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(54) **Method of preserving composition for silver halide photographic light-sensitive material.**

(57) A method for preserving a composition for silver halide photographic light-sensitive material is disclosed. In the method, the composition is preserved in a temperature within the range of from 0 °C to the freezing point of the composition. The method is preferably applied for preserving a silver halide photographic emulsion, a oil-in-water type dispersion such as a oil-soluble coupler dispersion or a coating solution of the emulsion prepared to be coated.

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METHOD OF PRESERVING COMPOSITION FOR SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a method of preserving the composition for silver halide photographic light-sensitive material, and more particularly to the method of preserving a silver halide emulsion, an oil-in-water type dispersion or an emulsion coating solution of which properties are prepared for coating to make an emulsion layer of light-sensitive material.

BACKGROUND OF THE INVENTION

A silver halide photographic light-sensitive material (hereinafter referred to light-sensitive material) is usually produced by the following steps.

1. The first ripening:

Formation of silver halide emulsion (hereinafter referred to emulsion)

2. Desalting of the emulsion

3. The second ripening:

Chemical sensitization of the emulsion

The emulsion essentially consists of silver halide grains, a binder and water at the steps of 1 to 3.

4. Preparation of coating solution of the emulsion:

Coating solution of the emulsion (hereinafter referred to coating solution) is prepared in such a manner that: predetermined various additives are added to the chemically sensitized silver halide emulsion in order to provide photographic properties; and the concentration and viscosity of the solution are adjusted to necessary values for coating. When an oil soluble additive such as a color forming coupler or a development inhibitor releasing compound (DIR) is added to the solution, the oil soluble additive is dissolved in a high boiling solvent and dispersed in a hydrophilic colloid solution; and thus obtained oil-in-water type dispersion is added to the coating solution.

5. Coating and drying of the coating solution (hereinafter referred to suspension)

Prepared coating solution is coated on a support and dried.

In the industrial production of photosensitive materials, from the viewpoint of procedure and quality control, an emulsion needs to be preserved for a predetermined period of time during the above-described manufacturing processes. An emulsion may be preserved at the stage after desalting, after the second ripening, or after the preparation of a coating solution. The preservation of an emulsion at the stage after the preparation of a coating solution is advantageous in that: (1) it is possible to inspect the coating solution itself and the photographic characteristics of the coating solution can be checked before coating; (2) only an operation for melting the emulsion must be conducted at the stage of coating, so that deterioration of the photographic characteristics of the emulsion due to standing for prolonged time before coating can be avoided; and (3) a large amount of uniform emulsion can be obtained by blending the preserved emulsions.

Since the photosensitive material have been produced on a large scale and the coating speed has been increased, it is desirable to stably preserve the coating solution as well as the emulsion and dispersion into practical use.

However, from the viewpoint of stability of the emulsion which has been preserved, many problems are caused. When a composition such as an emulsion, dispersion or a coating solution is preserved, it is usually refrigerated in order to prevent the chemical reaction and denaturation by bacteria which are caused during preservation. In order to prevent breeding of bacteria and decrease in photographic sensitivity, the lower the temperature is, the higher the effect is. However, the above-described composition freezes at a temperature of about -6°C and water is separated in a form of ice from the composition. When it is defrosted, the characteristics of the composition can not be recovered in many cases. In the case of a

photographic emulsion and coating solution, fogging is increased and the viscosity is varied due to deterioration of gelatin. In the case of a dispersion, pinhole-like spots are given and the viscosity of the dispersion is varied. When a coating solution containing silver halide grains and a dispersion of high boiling solvent, in which an oil soluble additive such as a coupler is dissolved, is refrigerated for preservation, these
 5 problems are simultaneously raised. Therefore, it is difficult to preserve an emulsion after it has been made into a coating solution.

SUMMARY OF THE INVENTION

10 It is a primary object of the invention to provide a method of preserving compositions for silver halide photographic light-sensitive material in which photographic and physical properties of the composition are preserved; and further the coating solution can be simply and quickly prepared so that reliability and productivity of the coating solution can be improved.

The above-described object of the present invention can be accomplished by the method of preserving
 15 the above-described composition at a temperature within the range of from 0 °C to the freezing point, and further the embodiment of the present invention is effective in the case where the above-described component is an oil-drop-in-water type of dispersion, a photographic light-sensitive silver halide emulsion essentially consisting of silver halide grains, a binder and water and a coating solution of an silver halide emulsion of which photographic characteristics and physical properties are prepared so that it can be
 20 coated. The coating solution usually contains various addenda.

