocations were scarcely found at the peripheral portion (silver iodobromide portion) in the major surface region of the host tabular grain, and was found in the inner portion (silver bromide portion). Also, the dislocation density was found to be higher in emulsions 2-C and 2-D prepared by using a solution of KI than in emulsion 2-B. Further, the distribution of the dislocation density among the grains was narrower in emulsions 2-E and 2-F than in emulsions 2-C and 2-D prepared by using a solution of KI. In other words, the method of introducing dislocations employed for the preparation of emulsions 2-E and 2-F permits more uniform dislocations introduction. On the other hand, dislocations were not recognized at all in emulsion 2-G. Also, dislocations were concentrated in the edge region alone of the tabular grain in emulsion 2-H.

Preparation of Emulsion-Coated Sample

Each of emulsions 2-B to 2-H was subjected to an optimum chemical sensitization at 60° C with sodium thiosulfate, potassium thiocyanate and chloroauric acid.

A triacetyl cellulose film support having an undercoating layer was coated with a plurality of superposing layers of the compositions given below so as to prepare samples 201 to 207. In these samples, emulsions 2-B to 2-H subjected to optimum gold sulfur sensitization were used for forming the 1st green-sensitive layer included in the multi-layered color light-sensitive material.

(Composition of Light-sensitive Layer)

Numerals corresponding to the respective components indicate coating amount in units of g/m^2. The coating amount of silver halide is represented by a silver amount. Further, the coating amount of the sensitizing dye is represented in units of mols per mol of silver halide in the same layer.

(Sample 201)

Layer 1: Antihalation layer

Black colloid silver	(silver)	0.18
Gelatin		1.40

Layer 2: Interlayer

2,5-di-t-pentadecylhydroquinone		0.18
EX-1		0.070
EX-3		0.020
EX-12		2.0×10^{-3}
U-1		0.060
U-2		0.080
U-3		0.10
HBS-1		0.10
HBS-2		0.020
Gelatin		1.04

Layer 3: 1st red-sensitive emulsion layer

Emulsion A	(silver)	0.25
Emulsion B	(silver)	0.25
Sensitizing dye I		6.9×10^{-5}
Sensitizing dye II		1.8×10^{-5}
Sensitizing dye III		3.1×10^{-4}
EX-2		0.34
EX-10		0.020
U-1		0.070
U-2		0.050

U-3		... 0.070
HBS-1		... 0.060
Gelatin		... 0.87

Layer 4: 2nd red-sensitive emulsion layer

Emulsion G	(silver)	... 1.00
Sensitizing dye I		... 5.1×10^{-5}
Sensitizing dye II		... 1.4×10^{-5}
Sensitizing dye III		... 2.3×10^{-4}
EX-2		... 0.40
EX-3		... 0.050
EX-10		... 0.015
U-1		... 0.070
U-2		... 0.050
U-3		... 0.070
Gelatin		... 1.30

Layer 5: 3rd red-sensitive emulsion layer

Emulsion D	(silver)	... 1.60
Sensitizing dye I		... 5.4 × 10-5
Sensitizing dye II		... 1.4×10^{-5}
Sensitizing dye III		... 2.4×10^{-4}
EX-2		... 0.097
EX-3		... 0.010
EX-4		... 0.080
HBS-1		... 0.22
HBS-2		... 0.10
Gelatin		... 1.63

Layer 6: Interlayer

EX-5		... 0.040
HBS-1		... 0.020
Gelatin		... 0.80

Layer 7: 1st green-sensitive emulsion layer

Emulsions 2B to 2H	(silver)	... 0.15
Emulsion B	(silver)	... 0.15
Sensitizing dye IV		... 3.0×10^{-5}
Sensitizing dye V		... 1.0×10^{-4}
Sensitizing dye VI		... 3.8×10^{-4}
EX-1		... 0.021

EX-6		... 0.26
EX-7		... 0.030
EX-8		... 0.025
HBS-1		... 0.10
HBS-3		... 0.010
Gelatin		... 0.63

Layer 8: 2nd green-sensitive emulsion layer

Emulsion C	(silver)	... 0.45
Sensitizing dye IV		... 2.1×10^{-5}
Sensitizing dye V		... 7.0×10^{-5}
Sensitizing dye VI		... 2.6×10^{-4}
EX-6		... 0.094
EX-7		... 0.026
EX-8		... 0.018
HBS-1		... 0.16
HBS-3		... 8.0×10^{-3}
Gelatin		... 0.50

Layer 9: 3rd green-sensitive emulsion layer

Emulsion E	(silver)	... 1.20
Sensitizing dye IV		... 3.5×10^{-5}
Sensitizing dye V		... 8.0×10^{-5}
Sensitizing dye VI		... 3.0×10^{-4}
EX-1		... 0.025
EX-11		... 0.10
EX-13		... 0.015
HBS-1		... 0.25
HBS-3		... 0.10
Gelatin		... 1.54

Layer 10: Yellow filter layer

Yellow colloid silver	(silver)	... 0.050
EX-5		... 0.080
HBS-1		... 0.030
Gelatin		... 0.95

Layer 11: 1st blue-sensitive emulsion layer

Emulsion A	(silver)	... 0.015
Emulsion F	(silver)	... 0.070
Sensitizing dye VII		... 3.5×10^{-4}

EX-8 ... 0.042
EX-9 ... 0.72
HBS-1 ... 0.28
Gelatin ... 1.10

Layer 12: 2nd blue-sensitive emulsion layer
Emulsion G (silver) ... 0.45
Sensitizing dye VII ... 2.1×10^{-4}
EX-9 ... 0.15
EX-10 ... 7.0×10^{-3}
HBS-1 ... 0.050
Gelatin ... 0.78

Layer 13: 3rd blue-sensitive emulsion layer
Emulsion H (silver) ... 0.77
Sensitizing dye VII ... 2.2×10^{-4}
EX-9 ... 0.20
HBS-1 ... 0.070
Gelatin ... 0.69

Layer 14: 1st protective layer
Emulsion I (silver) ... 0.20
U-4 ... 0.11
U-5 ... 0.17
HBS-1 ... 5.0×10^{-2}
Gelatin ... 1.00

Layer 15: 2nd protective layer
H-1 ... 0.40
B-1 (diameter 1.7 μm) ... 5.0×10^{-2}
B-2 (diameter 1.7 μm) ... 0.10
B-3 ... 0.10
S-1 ... 0.20
Gelatin ... 1.20

Further, in order to improve the storage capability, processing capability, pressure resistance, resistance to mold and bacteria, antistatic property and coating property, each layer was allowed to contain compounds W-1, W-2, W-3, B-4, B-5, F-1, F-2, F-3, F-4, F-5, F-6, F-7, F-8, W-9, W-10, W-11, F-12, F-13, iron salt, lead salt, gold salt, platinum salt, iridium salt and rhodium salt.

Table 2 shows the details of emulsions A to I contained in the light-sensitive layer described above.

Further, the structual formulas of the compounds identified using symbols are listed in Table C below.

Table 2

Emulsion	Average AgI content (%)	Average grain size (µm)	Variation coefficient in grain size (%)	size/ thickness ratio	Silver amount ratio (AgI content %)
A	4.0	0.45	27	1	core/shell = 1/3(13/1) double layered grain
B	8.9	0.70	14	1	core/shell = 3/7(25/2) double layered grain
C	10	0.75	30	2	core/shell = 1/2(24/3) double layered grain
D	6	1.05	35	2	core/shell = 4/6(40/0) double layered grain
E	10	1.05	35	3	core/shell = 1/2(24/3) double layered grain
F	4.0	0.25	28	1	core/shell = 1/3(13/1) double layered grain
G	14.0	0.75	25	2	core/shell = 1/2(42/0) double layered grain
H	14.5	1.30	25	3	core/shell = 37/63(34/3) double layered grain
I	1	0.07	15	1	uniform grains

Samples 201 to 207 thus prepared were exposed to light through an "SC-52 Fuji Filter" (trademark) which transmits light of wavelength longer than 520 nm and subjected the processing by the methods given below by using an automatic developing machine. The processing was continued until the accumulated replenishing amount of the bleaching solution reached three times as much as the volume of the mother liquid tank.

