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(54) A process for preparing a silver halide photographic emulsion.

(57) A process for preparing a silver halide photographic emulsion, which comprises :

forming silver halide grains to produce a silver halide emulsion ;

adding a silver halide solvent to said silver halide emulsion after completion of the formation of the silver halide grains ; and

adding a spectral sensitizing dye to said silver halide emulsion containing said silver halide solvent over a period of time which is equal to or longer than the mean mixing time of a mixing system in which said silver halide emulsion is mixed with said spectral sensitizing dye.

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FIELD OF THE INVENTION

The present invention relates to a process for preparing a silver halide emulsion and a silver halide light-sensitive material containing the emulsion.

BACKGROUND OF THE EMULSION

In a process of preparing a silver halide photographic emulsion (hereinafter called merely emulsion), for the purpose of adjusting and improving its photographic characteristics and providing it with specific characteristics, various additives are added thereto to thereby finish up a final emulsion for coating.

As is well known, the emulsion is a suspension comprising a hydrophilic high-molecular solution, generally gelatin and silver halide (hereinafter sometimes called AgX) crystal grains suspended in the solution.

The basic characteristics required for a silver halide photographic light-sensitive material constituted by the emulsion are a high sensitivity, a low fog, a high developability and an excellent preservability.

In order to make a light-sensitive material highly sensitive, it is required to increase the sensitivity of silver halide grains as a basic element for composing the light-sensitive layers of the light-sensitive material. To meet the requirement, various chemical sensitization methods have so far been studied to date. Typical methods are sulfur sensitization, selenium sensitization, noble-metal sensitization, and reduction sensitization methods, and combinations of these methods.

Also, various investigations have conventionally been made to increase the inherent sensitivity of silver halide grains. The inherent light-absorbability of silver halide turns larger in the order of AgCl, AgBr and AgI, while the developability of the same turns lower in the above described order. To make the reciproal characteristics of silver halide compatible, Japanese Patent Examined Publication No. 18939/1981 discloses a method for deriving separately the respective useful intrinsic characteristics of a silver halide core phase and a different silver halide shell phase from a core/shell type silver halide emulsion. Particularly, to provide the core/shell type silver halide emulsion with an increased sensitivity by raising its light absorbance and a well-maintained processability, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP O.P.I.) Nos. 14331/1985 and 245151/1986 disclose examples of the grain structure composed of a core phase having a high AgI content and an AgBrI shell phase having a low AgI content. For photographic papers and graphic arts light-sensitive materials that require high developabilities, Japanese Patent Examined Publication No. 18939/1981 and JP O.P.I. No. 215540/1986 describe examples of AgBrCl grains composed of a high silver bromide-content core phase and a low silver bromide-content shell phase. The intrinsic absorption edge of a silver halide such as AgBr, AgBrI and AgBrCl is in the blue-ultraviolet light region, so that they absorb only a limited part of the visible rays. Accordingly, where silver halide is applied to a photographic light-sensitive material for practical use, silver halide grains are usually subjected to an appropriate dye adsorption treatment; so-called spectral sensitization. Generally, where the adsorption of a dye to silver halide is weak, the desorption of or changes in the condition of adsorbing state of the dye may sometimes occur during the storage of a light-sensitive material containing the silver halide, which makes the light-sensitive material liable to undergo changes in its photographic characteristics. Particularly, the changes are conspicuous under high temperature/high humidity conditions; in a color photographic light-sensitive material, there are cases where a spectral sensitizing dye to a certain color-sensitive layer diffuses into an adjacent different color-sensitive layer to bring about a color impurity, thus resulting in a conspicuous deterioration of the photographic characteristics.

The adsorption of a spectral sensitizing dye to silver halide turns stronger normally in the order of silver chloride < silver bromide < silver iodide, but in view of this tendency, grains having the aforementioned grain structure are disadvantageous in respect of the dye adsorption. Even JP O.P.I. No. 273033/1989 points out that the double-structure grain disclosed in JP O.P.I. No. 14331/1985 is an essential disadvantage in this respect.

On the other hand, attempts have hitherto been made to strengthen the adsorption of spectral sensitizing dyes by the selection of the position of the addition thereof in the silver halide emulsion production line. U.S. Patent Nos. 2,735,766, 3,628,960, 4,183,756 and 4,225,666, JP O.P.I. Nos. 26589/1980 and 184142/1983 disclose techniques for the addition of the dye in the course of grain formation or physical ripening.

The above techniques, although capable of improving the adsorption amount and retainability of the dye under various environmental conditions, however, have the problem that the dye is adsorbed to the surface of the grain in the midst of growing to prevent the grain crystal from properly growing.

JP O.P.I. Nos. 103149/1986 and 196238/1986 disclose techniques to add the dye during the period including the latter half of the grain growing process wherein the grain form does substatially not change and the process from completion of the grain formation until before the desalting process, and further, JP O.P.I. No. 52137/1989 discloses a technique to add the dye in the desalting process. The addition of the dye in these techniques surely more strengthen the dye adsorption than the addition made during the period of from after completion of the desalting process until before the coating process, but is not sufficient for providing an improved level, and not advantageous, either, in the aspect of production efficiency.

As a means to strengthen the dye adsorption on the silver halide grain side, JP O.P.I. No. 106745/1988 describes raising to not less than 5 mol% the surface AgI content of an inside high AgI-content core/shell-structure grain. It is well-known, however, that, generally, if the surface AgI content is increased, then the grain's aptitude for chemical sensitization is deteriorated to reduce its sensitivity and developability, and therefore it is difficult to satisfy both requirements for improving the sensitivity and dye adsorbability at the same time. In addition, the above publication makes no mention at all of how to solve this problem. JP O.P.I. No. 273033/1989 discloses a technique for a high surface AgI content grain, in which the same index surface of the grain is partially made into a surface of a different compositon, i.e., a low AgI content, to thereby improve the grain's aptitude for chemical sensitization. However, the grain having such a structure is inferior in the preservability as well as in the stability in the manufacturing process.

In addition to the above macro-equilibrium problem, the uniformity and heterogeneity of the adsorption to the emulsion grain from the view point of the reaction rate and microscopic reaction on the basis of the grain come into question.

When such an additive is added in the form of a solution, suspension or powder to an emulsion liquid, it is quickly or gradually according to a stirring condition and uniformly distributed in the emulsion liquid, and after a certain period of time from the added point of time, it comes to a completely uniformly distributed condition.

However, where the additive is slowly uniformly distributed over the whole emulsion liquid, rapidly dissolved, rapidly adsorbed, and/or relatively abundantly adsorbable in a small adding amount to silver halide, the additive is adsorbed to only the silver halide grains located in the proximity of the place where the additive is added. When several kinds of the additive are used, the respective additives and their amounts used differ to constitute a large variety of groups of grains different in the photographic behavior.

Furthermore, the above uncontrollable situation could be doubled if it is necessary to use a polydispersed emulsion comprising a group of grains different in the crystal phase and/or grain size, which represents a technical system lacking in reliability.

Accordingly, if reproducible photographic characteristics are required for an emulsion, it is compelled to wait for the adsorption equilibrium of all the additives added, but the emulsion preparation period of time is too short to wait for the equilibrium to come, while the transit to the adsorption equilibrium in the coated and composed dry-colloid state on a light-sensitive material gradually but securely makes progress to cause the characteristics to change with time.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for preparing an emulsion and an emulsion which is prepared according to the method and possesses the following characteristics:

(1) Equal functions provided to all the silver halide grains by uniformly distributing a spectral sensitizing dye thereto,
(2) Decreased difference in the function between the silver halide grains,
(3) Excellent reproduciblity with less changes in the characteristics in the state of an emulsion, and
(4) A high sensitivity and a good preservability.

The above object of the invention is accomplished by the following process for preparing a silver halide emulsion and a silver halide photographic light-sensitive material using a silver halide emulsion prepared by the process.

The process comprises steps of

forming silver halide grains to make a silver halide emulsion,

adding a silver halide solvent to the silver halide emulsion after completion of the formation of silver halide grains, and

adding a spectral sensitizing dye to the silver halide emulsion containing the silver halide solvent during a period of time equal to or longer than the mean mixing time of a mixing system in which the silver halide emulsion is mixed with the spectral sensitizing dye.

DETAILED DESCRIPTION OF THE INVENTION

In the preparing process of the invention, the spectral sensitizing dye is added to and mixed with a silver halide emulsion under specific conditions. That is, the dye is added to the emulsion, spending a longer period of time than the mean mixing time T for the mixture system thereof. The mean mixing time, when a certain substance is added to the emulsion being stirred under definite conditions, is a time required for the substance to be uniformly mixed in the emulsion, and is determined according to many factors such as the physical characteristics and volume of the emulsion, the form of the mixing pot used, the form of the stirrer, and the stirring rate. In the invention, the mean mxing time is defined as a period of time measured in the following manner for each individual mixure system actually used.