DETAILED DESCRIPTION OF THE INVENTION

In the dispersion relating to the present invention, oil soluble additives which are added to a high boiling
 25 solvent are not limited to specific ones. The following are included in the oil soluble additives: various kinds of color-forming couplers; DIR couplers; UV absorbents; and color contamination preventing agents. Oil soluble additives are dissolved in a high boiling solvent and dispersed in a hydrophilic colloid water solution so that it is added to an emulsion in the form of a dispersion. In this case, various low-boiling solvents may be used together with the high-boiling solvent so that the oil soluble additives can be dissolved easily or the
 30 high-boiling solvent solution can be dispersed easily. The high-boiling solvent is not limited to a specific one. Various high-boiling solvents which are known to be used for this object, such as dibutyl phthalate, dioctyl phthalate and tricresyl phosphate, may be used. The hydrophilic colloid which is used for dispersing a high boiling solvent solution includes gelatin, gelatin derivatives, and various kinds of water-soluble polymers. It is preferable to use gelatin. The high-boiling solvent solution is dispersed in the hydrophilic
 35 colloid solution by a dispersing apparatus such as a homogenizer and an ultrasonic dispersing machine. The high boiling solvent solution is preferably dispersed under the presence of a surface active agent.

In the present invention, silver halide usually used for the silver halide emulsion, such as silver bromide, silver chloride, silver iodobromide, silver chlorobromide and silver chloriodobromide, can be used. In the silver halide emulsion used in the present invention, widely known methods can be applied to the processes
 40 of formation of silver halide particles, desalting and chemical ripening. The chemically ripened emulsion can be spectrally sensitized by a widely known sensitizing dye, and other than the above-described high-boiling solvent dispersion, various kinds of widely known additives for photographic emulsion use such as a stabilizer, a sensitizer, an fog inhibitor, and an antistain agent can be optionally added.

The compositions relating to the present invention such as the above-described emulsion dispersion,
 45 photosensitive emulsion and coating solution are cooled, set, and preserved at the temperature within the range of from 0 °C to the freezing point thereof. It is preferable to set the preserving temperature at a point slightly higher than the freezing point of the coating solution, concretely -3 °C to -5 °C. When the preserving temperature is 0 °C or higher, problems are caused such as, the deterioration of the photographic characteristics including the decrease in sensitivity and increase in fog, and the breeding of bacteria. When
 50 the preserving temperature is freezing point or lower, the emulsion is frozen and the dispersed oil drops of the high-boiling solvent containing the oil soluble additives become large in size, resulting in the occurrence of pin holes.

The freezing point of composition can be measured by a well known method as follows. The composition to be measured is put in a vessel and a temperature censer is set in the composition. The composition is
 55 cooled in a freezer and temperature lowering with the laps of time is recorded as a curve. Thus obtained curve has a plateau caused by the freezing latent heat of the composition. The freezing point of the composition is determined at the temperature at which the plateau on the temperature lowering curve is formed.

It is preferable to cool the emulsion rapidly for setting. For example, the following cooling method described in Japanese Patent Publication Open to Public Inspection No. 104937/1985, is preferably applied to the present invention, in which an emulsion, is boiled under a reduced pressure and cooled rapidly by deprivation of the latent heat of vaporization so that the emulsion can be gelled. The emulsion is preferably preserved in a refrigerator which can be controlled the temperature to a tolerance of $\pm 0.5^{\circ}\text{C}$.

In the method of the present invention, it is preferable that the addition, of all additives including the high boiling solvent dispersion, and adjustment of concentration and viscosity of the solution are carried out before setting the coating solution to be preserved. However, immediately effective additives such as a hardening agent, for example, which makes chemical reaction even when the emulsion is refrigerated, may be added when the emulsion is melted for coating.

The compositions which have been preserved by the method of the present invention, is melted when necessary. The coating solution is coated on a widely known support by a widely known coating method. It is preferable that the preserved composition is dissolved as rapidly as possible avoiding local heat.

EXAMPLES

The embodiment of the present invention will be explained as follows.

EXAMPLE 1

An oil-drop-in-water type magenta coupler dispersion, the recipe of which is shown as follows, was prepared, and preserved at a temperature shown in Table 1 for 6 months. Then the temperature was raised as high as a room temperature, and the viscosity of the emulsion dispersion was measured with a Brook Field Viscometer.