Process	Processing time (min:sec)	Processing temp. (°C)	Replenishing amount*	Tank volume (liters)
Color development	3:15	38	33 mℓ	20
Bleaching	6:30	38	25 mℓ	40
Washing	2:10	24	1200 mℓ	20
Fixing	4:20	38	25 mℓ	30
Washing (1)	1:05	24	ounter-current piping system from (2) to (1)	10
Washing (2)	1:00	24	1200 mℓ	10
Stabilization	1:05	38	25 mℓ	10
Drying	4:20	55		

* Replenishing amount per 35 mm × 1 m

The compositions of the processing solutions were as follows:

(Color Developing Solution)

	Mother liquid (g)	Replenishing liquid (g)
Diethylenetriaminepentaacetate	1.0 g	1.1 g
1-hydroxyethylidene-1,1-diphosphonic acid	3.0 g	3.2 g
Sodium sulfite	4.0 g	4.4 g
Potassium carbonate	30.0 g	37.0 g
Potassium bromide	1.4 g	0.7 g
Potassium iodide	1.5mg	-
Hydroxylamine sulfate	2.4 g	2.8 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g	5.5 g

Water to make	1.0 ℓ	1.0 ℓ
pH	10.05	10.10

(Bleaching Solution)

	Mother liquid (g)	Replenishing liquid (g)
Ferric ammonium ethylenediaminetetraacetate trihydrate	100.0	120.0
Disodium ethylenediamine tetraacetate	10.0	11.0
Ammonium bromide	140.0	160.0
Ammonium nitrate	30.0	35.0
Ammonia water (27%)	6.5mℓ	4.0mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.0	5.7

(Fixing Solution)

	Mother liquid (g)	Replenishing liquid (g)
Disodium ethylenediamine tetraacetate	0.5	0.7
Sodium sulfite	7.0	8.0
Sodium bisulfite	5.0	5.5
Aqueous solution (70%) of ammonium thiosulfate	170.0mℓ	200.0mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.7	6.6

(Stabilizing Solution)

	Mother liquid (g)	Replenishing liquid (g)
Formalin (37%)	2.0mℓ	3.0mℓ
Polyoxaethylene-p-monononyl phenyl ether (mean polymerization degree 10)	0.3	0.45
Disodium ethylenediamine tetraacetate	0.05	0.08
Water to make	1.0 ℓ	1.0 ℓ
pH	5.0-8.0	5.0-8.0

Concentration of the sample thus processed was measured with a green filter. The results of the photographic performance were summarized in Table 3 below.

Further, the pressure sensitive characteristics were evaluated by the same method as employed in Example 1. The folded sample was subjected to the processings as above. The results were also summarized in Table 3 below.

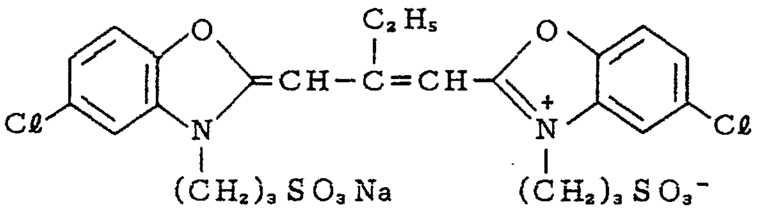
Table 3

Sample	Emulsion	Sensitivity	Fogging	Pressure mark Δ Fog/Dm (%)
201	2-B (present invention)	140	0.17	2
202	2-C (present invention)	150	0.18	1
203	2-D (present invention)	155	0.18	0
204	2-E (present invention)	150	0.17	0
205	2-F (present invention)	155	0.17	0
206	2-G (comparative example)	100	0.18	6
207	2-H (comparative example)	130	0.18	3

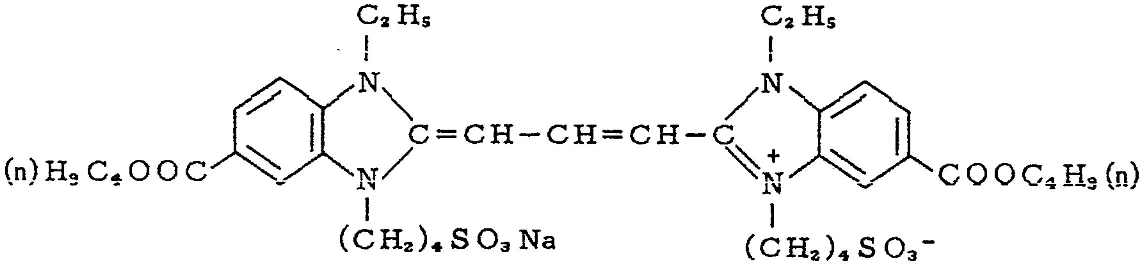
As seen from Table 3, samples 201 to 205 coated with the emulsion of the present invention exhibit a higher sensitivity and a lower pressure mark, compared with comparative samples 206 and 207.

Table A

Spectral Sensitizing Dye A

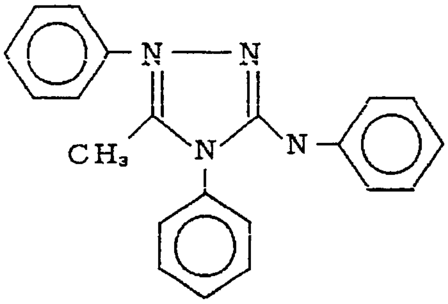


Spectral Sensitizing Dye B



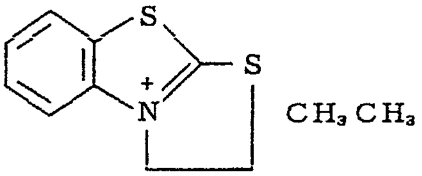
TableB

Additive－1



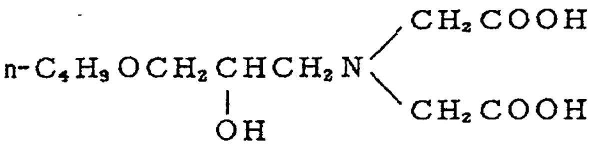
150mg

Additive－2



70mg

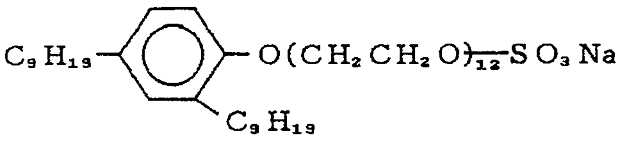
Additive－3



$$n\text{-}C_4H_9OCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2N\begin{matrix} \diagup CH_2COOH \\ \diagdown CH_2COOH \end{matrix}$$

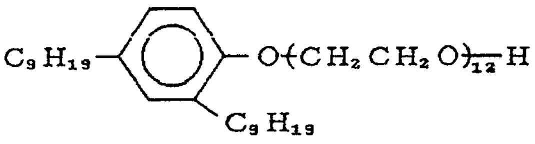
1 g

Additive－4



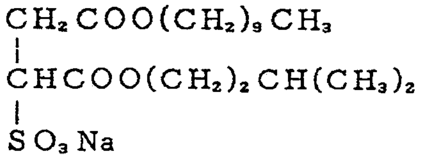
1.0 g

Additive－5



0.4 g

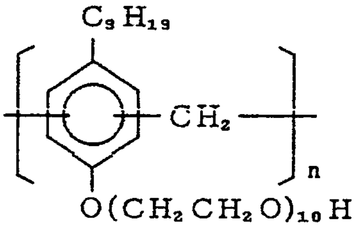
Additive－6



$$\begin{array}{l} CH_2COO(CH_2)_9CH_3 \\ | \\ CHCOO(CH_2)_2CH(CH_3)_2 \\ | \\ SO_3Na \end{array}$$