A prescribed amount of the emulsion is put in a mixing vessel and stirred under definite conditions, and to the emulsion with stirring is added a 3N potassium bromide solution in an amount of 1/100 of that of the emulsion, and the silver ion potential of the emulsion is measured with a detection electrode that is set in a position symmetrical about the stirring center to the potassium bromide solution adding position. As the mixing of the potassium bromide solution proceeds, the silver ion potential changes to reach a constant equilibrium value; the period of time required from the addition of the potassium bromide solution until the silver ion potential reaches 95% of the equilibrium value is defined as the mean mixing time of the mixture system.

In the invention, the dye-adding time Ta is equal to or longer than T.

The upper limit of Ta may be determined practically in consideration of the number of dyes used, a necessary point of time for the addition, and allowable process time.

A solution of the dye may be added through either a single nozzle or a plurality of nozzles, and the position of the solution-pouring tip of the nozzle may be either above or below the surface of the liquid.

The adding rate during the addition time Ta may be constant or smoothly or stepwise varied. Or the solution may be added by instalments.

The emulsion liquid of the invention differs in the liquid characteristics such as gelatin concentration, silver halide content, grain size, viscosity and temperature according to its prescription, so that when a dye is added to the emulsion it is necessary to determine suitable stirring and mixing conditions for the liquid characteristics of the emulsion used.

In this instance, the dye's mixing progress differs depending on whether the fluid behavior of the emulsion is an over-all circulation flow throughout the emulsion liquid or a locally circulated turbulent flow, so that it is necessary to take the liquid flow in a stirring system.

Such a fluid behavior of the emulsion liquid connects with an agitation Reynolds number $Re = \rho d^2 n/\eta$, which correlates with various characteristics such as a motive power for stirring and heat transfer characteristics.

In a mixing vessel used for accelerating and uniformalizing the dye adsorption, it is necessary to select a fluid behavior or agitating condition of the emulsion settled according to the adsorption characteristics of the dye.

On the other hand, the liquid charactersitics of the emulsion and the motive power required for stirring P connect with a power number Np defined by $Np \equiv P/\rho n^3 d^5$, and further, the Np connects with an agitation Reynolds number defined by $Np = A/Re$, wherein A is constant.

When the value of Re exceeds several thousands, a conspicuous turbulent flow appears through the turbulent flow transition region, and a circulation flow extends over the whole liquid, while when Re is less than several hundreds, the part located far from the stirring blade forms a laminar flow, and when Re is still less, only the part close to the blade is fluid.

In the turbulent flow region where Re is sufficiently developed, Np comes to a substantially constant value $Np\,\infty$.

In the invention, the addition of the dye is preferably made under the emulsion's fluid condition with Np put in the $Np\,\infty$ region.

In this region, the rapid and uniform mixing of the dye into the emulsion liquid are attained, and the reproducibility in the characteristics of the emulsion can be obtained when the preparation is repeated in different scales as well as in the same scale. Furthermore, the first step of the homogeneity assurance of the continuous preparation can be made under such conditions.

The foregoing ρ represents an emulsion liquid density, η is a viscosity, n is a number of revolutions of the stirrer blade and d is the diameter thereof.

The invention is further detailed below.

In the invention, the 'completion of the formation of emulsion grains' implies the situation that the whole quantities of a soluble silver salt and a halide necessary to form a given amount of silver halide crystals have been added to an emulsion.

As for the adding order of a silver halide solvent, a dye and a chemical sensitizer, the first is the addition of the silver halide solvent, which is preferably made after the desalting process and before subjecting the silver halide crystal surface to chemical sensitization treatment.

The dye is added after the addition of a silver halide solvent, and the interval between both additions depends on the type of the silver halide solvent used and conditions of temperature, pH and pAg, but is preferably not less than one minute, and more preferably not less than 5 minutes, provided that it is essential to add the silver halide solvent prior to the addition of the spectral sensitizing dye, but the addition of the solvent together with a gold sensitizer may be made after the addition of the dye.

The dye-adding period of time Ta is longer than the mean mixing time, preferably at least one minute and more preferably at least 5 minutes larger than the mean mixing time.

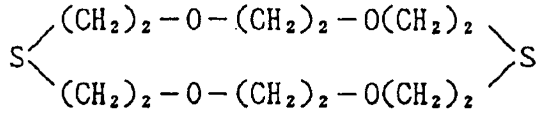
A chemical sensitizer is added simultaneously with or after the silver halide solvent, preferably after the addition of the dye, more preferably 5 minutes after and most preferably 15 minutes after the passage of the dye-adding period of time Ta.

Subsequently, the silver halide solvent added prior to the addition of the dye in this invention is explained. As the solvent there may be used various solvents capable of solving silver halide, but those useful for the invention include (a) the organic thioethers described in U.S. Patent Nos. 3,271,157, 3,531,289 and 3,574,628, JP O.P.I. Nos. 1019/1979, 158917/1979 and 14646/1987, (b) the thiourea derivatives described in JP O.P.I. Nos. 82408/1978, 77737/1980 and 29829/1980, (c) the silver halide solvents having a thiocarbonyl group between an oxygen or sulfur atom and a nitrogen atom described in JP O.P.I. No.144319/1978, (d) the imidazoles described in JP O.P.I. No. 100717/1979, (e) sulfites, (f) thiocyanates, (g) the hydroxyalkyl-substituted ethylenediamines described in JP O.P.I. No. 196228/1982, and (h) the substituted mercaptotetrazoles described in JP O.P.I. No. 202531/1982.

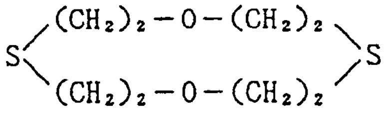
The following are the examples of the above silver halide solvents (a) to (h), but usable silver halide solvents for the invention are not limited thereto.

(a)

A - 1



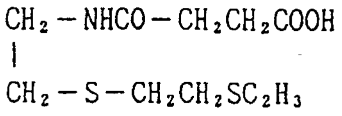
A - 2



A - 3

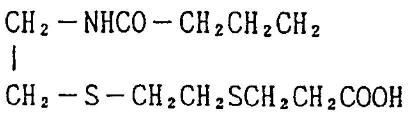
$HO-(CH_2)_2-S-(CH_2)_2-S-(CH_2)_2-OH$

A - 4



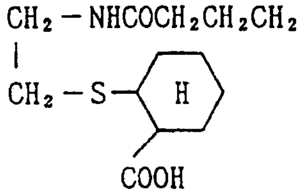
$$\begin{array}{l} CH_2-NHCO-CH_2CH_2COOH \\ | \\ CH_2-S-CH_2CH_2SC_2H_3 \end{array}$$

A - 5

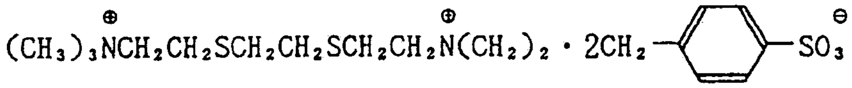


$$\begin{array}{l} CH_2-NHCO-CH_2CH_2CH_2 \\ | \\ CH_2-S-CH_2CH_2SCH_2CH_2COOH \end{array}$$

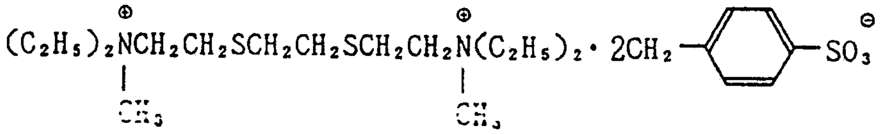
A − 6



A − 7

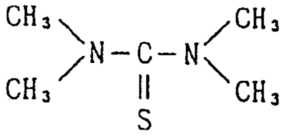


A − 8

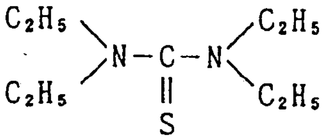


(b)

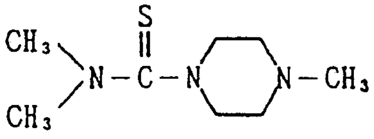
B − 1



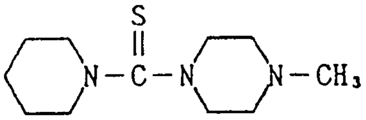
B − 2



B − 3

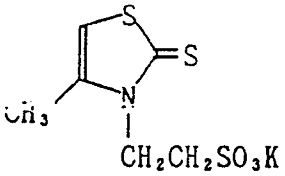


B − 4

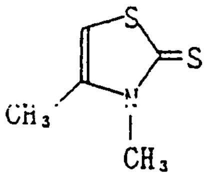


(c)

C − 1

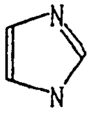


C − 2

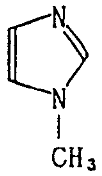


(d)

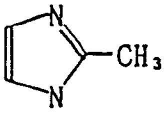
D − 1



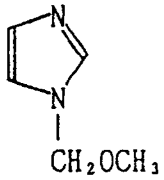
D − 2



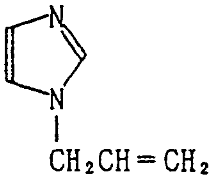
D − 3



D − 4



D − 5



(e)

E − 1

K_2SO_3

(f)

F - 1

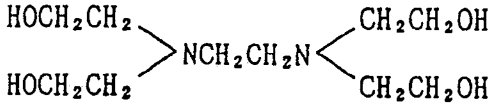
NH_4SCN

F - 2

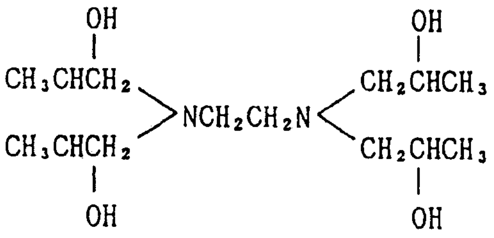
$KSCN$

(g)

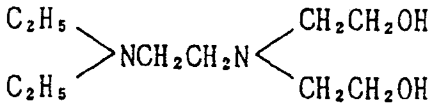
G - 1



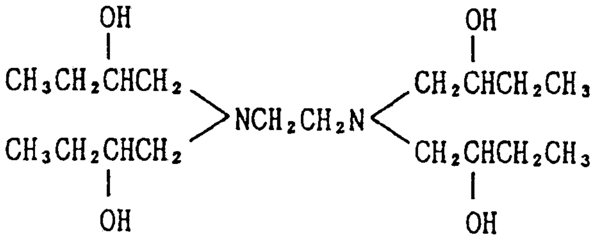
G - 2



G - 3

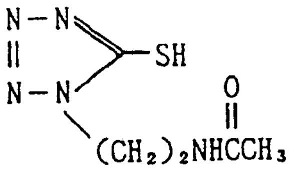


G - 4

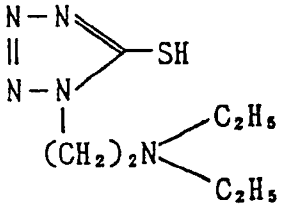


(h)

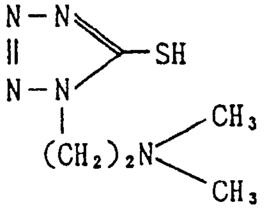
H - 1



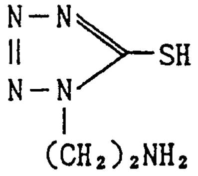
H - 2



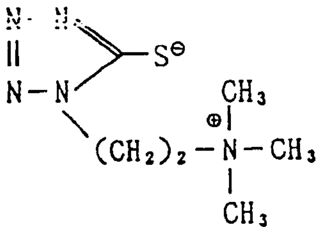
H - 3



H - 4



H - 5



Among these silver halide solvents, thiocyanates, tetra-substituted thioureas and thioethers are preferably used, in which potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate are particularly preferable.

In the preparation method of the invention, the adding amount of the silver halide solvent is determined so as to obtain a desired effect, but preferably 0.0005 to 1.0g, more preferably 0.001 to 0.5g and most preferably 0.005 to 0.2g per mol of silver halide.

Usable examples of the spectral sensitizing dye in the invention include methine dyes, cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly preferred among these dyes are cyanine dyes, mero-cyanine dyes and complex merocyanine dyes. To these dyes may be applied any of those nucleus usually used for cyanine dyes, including pyrroline nucleus, oxazoline nucleus, thiazoline nucleus, pyrrole nucleus, oxazole nucleus, thiazole nucleus, selenazole nucleus, imidazole nucleus, tetrazole nucleus and pyridine nucleus; nuclei formed by fusing an alicyclic hydrocarbon ring with these nuclei; and nuclei formed by fusing an aromatic hydrocarbon ring with these nuclei, such as indolenine nucleus, benzindolenine nucleus, indole nucleus, benzoxazole nucleus, naphthooxazole nucleus, benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, benzimidazole nucleus and quinoline nucleus. These nuclei may be substituted onto a carbon atom. To the merocyanine dyes or complex merocyanine dyes may be applied a ketomethylene structure-having nucleus, e.g., a 5- or 6-member heterocyclic nucleus such as pyrazoline-5-one nucleus, thiohydantoin nucleus, 2-thiooxazolidine-2,4-dione nucleus, thiazolidine-2,4-dione nucleus, rhodanine nucleus and thiobarbituric acid nucleus.

Useful sensitizing dyes include those described in West German Patent No. 929,080, U.S. Patent Nos. 2,231,658 and 4,046,572, British Patent No. 1,242,588, and Japanese Patent Examined Publication Nos. 14030/1969 and 24844/1977.

These sensitizing dyes may be used alone or in combination. Combination of sensitizing dyes is often used for the purpose of supersensitization. Examples of the combination are described in U.S. Patent Nos. 2,688,545 and 4,026,707, British Patent Nos. 1,344,281 and 1,507,803, Japanese Patent Examined Publication Nos. 4936/1968 and 12375/1978, and JP O.P.I. Nos. 110618/1977 and 109925/1977.

A dye which in itself has no spectral sensitization effect or a substance which does substantially not absorb any visible light but shows a supersensitization effect may be contained together with the above sensitizing dye in the emulsion of the invention.

The sensitizing dye, if water-soluble, may be added in the form of a solution of water or an organic solvent such as methanol or ethanol, miscible with water. Further, water-insoluble one may be solubilized by a surfactant and then added in the form of a solution, or else may be dispersed in water and then added in the form of a dispersion.

The adding amount of the spectral sensitizing dye of the invention, although not restricted, is preferably 1×10^{-6} to 1×10^{-4} mol per mol of silver.

As the chemical sensitizer there may be used any arbitrary one; preferably an instable chalcogen compound or a combination of it with an instable metallic compound.

The chalcogen compound is preferably a sulfur compound or selenium compound.

The metallic compound is preferably a compound of gold, platinum, palladium, iridium or rhodium.

Particularly preferred chemical sensitization means is sulfur sensitization or a combined use of sulfur sensitization and gold sensitization, which provides a remarkable sensitization effect. The combined use of sulfur sensitization and gold sensitization is very useful because it provides not only the remarkable sensitization effect but also a fog-restraining effect.

For the above sulfur sensitization there may be used various sulfur sensitizers including thiosulfates, allylthiocarbamidothiourea, allylisothiacyanate, cystine, p-toluenethiosulfonates and rhodanine. Further, the sulfur sensitizers described in U.S. Patent Nos. 1,574,944 and 3,656,955, West German Patent No. 1,433,869, Japanese Patent Examined Publication No. 24937/1981, and JP O.P.I. No. 45016/1980 may also be used. The sulfur sensitizer is added in an amount enough for effectively increasing the sensitivity of the emulsion. The amount considerably varies according to conditions such as pH, temperature and the silver halide grain size used, but is preferably about 10^{-7} to about 10^{-1} mol per mol of silver halide.

The above gold sensitizer may be ordinary one having a gold oxidation number of +1 or +3. Typical examples of the gold sensitizer include chloroauric acid, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate and pyridyl trichlorogold.

The adding amount of the gold sensitizer also differs according to various conditions, but preferably about 10^{-7} mol to about 10^{-1} mol per mol of silver halide.

The chemical ripening of the emulsion of the invention may be carried out at a temperature of preferably 90°C to 20°C, more preferably 80°C to 30°C and most preferably 70°C to 35°C.

The composition of the silver halide grains in the emulsion of the invention is, e.g., AgClBrI, AgCl, AgClBr, AgBr or AgBrI. The average grain diameter of the above silver halide grains is preferably 0.1 to 8.0μm, more preferably 0.2 to 3.0 μm, and most preferably 0.6 to 3.0μm. The inside structure of the silver halide grain is discretionary, but preferably a multi-phase structure as described in JP O.P.I. No. 245151/1986. The silver halide grain may have either a regular crystal form such as a hexahedral, octahedral, dodecahedral or tetradeca-hedral form, or an irregular crystal form such as a spherical or tabular form. The emulsion of the invention may be of either a wide silver halide grain size distribution, a so-called polydispersed emulsion, or a narrow silver halide grain size distribution, a so-called monodispersed emulsion.

The term 'monodispersed' means that, where the distribution width is defined by the AgX grain diameters' variation coefficient:

$$\text{variation coefficient(v)} = \frac{\text{standard deviation}}{\text{average grain diameter}} \times 100(\%),$$

the v of the AgX grain sizes is not more than 20%, and more preferably not more than 15%.

The above average grain diameter is the average of silver halide grain diameters each of which, in the spherical grain, is its diameter or, in the cubic or tabular grain, is the diameter of a circular image equivalent in the area to its projection image, and the average grain diameter $\bar{r}$ is defined by the following equation:

$$\bar{r} = \frac{\Sigma niri}{\Sigma ni}$$

wherein ri is the diameter of each individual grain and ni is the number of grains.