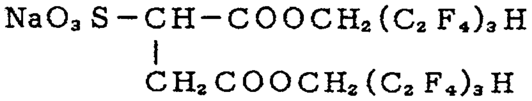
0.3 g

Additive－7



2.5 g

Additive－8



$$\begin{array}{l} NaO_3S-CH-COOCH_2(C_2F_4)_3H \\ \qquad\quad\ | \\ \qquad\quad\ CH_2COOCH_2(C_2F_4)_3H \end{array}$$

0.5 g

Additive－9

$F_{19}C_9-O(CH_2CH_2O)_{10}CH_2CH_2-OH$ 3 mg

Additive－10

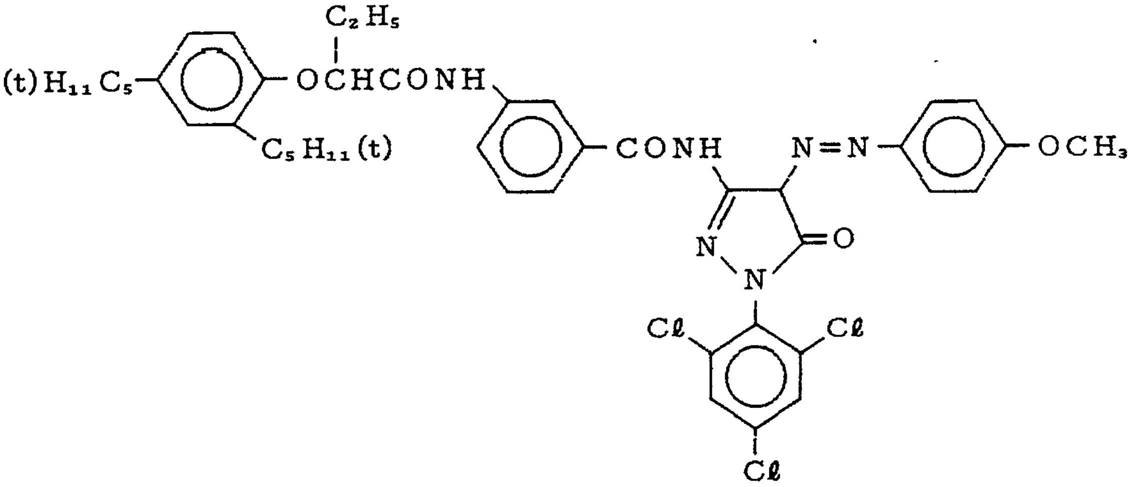
$C_4F_9SO_3K$ 2 mg

Additive－11

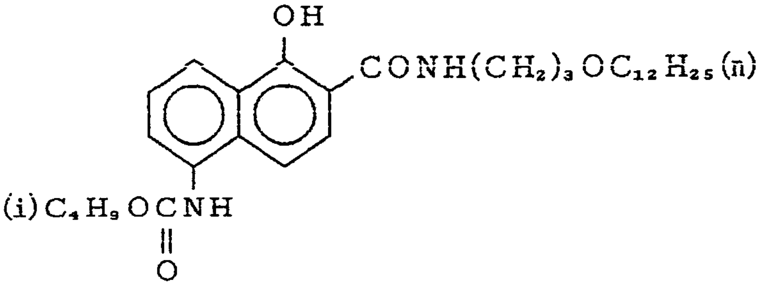
$C_{10}H_{21}CONH(CH_2CH_2O)_6H$ 3 g

Table C

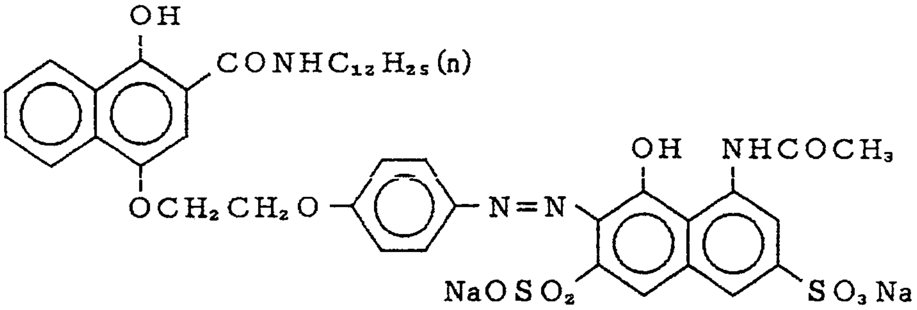