The silver halide grain of the invention may be formed in the presence of a cadmium salt, a zinc salt, a lead salt, an iron salt, a thalium salt, an iridium salt, a rhodium salt, an osmium salt, a ruthenium salt or a complex salt of these metals.

To the silver halide emulsion may be added an antifoggant or a stabilizer. As the binder for the emulsion, gelatin may be advantageously used.

Where the emulsion of the invention is used to produce a light-sensitive material, the emulsion layers and other hydrophilic colloid layers thereof may be hardened and may contain a plasticizer and a water-insoluble or less-soluble synthetic polymer dispersion (latex).

Where the emulsion is used to produce a color photographic light-sensitive material, appropriate couplers are used in the emulsion layers thereof.

Further, there may be used compounds capable of releasing photographically useful fragments such as colored couplers having color correction effects, competing couplers, development accelerators that effect a coupling reaction with the oxidant of a developing agent to thereby accelerate development, bleaching accelerators, developing agents, toning agents, hardeners, fogging agents, antifoggants, chemical sensitizers, spectral sensitizers and desensitizers.

The light-sensitive material may have auxiliary layers such as a filter layer, an antihalation layer and an antiirradiation layer. These layers and/or emulsion layers may contain a dye that may be bleached or dissolved out of the light-sensitive material while its development is in progress.

Further, to the light-sensitive material may be added a formalin scavenger, a matting agent, a lubricant, an image stabilizer, a surfactant, a development accelerator, a development retarder and a bleaching accelerator.

Materials useful as the support of the light-sensitive material include polyethylene-laminated paper, polyethylene terephthalate film, baryta paper and cellulose triacetate film.

The formation of a dye image with use of a light-sensitive material containing the emulsion of the invention is carried out by subjecting the light-sensitive material to imagewise exposure and then to generally known photographic processing.

EXAMPLES

Example 1

The following eight different solutions were used to prepare a silver iodobromide emulsion EM-1 containing core/shell type grains having an average grain diameter of 0.81μm and each having AgI contents of, in the order from the innermost part thereof, 15 mol%, 5 mol% and 3 mol%, averaging 7.16 mol%.

Solution A-1

Osein gelatin	10.8 g
Propanone, 10% ethanol solution	20.0 ml
4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene (hereinafter called TAI)	200 mg
56% acetic acid aqueous solution	32.5 ml
28% ammonia aqueous solution	58.7 ml
Seed emulsion (silver iodobromide containing 2 mol% AgI, having an average grain diameter of 0.33μm and a variation coefficient of 26%) An amount equivalent to Ag	0.4673 mol

Distilled water to make 4,000 ml.

An amount equivalent to Ag 0.4673 mol Distilled water to make 4,000 ml.

Solution B-1

Osein gelatin	40 g
Potassium bromide	404.6 g
Potassium iodide	99.6 g
TAI	1224 mg

Distilled water to make 1,300 ml

Solution C-1

Osein gelatin	20 g
Potassium bromide	791.4 g
Potassium iodide	58.1 g
TAI	2142 mg

Distilled water to make 1,700 ml

Solution D-1

Osein gelatin	15 g
Potassium bromide	606.0 g
Potassium iodide	26.15g
TAI	1605 mg

Distilled water to make 800 ml

Solution E-1

Silver nitrate	310.4 g
28% ammonia water	253 ml

Distilled water to make 1,827 ml

Solution F-1

Silver nitrate	803.3 g
28% ammonia water	655 ml

Distilled water to make 1,351 ml

Solution G-1

20% potassium bromide solution	An amount necessary to adjust pAg

Solution H-1

56% acetic acid solution	An amount necessary to adjust pH

Solution E-1 and Solution B-1 were added at 40°C by a double-jet process to Solution A-1, using the same mixing stirrer as described in JP O.P.I. Nos. 92523/1982 and 92524/1982, and upon completion of the addition of Solution B-1, Solutions C-1 and F-1 were added, and further Solution D-1 was added upon completion of the addition of Solution C-1. The controlled values of pAg and pH, and the added rates of Solutions E-1, B-1, C-1, D-1 and F-1 are as shown in Table-1.

The controls of pAg and pH were performed by changing the flows of Solutions G-1 and H-1 with a flow-variable roller tube pump.

Table-1 Grain growling conditions

Time (min)	pH	pAg	Added rate of solution (ml/min)				
			Sol.B-1	Sol.C-1	Sol.D-1	Sol.E-1	Sol.F-1
0	9.00	8.40	-	-	-	-	-
6.58	9.00	8.40	81.5	-	-	82.8	-
10.13	9.00	8.40	100.1	-	-	101.7	-
15.30	9.00	8.40	123.1	-	-	125.7	-
21.62	9.00	8.40	140.5	-	-	145.2	-
22.07	9.00	8.40	-	44.7	-	-	42.8
24.06	8.87	8.85	-	59.2	-	-	52.0
26.94	8.64	9.63	-	197.4	-	-	98.2
27.11	8.62	9.71	-	119.9	-	-	119.3
29.97	8.22	9.71	-	110.4	-	-	109.9
32.03	7.97	9.71	-	-	90.1	-	89.7
34.92	7.70	9.71	-	-	68.1	-	67.8
37.30	7.50	9.71	-	-	68.1	-	67.8

Next, the emulsion was washed for desalting in the usual manner, 197.4g of osein gelatin were dispersed therein, and then distilled water was added to make the whole amount 3,000 ml. In the meantime, pH and pAg were adjusted at 40°C to 6.00 and 7.7, respectively.

Subsequently, Comparative emulsions EM-2, EM-3 and EM-4, and Emulsions EM-5 and EM-6 of the invention were prepared in accordance with the following procedures.

Preparation of Comparative emulsion EM-2

To Emulsion EM-1 in an amount equivalent to 1 mol of silver halide, which was stirred at 50°C for a mean mixing time of about 15 seconds, were added in a moment (2 seconds or less) 68 ml of the following spectral sensitizing dye solution, added 30 minutes later 6.5×10^{-6} mol of sodium thiosulfate, and further added 2 minutes later 2×10^{-6} mol of chloroauric acid and 6.0×10^{-4} mol of ammonium thiocyanate, and then the whole quantity was made 700 ml per mol of silver halide, and subjected to chemical ripening for a prescribed time.

To the emulsion was added 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene after a period of time of the chemical ripening enough to make the sensitivity-fog relation optimal, and at the same time its temperature was cooled to 40°C for stopping the chemical ripening. The optimal sensitivity was obtained in 130 minutes after the addition of the sodium thiosulfate. Further, a dispersion of the following magenta coupler M-1 was added, whereby Emulsion EM-2 was prepared. After that, a part of the emulsion was taken and its whole quantity was made 4000 ml per mol of silver halide. The emulsion, with continued stirring at 40°C, was measured for its reflection spectrum to determine the aging changes in the sensitizing dye adsorption condition.

To the other part of the emulsion was added a hardener, and it was coated on a cellulose triacetate film support and then dried, whereby a coated sample No.1 was obtained.

Preparation of Comparative emulsion EM-3

Emulsion EM-3 was prepared and coated in the same manner as in Emulsion EM-2 except that 5.5×10^{-4} mol of ammonium thiocyanate was added 15 minutes before the addition of the sensitizing dye solution, and the amount of the ammonium thiocyanate added simultaneously with the chloroauric acid was changed to 0.5×10^{-4} mol, whereby a coated sample No.2 was obtained.

Preparation of Comparative emulsion EM-4

Emulsion EM-4 was prepared and coated in the same manner as in Emulsion EM-2 except that the sensitizing dye solution was added, spending 20 minutes at a constant flow rate, and sodium thiosulfate was added 30 minutes after the addition of the dye solution, whereby a coated sample No.3 was obtained.

Preparation of Sample EM-5 of the invention

Emulsion EM-5 was prepared and coated in the same manner as in Emulsion EM-2 except that to Emulsion EM-1 was added sodium thiosulfate, and 2 minutes later added chloroauric acid and ammonium thiocyanate, and further, 10 minutes later added the sensitizing dye solution at a constant flow rate, spending 20 minutes, whereby a coated sample No.4 was obtained.

Preparation of Emulsion EM-6 of the invention

Emulsion EM-6 was prepared and coated in the same manner as in Emulsion EM-4 except that 5.5×10^{-4} mol of ammonium thiocyanate was added 15 minutes before the addition of the sensitizing dye solution, and the amount of the ammonium thiocyanate added simultaneously with the chloroauric acid was changed to 0.5×10^{-4} mol, whereby a coated sample No.5 was obtained.