EX-1



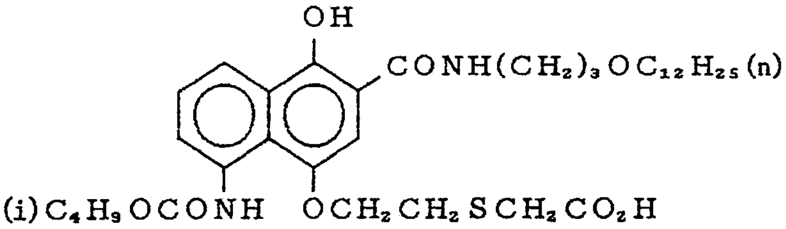
EX-2



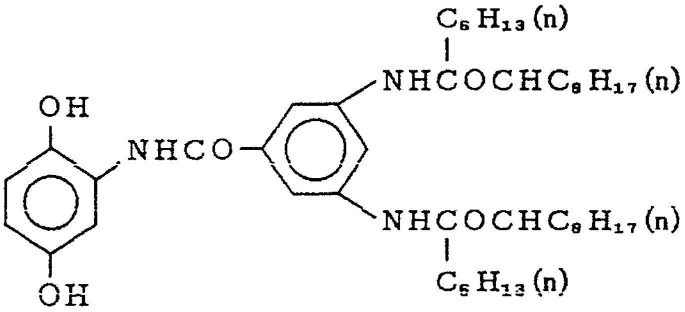
EX－3



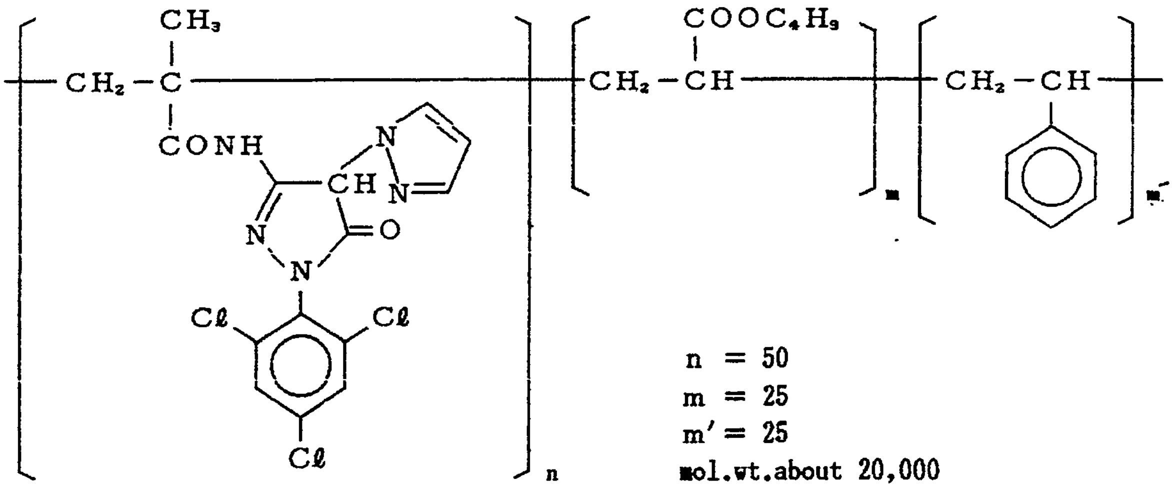
EX－4



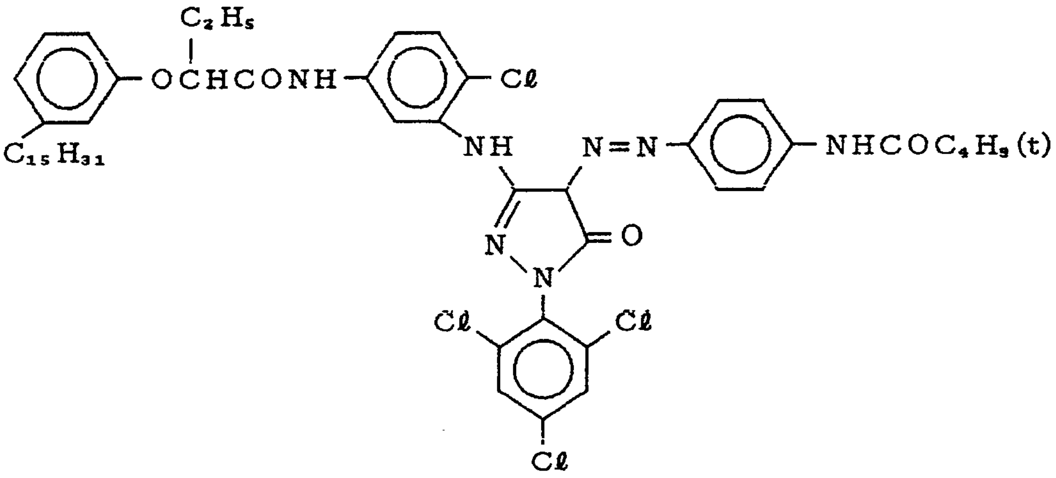
EX－5



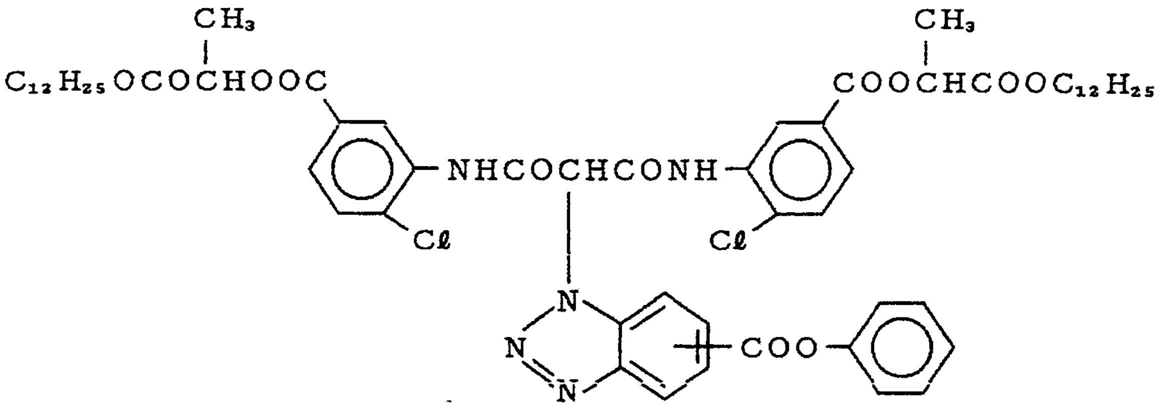
EX-6



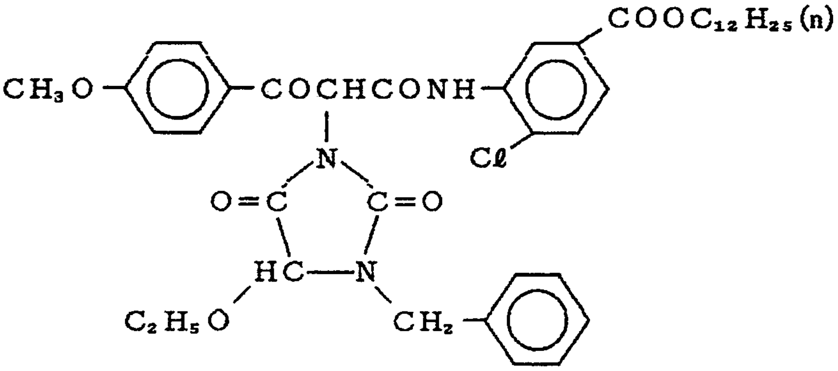
EX-7



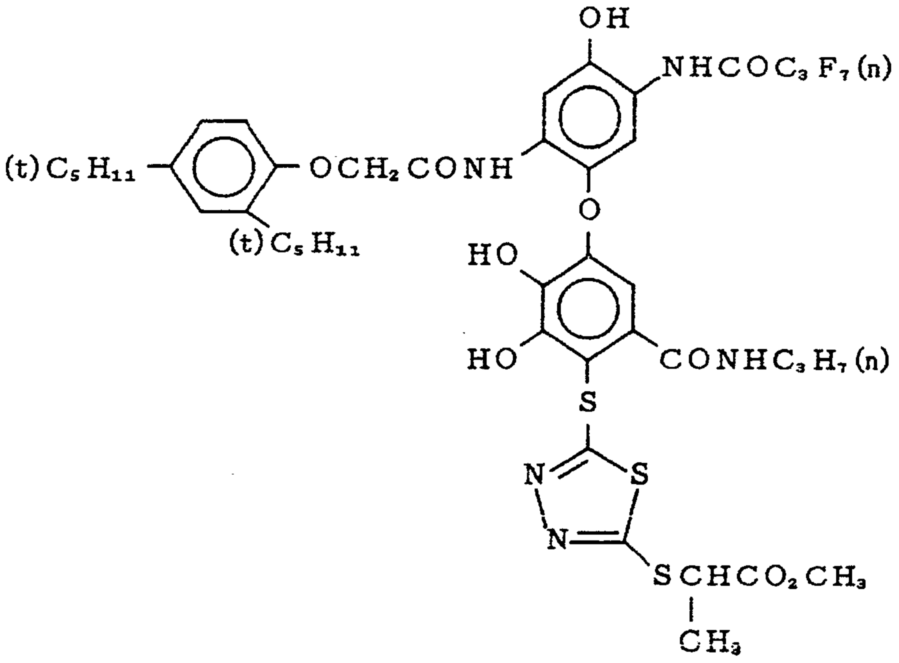
EX-8



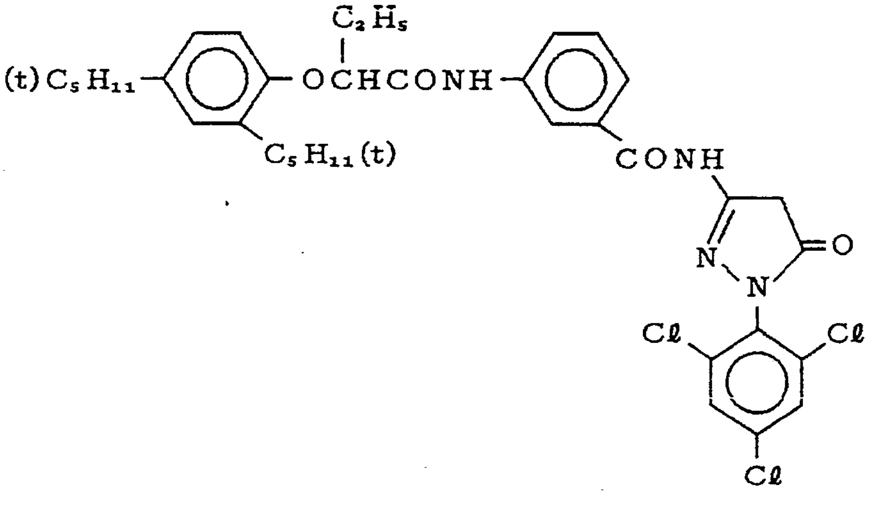
EX-9



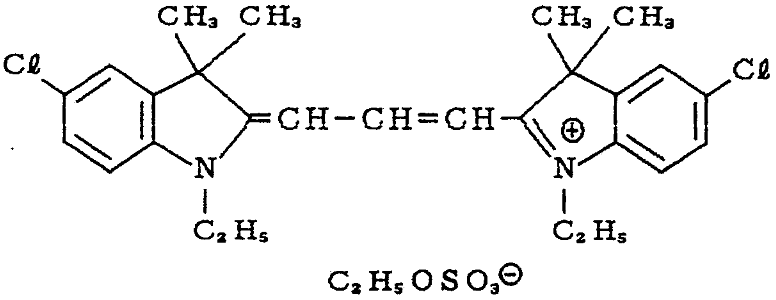
EX−10


OH
NHCOC₃F₇(n)
(t)C₅H₁₁
OCH₂CONH
(t)C₅H₁₁
O
HO
HO
CONHC₃H₇(n)
S
N
S
N
SCHCO₂CH₃
CH₃

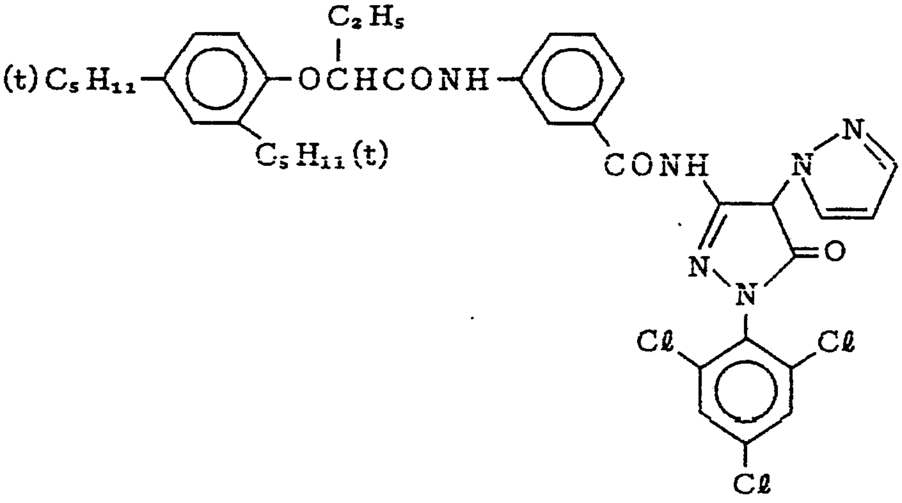
EX−11


C₂H₅
(t)C₅H₁₁
OCHCONH
C₅H₁₁(t)
CONH
N
N
O
Cl
Cl
Cl

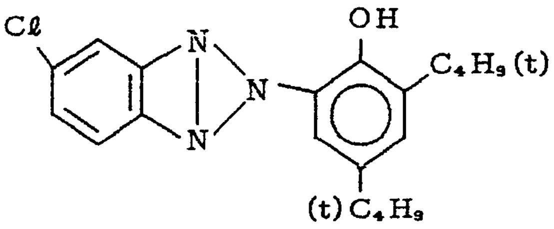
EX-12



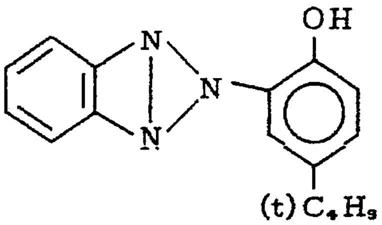
EX-13



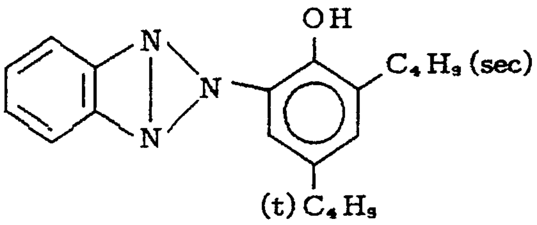
U－1



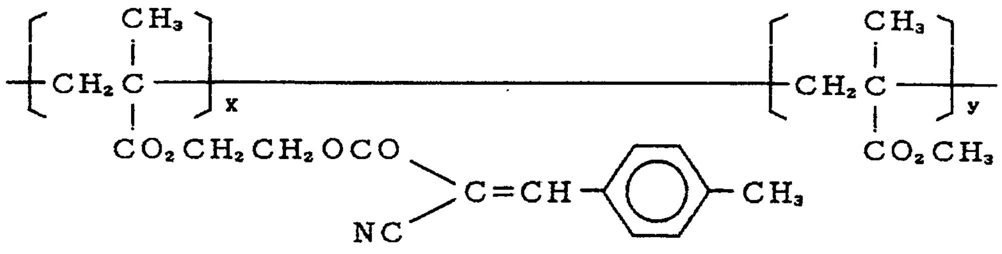
U－2



U－3

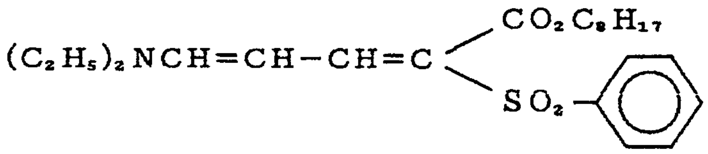


U−4



x : y = 70 : 30 (wt%)