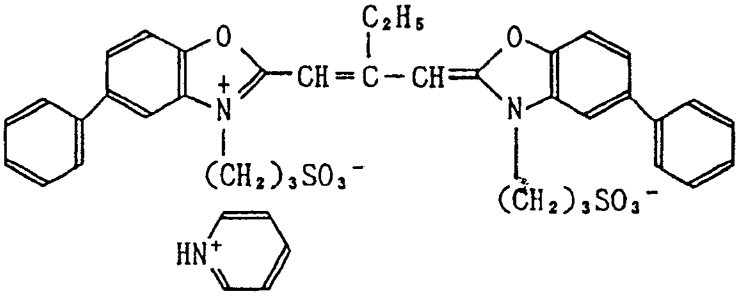
As an index for showing the stability of the emulsion in the process of its preparation, the changes, during the period of from the stop of the chemical ripening under the dye adsorption condition, in the reflection spectrum of the emulsion in the absorption band of dyes when its whole amount was made 4000 ml per mol of silver and its stirring was continued at 40°C were evaluated. The measurement was made with a spectrophotometer UV-2100 equipped with an integrating sphere, manufactured by Shimazu Seisakusho, Ltd.

The attenuation rate of the absorbance after 2 hours of stirring to the absorbance at a wavelength of 560 nm of each emulsion immediately after its preparation is shown in Table-2. From the table it is understood that the emulsions of the invention show smaller attenuation rates and more excellent stabilities in the emulsion preparation process than the comparative emulsions.

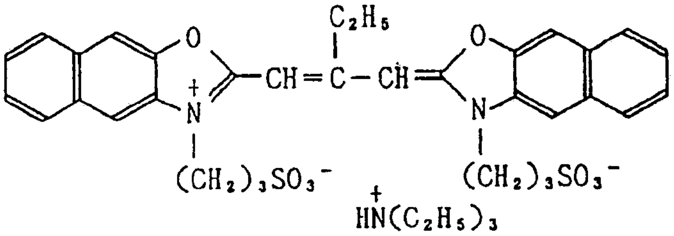
Sensitizing dye solution

Sensitizing dye S-1	2.7×10^{-4} mol
″ S-2	1.9×10^{-4} mol
$HCF_2-CF_2-CH_2OH$	20 ml
CH_3OH	80 ml

S-1



S-2



Coated samples No.1 to No.5 were used to evaluate the sensitivities and preservabilities of Emulsions EM-2 to EM-6.

Each coated sample was exposed through a green filter, and then processed according to the following steps:

Processing step (38°C)	
Color developing	2 min. 50 sec.
Bleaching	6 min. 30 sec.
Washing	3 min. 15 sec.
Fixing	6 min. 30 sec.
Washing	3 min. 15 sec.
Stabilizing	1 min. 30 sec.
Drying	

The compositions of the processing solutions used are as follows:

Color developer

4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.75g
Sodium sulfite anhydride	4.25g
Hydroxylamine 1/2 sulfate	2.0 g
Potassium carbonate anhydride	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate, monohydrate	2.5 g
Potassium hydroxide	1.0 g

Water to make 1 liter

Bleaching bath

Ferric-ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml

Water to make 1 liter.

Adjust pH to 6.0 with ammonia water

Fixer bath

Ammonium thiosulfate	175.0 g
Sodium sulfite anhydride	8.5 g
Sodium metasulfite	2.3 g

Water to make 1 liter.

Adjust pH to 6.0 with acetic acid.

Stabilizer bath

Formalin (37% aqueous solution)	1.5 ml
Koniducks (product of KONICA Corp.)	7.5 ml

Water to make 1 liter.

The sensitivity is the receprocal of an exposure amount necessary to give a density of fog plus 0.3. The sensitivity of each sample is shown with a value relative to that of Sample No.1 set at 100 in Table-2.

As for the preservability, the sensitivity and the absorbance at a wavelength of 560 nm of each coated sample that was allowed to stand under 40°C/80%RH conditions for 7 days were compared with those of the same sample immediately after its preparation, and the differenes between them were evaluated. The results are shown in Table 2.

As is apparent from Table 2, Emulsions EM-5 and EM-6 of the invention and the light-sensitive materials containing the emulsions are excellent in the dye adsorbability as well as in the sensitivity. In addition, EM-6 has more excellent characteristics than EM-5, and the addition of the sensitizing dye prior to the addition of the chemical sensitizer provides better results in respect of giving a higher sensitivity.

M-1

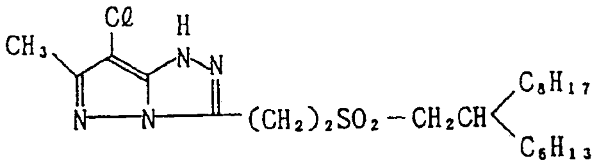


Table-2

Sample	Attenuation rate*¹ of absorbance of EM at 560nm	Attenuation rate*² of absorbance of coated sample at 560nm	Sensitivity of sample right after coating	Sensitivity after aging 7 days at 40°C/80%RH
EM-2	0.18	-	-	-
EM-3	0.08	-	-	-
EM-4	0.10	-	-	-
EM-5 (Inv.)	0.05	-	-	-
EM-6 (Inv.)	0.04	-	-	-
No.1	-	0.26	100	83
No.2	-	0.22	109	89
No.3	-	0.17	105	88
No.4 (Inv.)	-	0.14	100	101
No.5 (Inv.)	-	0.14	117	114

*¹: Defined by $1 - \frac{A^2}{A^1}$, wherein A^1 is the absorbance one minute after adding a coupler dispersion and adjusting the whole amount, and A^2 is the absorbance after stirring at 40°C for 2 hours.

*²: Defined by $1 - \frac{B^2}{B^1}$, wherein B^1 is the absorbance immediately after preparing the coated sample, and B^2 is the absorbance of the sample aged for 7 days at 40°C/80%RH.

Example 2

Multilayer color light-sensitive material samples No.6 (comparative), No.7 (comparative) and No.8 (invention) were each prepared by coating the following layers on a subbed triacetyl cellulose film support, wherein the layer 8 is a high-speed green-sensitive silver halide emulsion layer, to which were applied Emulsion EM-2 of Example 1 for Sample No.6, Emulsion EM-3 for Sample No.7 and Emulsion EM-6 for Sample No.8.

Regarding the coated amounts of components, the following prescriptions show amounts in g/m^2 equivalent to silver for silver halide and colloidal silver, in g/m^2 for additives and gelatin, and in molar amounts per mol of silver halide inside the same layer for sensitizing dyes, couplers and DIR compounds.

The emulsion contained in each color-sensitive emulsion layer was optimally sensitized with sodium thiosulfate and chloroauric acid.

Layer 1: Antihalation layer HC-1

Black colloidal silver	0.20
UV absorbing agent UV-1	0.20
High-boiling solvent Oil-1	0.20
Gelatin	1.5

Layer 2: Intermediate layer I.L-1

UV absorbing agent UV-1	0.01
High-boiling solvent Oil-1	0.01
Gelatin	1.5

Layer 3: Low-speed red-sensitive emulsion layer RL

Silver iodobromide emulsion (the following emulsion A)	0.9
Silver iodobromide emulsion (the following emulsion B)	0.6
Sensitizing dye III	$2.5\text{x}10^{-4}$
Sensitizing dye IV	$2.5\text{x}10^{-4}$
Sensitizing dye V	$0.5\text{x}10^{-4}$
Cyan coupler C-1	1.0
Cyan coupler C-2	0.05
Colored cyan coupler CC-1	0.05
DIR compound D-1	0.002
High-boiling solvent Oil-1	0.5
Gelatin	1.5

Layer 4: High-speed red-sensitive emulsion layer RH

Silver iodobromide emulsion EM-1	2.0
Sensitizing dye III	2.0×10^{-4}
Sensitizing dye IV	2.0×10^{-4}
Sensitizing dye V	0.1×10^{-4}
Cyan coupler C-2	0.015
Cyan coupler C-3	0.25
Colored cyan coupler CC-1	0.015
DIR compound D-2	0.05
High-boiling solvent Oil-1	0.3
Gelatin	1.5

Layer 5: Intermediate layer I.L-2

Gelatin	0.5

Layer 6: Low-speed green-sensitive emulsion layer GL

Silver iodobromide emulsion (the following emulsion A)	1.0
Sensitizing dye VI	5×10^{-4}
Sensitizing dye VII	1×10^{-4}
Magenta coupler M-2	0.5
Colored magenta coupler CM-1	0.01
DIR compound D-3	0.02
DSR compound D-4	0.02
High-boiling solvent Oil-2	0.4
Gelatin	1.0

Layer 7: Intermediate layer I.L-3

Gelatin	0.8

Layer 8: High-speed green-sensitive emulsion layer GH

Silver iodobromide emulsion	1.8
Magenta coupler M-3	0.05
Magenta coupler M-4	0.15
Colored magenta coupler CM-2	0.05
DIR compound D-3	0.01
High-boiling solvent Oil-3	0.5
Gelatin	1.0