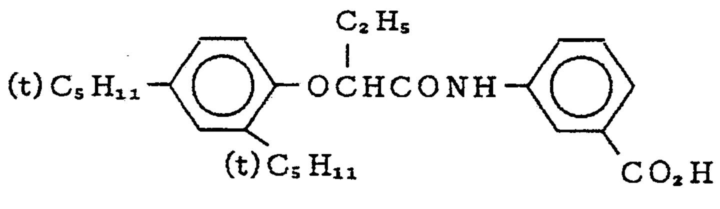
U−5



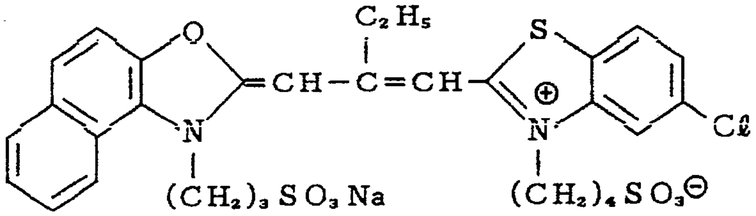
HBS−1 Tricresylphosphate

HBS−2 Di-n-butylphthalate

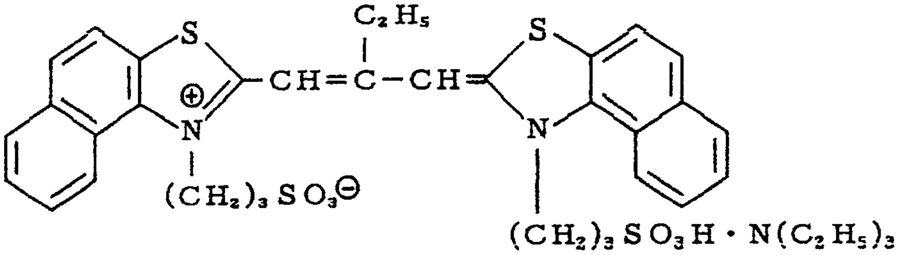
HBS−3



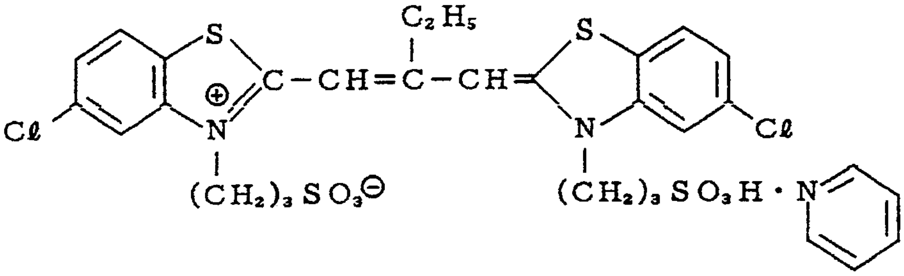
Sensitizing Dye I



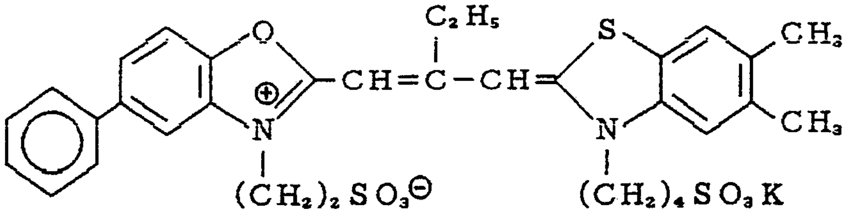
Sensitizing Dye II



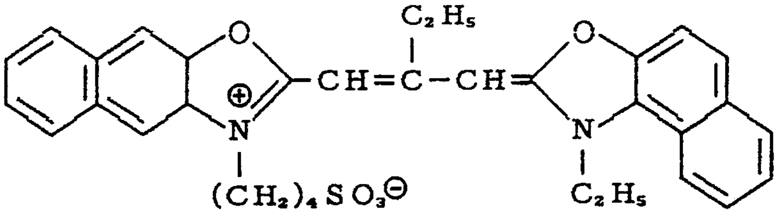
Sensitizing Dye III



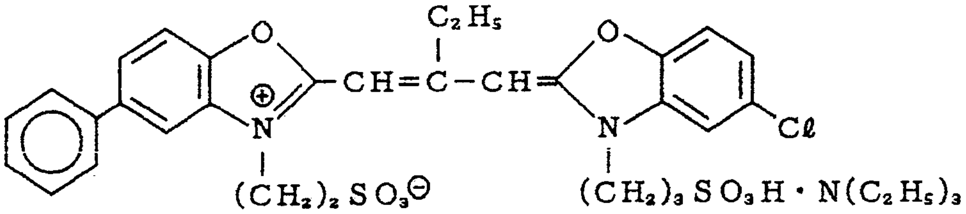
Sensitizing DyeⅣ



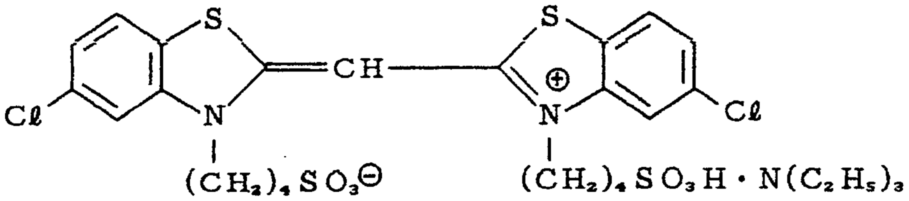
Sensitizing Dey V



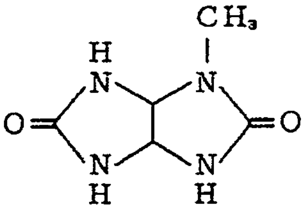
Sensitizing DyeⅥ



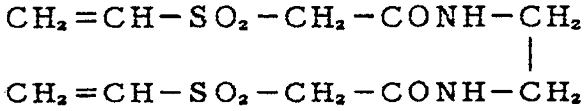
Sensitizing DyeⅦ



S－1

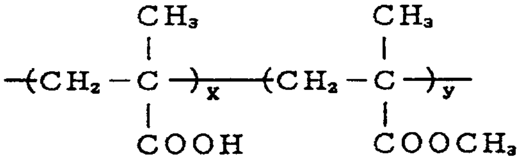


H－1



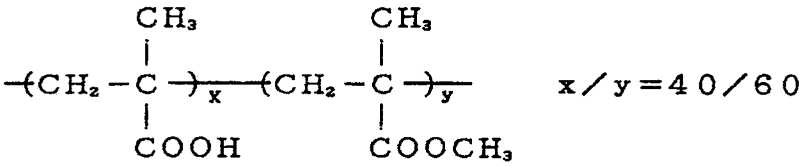
$$\begin{array}{l} CH_2=CH-SO_2-CH_2-CONH-CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2=CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

B－1



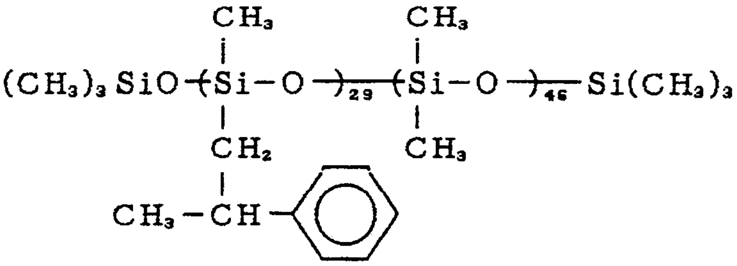
$$\left(CH_2-\underset{COOH}{\overset{CH_3}{C}}\right)_x\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_y \qquad x/y=10/90$$

B−2

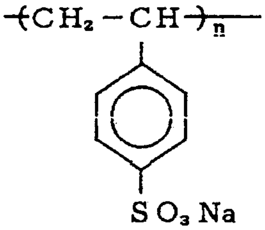


$$-\!\!(CH_2-\underset{COOH}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\!\!)_x\!-\!(CH_2-\underset{COOCH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\!\!)_y \qquad x/y=40/60$$

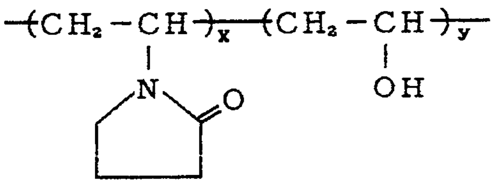
B−3



B−4

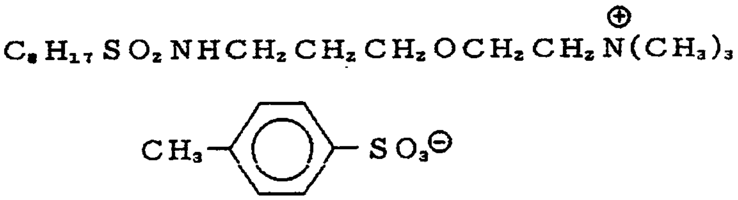


B−5



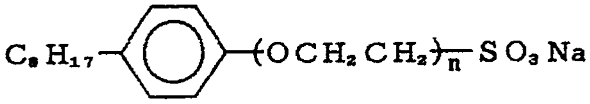
x／y＝70／30

W−1



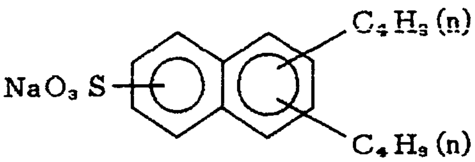
$C_8H_{17}SO_2NHCH_2CH_2CH_2OCH_2CH_2\overset{\oplus}{N}(CH_3)_3$