Layer 9: Yellow filter layer YC

Yellow colloidal silver	0.1
Antistain agent SC-1	0.1
High-boiling solvent Oil-3	0.1
Gelatin	0.8

Layer 10: Low-speed blue-sensitive emulsion layer BL

Silver iodobromide emulsion (the following emulsion A)	0.25
Silver iodobromide emulsion (the following emulsion B)	0.25
Sensitizing dye VII	7×10^{-4}
Yellow coupler Y-1	0.5
Yellow coupler Y-2	0.1
DIR compound D-2	0.01
High-boiling solvent Oil-3	0.3
Gelatin	1.0

Layer 11: High-speed blue-sensitive emulsion layer BH

Silver iodobromide emulsion (the following emulsion C)	0.4
Silver iodobromide emulsion (the following emulsion A)	0.3
Sensitizing dye IX	1×10^{-4}
Sensitizing dye VII	3×10^{-4}
Yellow coupler Y-1	0.3
Yellow coupler Y-2	0.05
High-boiling solvent Oil-3	0.1
Gelatin	1.1

Layer 12: First protective layer PRO-1

Fine-grained silver iodobromide emulsion average grain size: 0.08μm, AgI: 2 mol%	0.4
UV-absorbing agent UV-1	0.1
UV-absorbing agent UV-2	0.05
High-boiling solvent Oil-1	0.1
High-boiling solvent Oil-4	0.1
Formalin scavenger HS-1	0.5
Formalin scavenger HS-2	0.2
Gelatin	1.0

Layer 13: Second protective layer PRO-2

Surfactant Su-1	0.005
Alkali-soluble matting agent (average particle size: 3μm)	0.1
Gelatin	0.6

Emulsion A:

Monodispersed low surface silver iodide-content-type emulsion having an average grain size of 0.38 μm and an average silver iodobromide content of 8. 0 mol%.

Emulsion B:

Monodispersed uniform-composition emulsion having an average grain size of 0.27μm and an average silver iodide content of 2.0 mol%.

Emulsion C:

Monodispersed low surface silver iodide-content-type emulsion having an average grain size of 0.80 μm and an average silver iodide content of 9.0 mol %.

To each of the above layers were added coating aid Su-2, dispersing aid Su-3, hardeners H-1 and H-2, stabilizer Stab-1 and antifoggant AF-1 in addition to the above components.

A part of each multilayer light-sensitive material sample prepared above was aged under 23°C/55%RH conditions for 7 days and the other part of the same was aged under 40°C/80%RH for 7 days, and the sensitivities of both parts were compared for evaluation. The evaluation was carried out in accordance with the method in Example 1. The results are shown in Table-3, wherein the sensitivity is indicated with a value relative to the sensitivity of Sample No.6, aged under 23°C/55%RH conditions, set at 100.

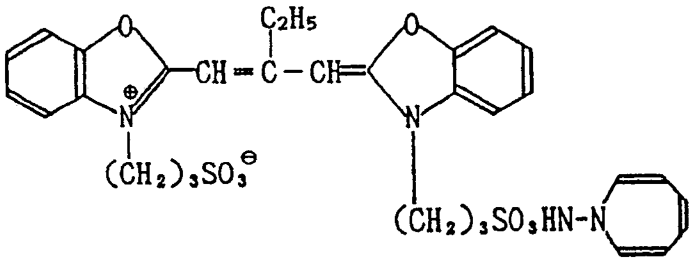
Further, the sample aged under 50°C/80%RH conditions for 7 days was exposed and processed in the manner shown in Example 1, and then the processed sample was measured for the formed cyan color density of an area thereof subjected to an exposure necessary to give a density of fog plus 0.6. The results are shown in Table-3.

Table-3

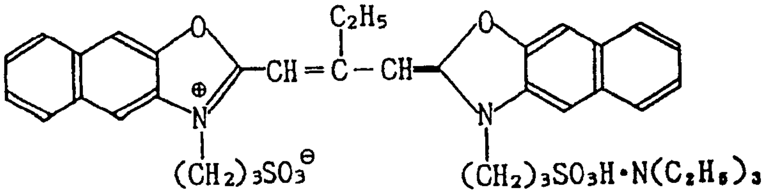
Sample	Sensitivity aged at 23°C/55%RH	Sensitivity aged at 40°C/80%RH	Cyan density aged at 50°C/80%RH
No.6	100	74	0.10
No.7	103	84	0.07
No.8 (Inv.)	109	100	0.02

The light-sensitive material containing the emulsion of the invention shows little fall of the sensitivity and little color impurity that is apparently attributable to the adsorbed dye's desorption and diffusion into other color-sensitive layers.