W−2

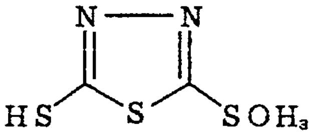


n＝2〜4

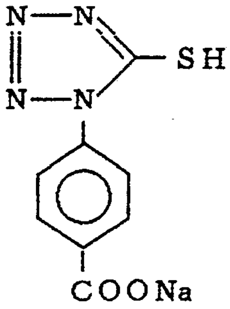
W−3



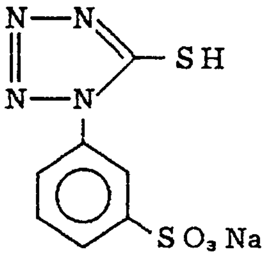
F－1



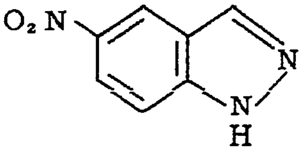
F－2



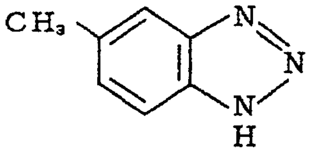
F－3



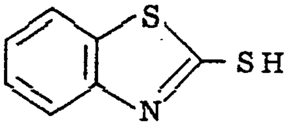
F－4



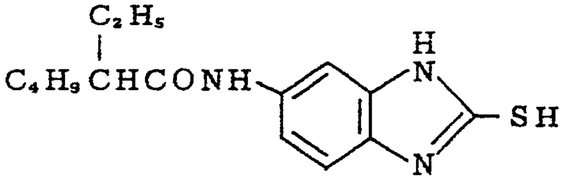
F－5



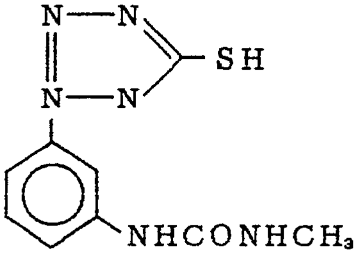
F－6



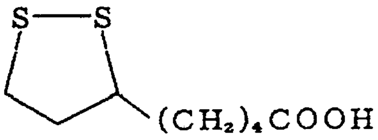
F－7



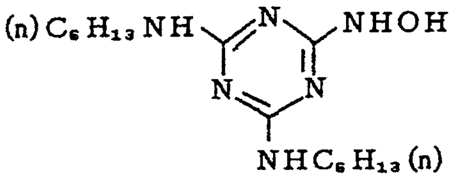
F－8



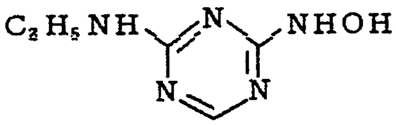
F－9



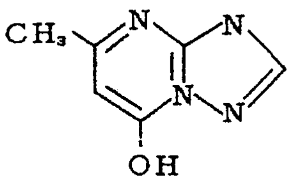
F－10



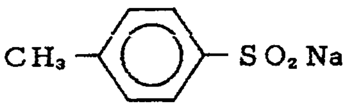
F－11



F－12



F－13



Claims

1. A silver halide photographic emulsion comprising a dispersant and silver halide grains, characterized in that at least 50% of the total projected surface area of the silver halide grains is occupied by tabular silver halide grains having an average aspect ratio of 2 or more, the mutually facing parallel major surfaces of the tabular silver halide grain are (111) faces, and at least 30% of the tabular silver halide grains have dislocations in the major surface region.

2. The silver halide photographic emulsion according to claim 1, characterized in that said tabular silver

halide grains having dislocations in the major surface region do not have any dislocation in the edge region of the major surface region.

3. The silver halide photographic emulsion according to claim 1, characterized in that said tabular silver halide grains having dislocations in the major surface region do not have dislocations localized in only the central region of the major surface region.

4. The silver halide photographic emulsion according to claim 1 or 2, characterized in that at least 70% of the total projected surface area of the silver halide grains is occupied by hexagonal tabular silver halide grains having mutually facing two parallel planes as the outer surfaces, the hexagonal shape being such that a ratio in length of the longest side to the shortest side of the hexagon is 2 or less, and the hexagonal tabular silver halide grains exhibit a mono dispersed size distribution.