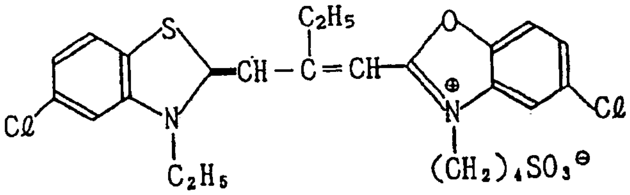
Sensitizind dye I



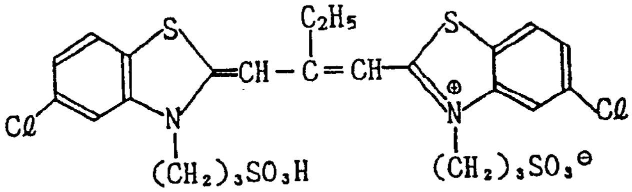
Sensitizing dye II



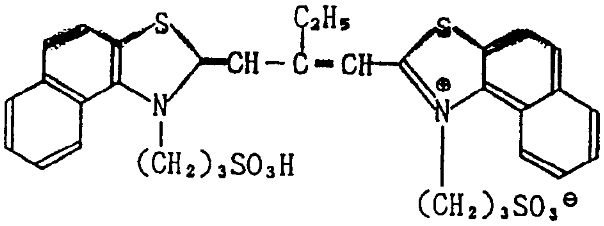
Sensitizing dye III



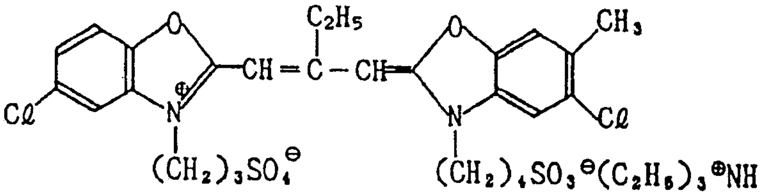
Sensitizing dye IV



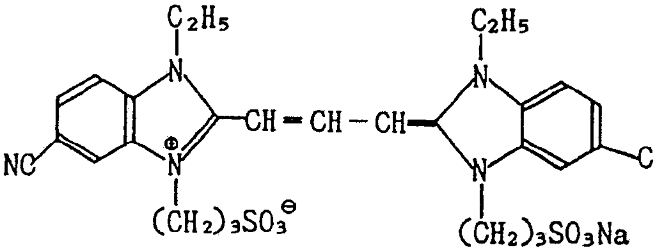
Sensitizing dye V



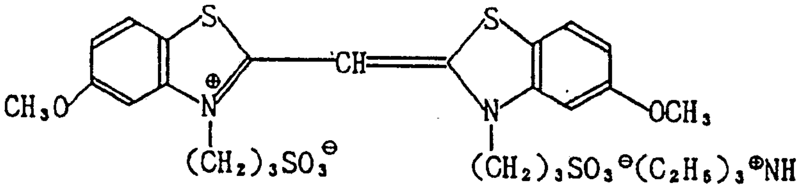
Sensitizing dye VI



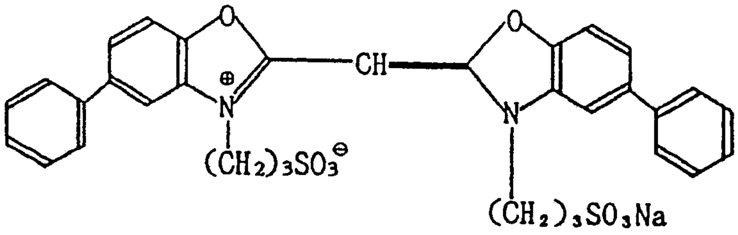
Sensitizing dye VII



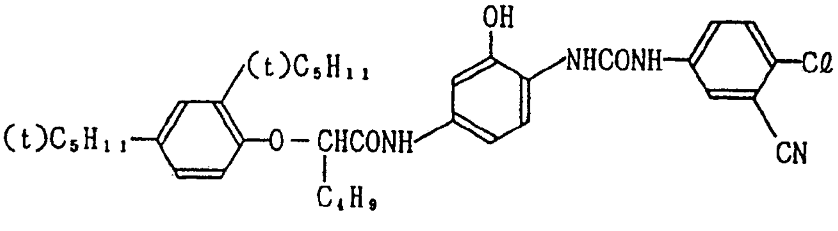
Sensitizing dye VIII



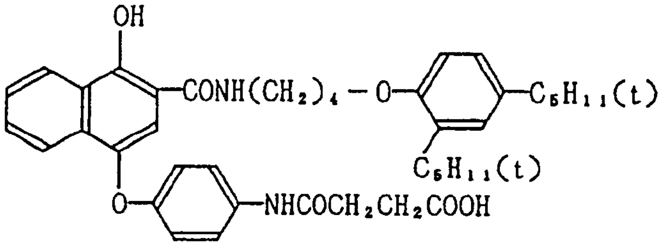
Sensitizing dye IX



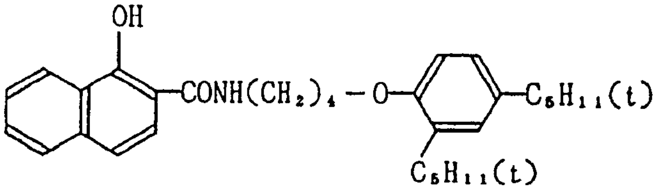
C - 1



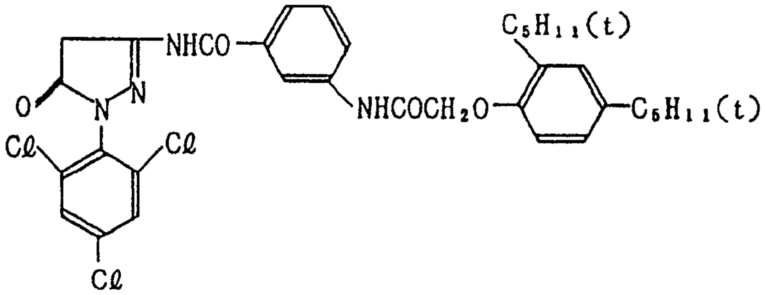
C － 2



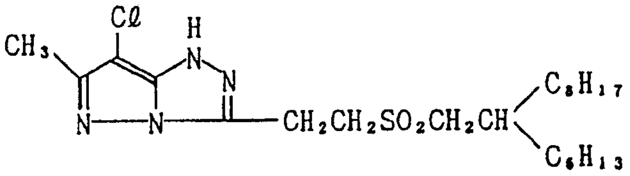
C － 3



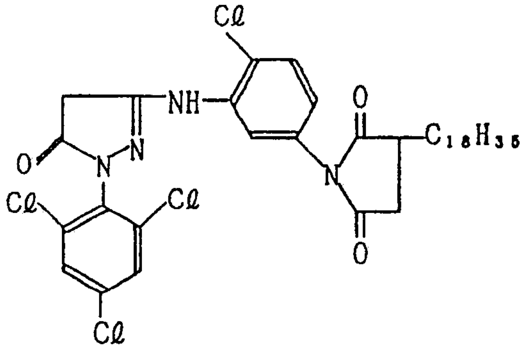
M － 1



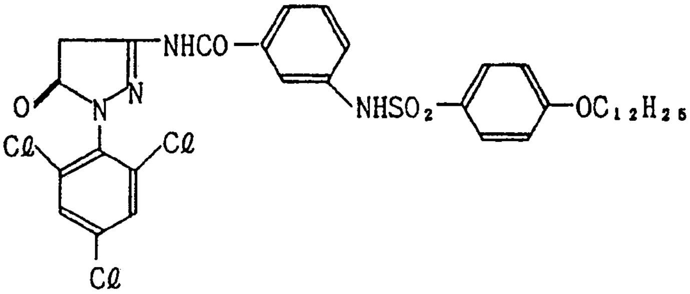
M － 2



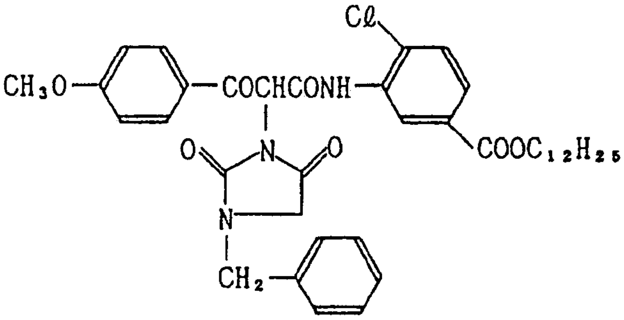
M - 3


Cℓ
NH
O
N
N
C₁₈H₃₅
O
Cℓ
Cℓ
N
O
Cℓ

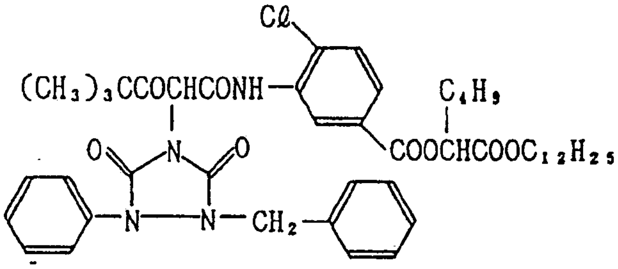
M - 4


NHCO
O
N
N
NHSO₂
OC₁₂H₂₅
Cℓ
Cℓ
Cℓ

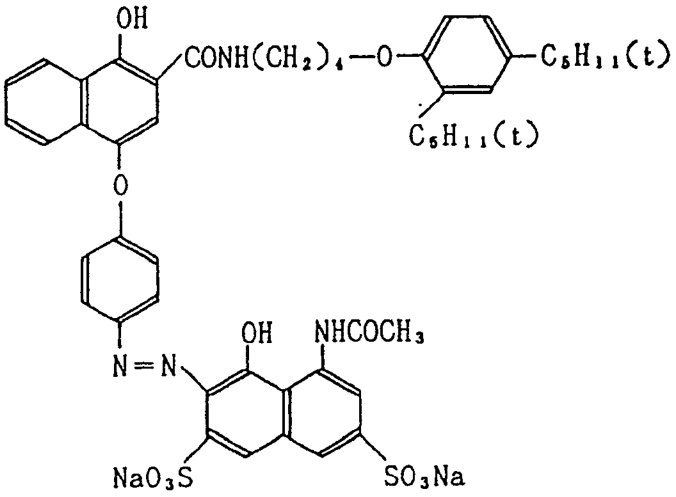
Y - 1


Cℓ
CH₃O
COCHCONH
O
N
O
COOC₁₂H₂₅
N
CH₂

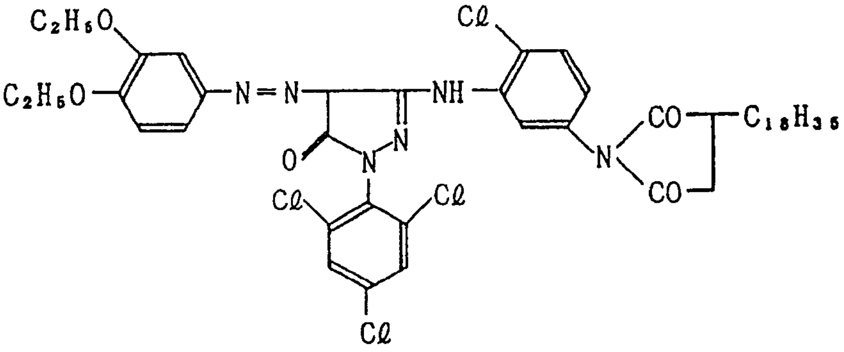
Y - 2


Cℓ
(CH₃)₃CCOCHCONH
C₄H₉
O
N
O
COOCHCOOC₁₂H₂₅
N
N
CH₂

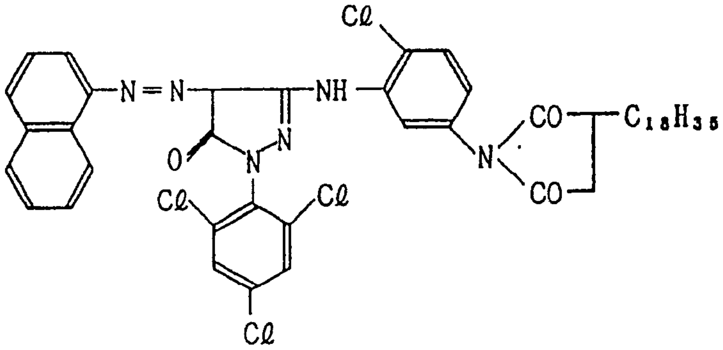
CC－ 1



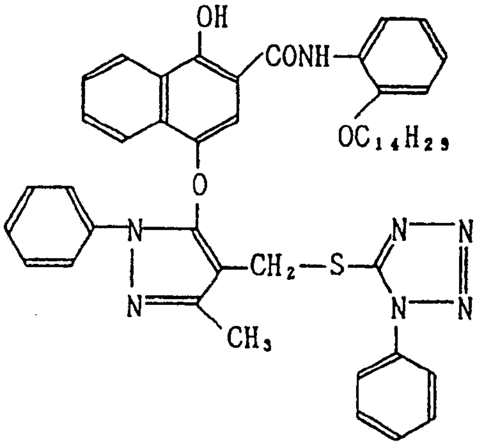
CM－ 1



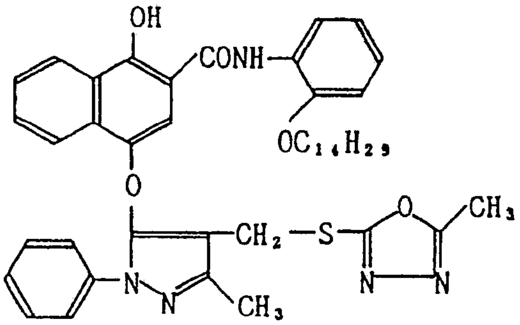
CM－ 2



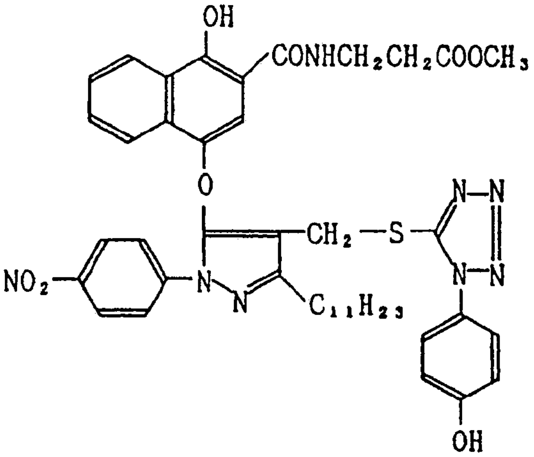
D - 1


OH
CONH
OC14H29
O
N
N
CH2—S
N
N
N
N
CH3

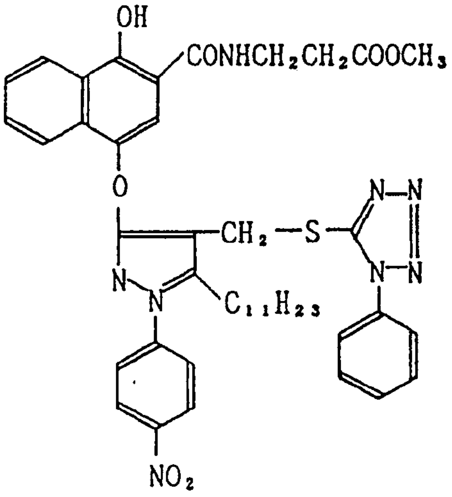
D - 2


OH
CONH
OC14H29
O
CH2—S
O
CH3
N
N
CH3
N
N

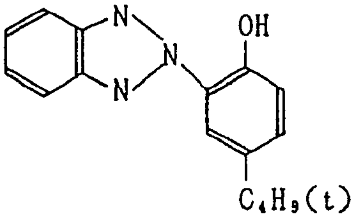
D - 3


OH
CONHCH2CH2COOCH3
O
CH2—S
N—N
NO2
N
N
C11H23
N—N
OH

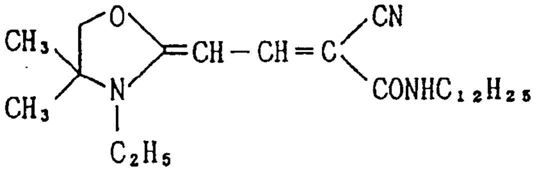
D－4



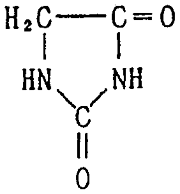
UV－ 1



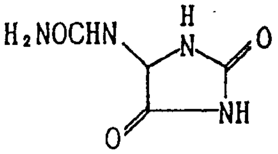
UV－ 2



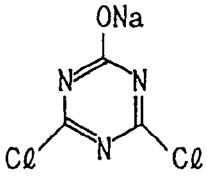
HS－ 1



HS－ 2



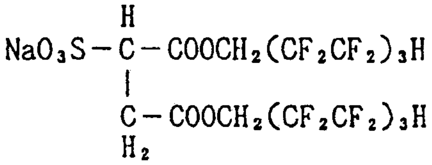
H－1



H－2

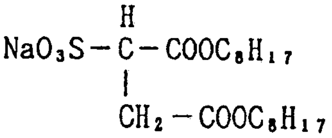
$[(CH_2=CHSO_2CH_2)_3CCH_2SO_2(CH_2)_2]_2N(CH_2)_2SO_3K$

Su－1



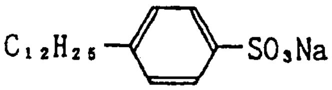
$$NaO_3S-\overset{H}{C}(-COOCH_2(CF_2CF_2)_3H)-\underset{H_2}{C}-COOCH_2(CF_2CF_2)_3H$$

Su－2

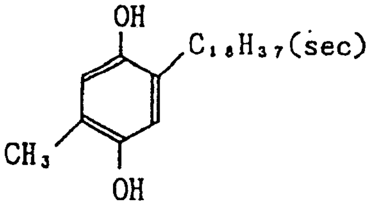


$$NaO_3S-\overset{H}{C}(-COOC_8H_{17})-CH_2-COOC_8H_{17}$$

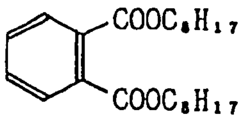
Su－3



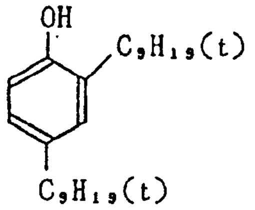
SC－1



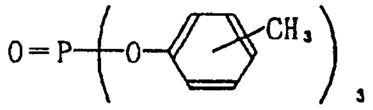
Oiℓ－1



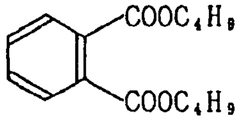
Oiℓ-2



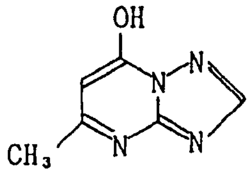
Oiℓ-3



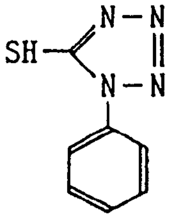
Oiℓ-4



Stab-1



AF-1



Claims

1. A process for preparing a silver halide photographic emulsion, which comprises:
   forming silver halide grains to produce a silver halide emulsion;
   adding a silver halide solvent to said silver halide emulsion after completion of the formation of the silver halide grains; and
   adding a spectral sensitizing dye to said silver halide emulsion containing said silver halide solvent over a period of time which is equal to or longer than the mean mixing time of a mixing system in which said silver halide emulsion is mixed with said spectral sensitizing dye.

2. A process according to claim 1, which further comprises desalting said silver halide emulsion between forming the silver halide grains and adding the silver halide solvent.

3. A process according to claim 1 or 2, which further comprises adding a chemical sensitizing agent to said silver halide emulsion after completion of adding the spectral sensitizing dye.

4. A process according to claim 3, wherein the chemical sensitizing agent is added not less than 5 minutes after completion of adding the spectral sensitizing dye.

5. A process according to any one of the preceding claims, wherein said silver halide solvent is a thiocyanate, tetra-substituted thiourea or organic thioether.

6. A process according to claim 5, wherein said silver halide solvent is potassium thiocyanate, sodium thiocyanate or ammonium thiocyanate.

7. A process according to any one of the preceding claims, wherein said silver halide solvent is added in an amount of from 0.005 g to 0.2 g per mole of silver contained in said silver halide emulsion.

8. A process according to any one of the preceding claims, wherein said spectral sensitizing dye is added to said silver halide emulsion over a period of time of at least one minute longer than said mean mixing time.

9. A process for preparing a silver halide photographic emulsion, which comprises:
   forming silver halide grains each substantially consisting of silver iodobromide and having a core/shell structure comprising at least two phases, the internal phase of which has a silver iodide content higher than that of the external phase, to produce a silver halide emulsion;
   adding a thiocyanate to said silver halide emulsion after completion of the formation of the silver halide grains;
   adding a spectral sensitizing dye to said silver halide emulsion containing said thiocyanate over a period of time which is at least five minutes longer than the mean mixing time of a mixing system in which said silver halide emulsion is mixed with said spectral sensitizing dye; and
   adding a chemical sensitizing agent to said silver halide emulsion after adding the spectral sensitizer.

10. A process according to any one of the preceding claims, which further comprises coating said emulsion on a support.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 3810

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 120 (P-846)(3468) 24 March 1989, & JP-A-63 292126 (KONICA CORPORATION) 29 November 1988, * the whole document *	1	G03C1/005
A		2-10	

X	PATENT ABSTRACTS OF JAPAN vol. 14, no. 35 (P-994)(3978) 23 January 1990, & JP-A-01 271743 (FUJI PHOTO FILM COMPANY LTD.) 30 October 1989, * the whole document *	1, 5-7	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 AUGUST 1991	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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