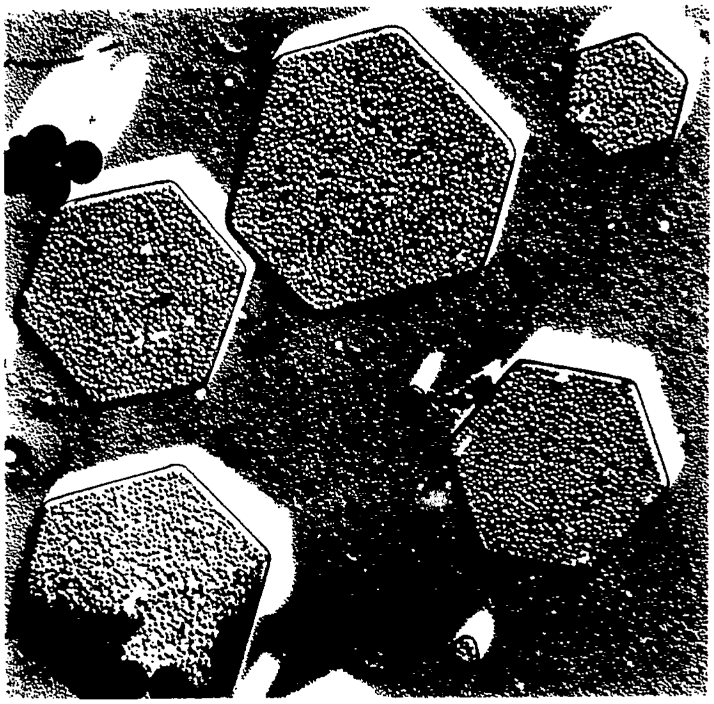


FIG. 1

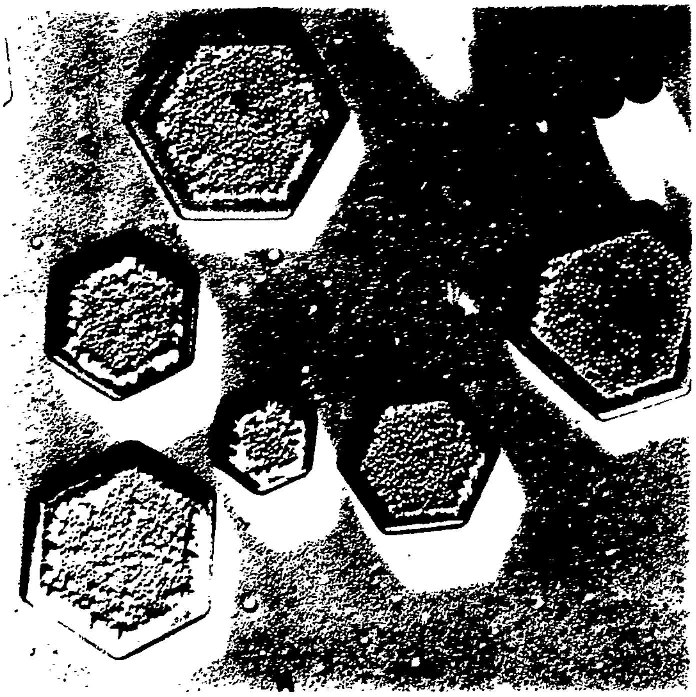


FIG. 2

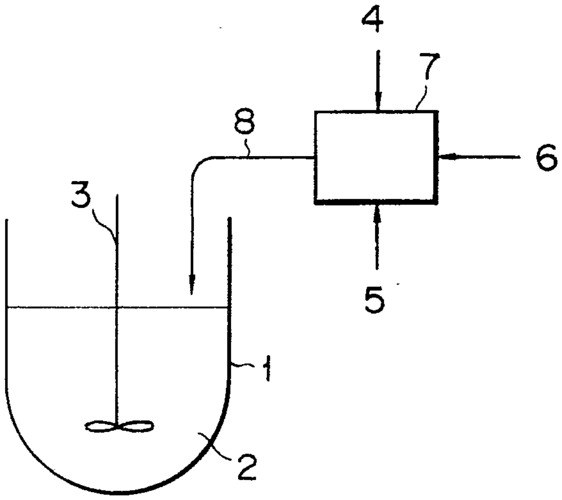


FIG. 3A

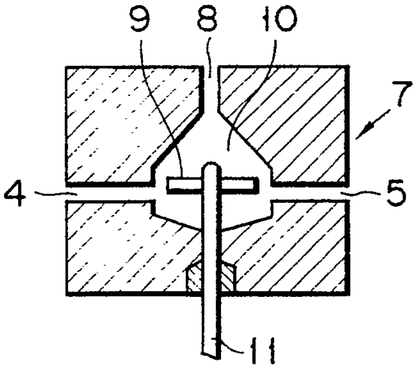


FIG. 3B

FIG. 4

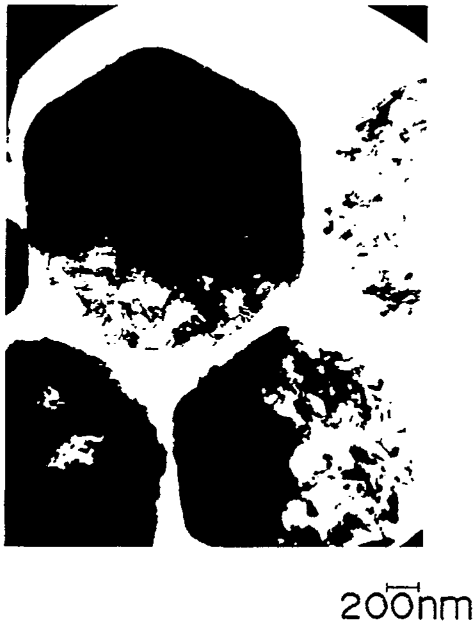


FIG. 5

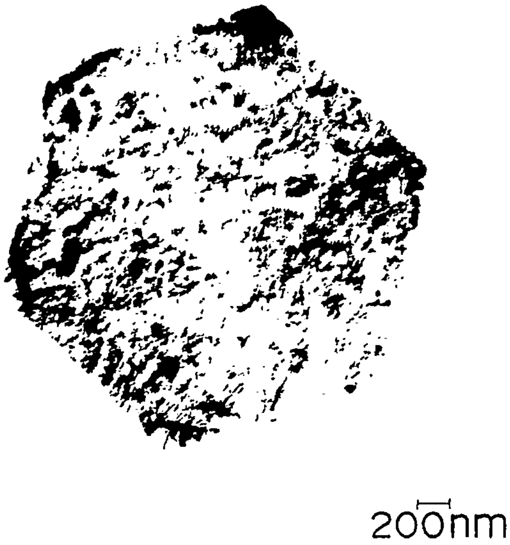


FIG. 6

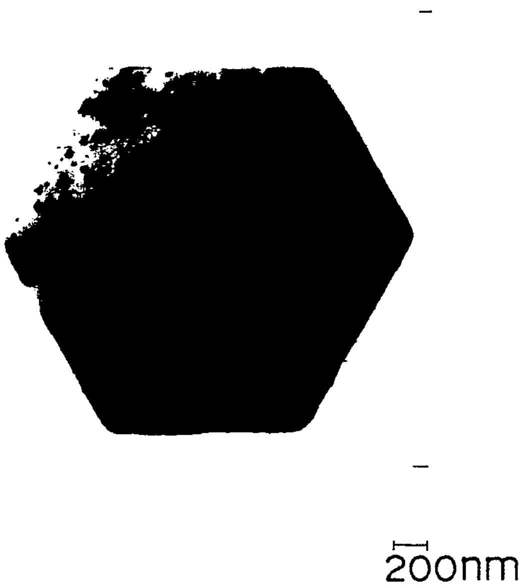


FIG. 7

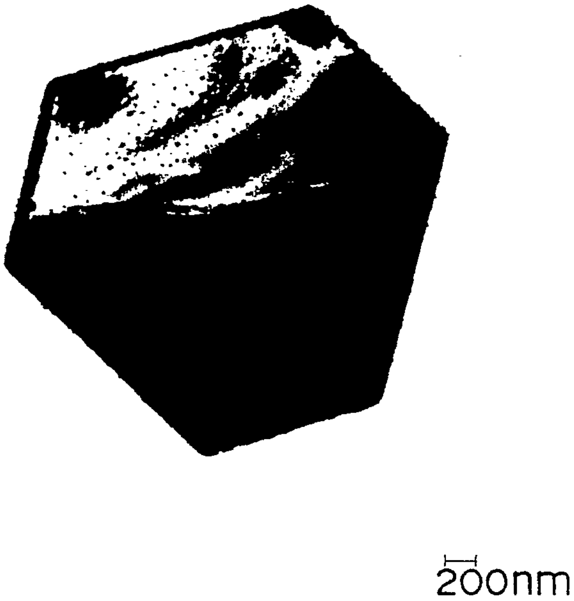


FIG. 8

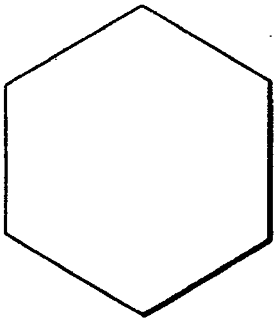


FIG. 9A

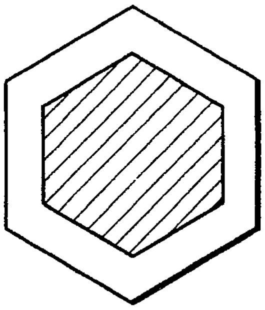


FIG. 9B

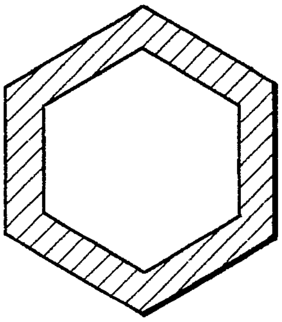


FIG. 9C

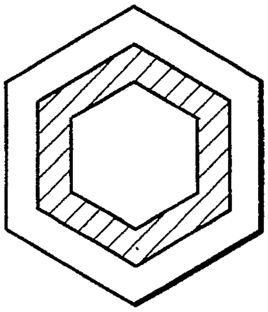


FIG. 9D

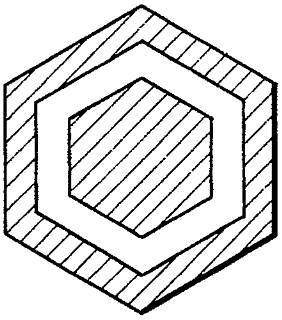


FIG. 9E

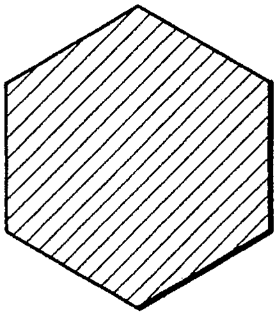


FIG. 9F

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 9266

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	JOURNAL OF IMAGING SCIENCE. vol. 32, no. 4, July 1988, SPRINGFIELD US pages 160 - 177; Joe E. Maskasky: "Epitaxial Selective Site Sensitization of Tabular Grain Emulsions" * figure 11 * – – –	1-4	G 03 C 1/035
Y	EP-A-0 244 356 (CIBA-GEIGY AG) * the whole document * – – –	1-4	
A,D	EP-A-0 282 896 (FUJI PHOTO FILM COMPANY LTD.) * claims & JP-A-632202388 * – – –	1-4	
D,A	US-A-4 879 208 (FUJI PHOTO FILM COMPANY LTD.) * claims 1-13; figures 1-4c * – – – – –	1-4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	19 July 91	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

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

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

& : member of the same patent family, corresponding document