Coupler dispersion

M-1	7.5g
CM-1	0.15g
Tricresyl phosphate	6g
4% Gelatin solution	375ml
Dispersing aid	
Su-1 10% solution	25ml

Further, the dispersion was coated alone on a support and dried. The coated surface was observed with a magnifying glass so that the number of pinholes were counted, the results of which are shown in Table 1, wherein the figures in the table represent the number of pinholes per m^2 .

Table 1

Preserving temperature ($^{\circ}\text{C}$)	(Reference)	7	0	-5.5	-6.5	-10	-20
Number of pinholes	1	5	2	1	1	39	30
Viscosity	40	38	40	40	40	29	28

In the above table, "reference" represents the sample which was not preserved.

According to Table 1, it can be recognized that: when the preserving temperature was so low that the

dispersion was frozen, the number of pinholes were remarkably increased and the viscosity was decreased.

EXAMPLE 2

5 The following chemically ripened silver halide emulsion was preserved for 6 months at a temperature shown in the Table 2.

Silver halide emulsion:

10 The core/shell type of silver iodobromide, the average particle size of which is $0.38\mu\text{m}$, was prepared by the double jet method, desalted by an ordinary method, and chemically sensitized with sodium thiosulfate and aurochloric so that the most optimum sensitivity could be obtained. The emulsion was optically sensitized in green region of spectrum by sensitizing dyes I and II, the amount of which were 5×10^{-4} mol and 1×10^{-4} mol per mol of silver contained in the emulsion, respectively. The freezing point of the emulsion was -6.5°C .

15 The emulsion was melted after preservation and the following dispersion and additives were added to prepare a coating solution.

A coupler dispersion was prepared according to the following formula and added to the above-described emulsion so that the amount of magenta coupler M-1 was 0.5 g per g of silver contained in the emulsion and the amount of colored magenta coupler was 0.01g per g of silver contained in the emulsion, wherein the dispersion was not preserved under the freezing condition, and further the following additives
20 were added to prepare the emulsion coating solution.

Other additives

25 Thickener V-1 4% solution was added so as
to make that the viscosity
to 32cp.
30 Coating assistant Su-2 1.2ml of the 1% solution was
added per 200ml of the
35 above-described emulsion.

The coating solution was coated on a subbed triacetate film base. The coated samples were exposed and developed under the following conditions, and the specific sensitivity and specific fogging were found,
40 the results of which are shown in Table 2.

Table 2

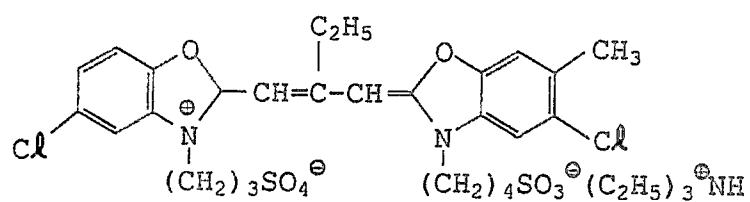
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Preserving temperature ($^\circ\text{C}$)	(Reference)	7	0	-4	-5	-10	-20
Specific sensitivity	100	95	98	99	99	99	99
Specific fog value	100	110	101	100	105	128	139

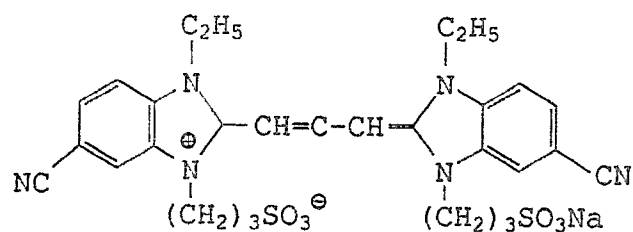
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As shown in Table 2, when the preserving temperature is low, the decrease in sensitivity is small. Specifically, when the preserving temperature is not more than 0°C , the decrease in sensitivity is not more than 2%. As far as fogging is concerned, in the range of 1 to -5°C , the increase in fogging can be hardly
55 observed. When the preserving temperature is lower than -5°C , the emulsion becomes frozen and fogging is sharply increased.

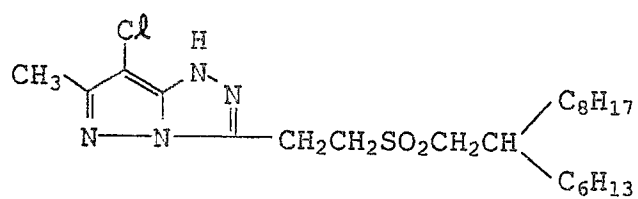
Sensitizing Dye I



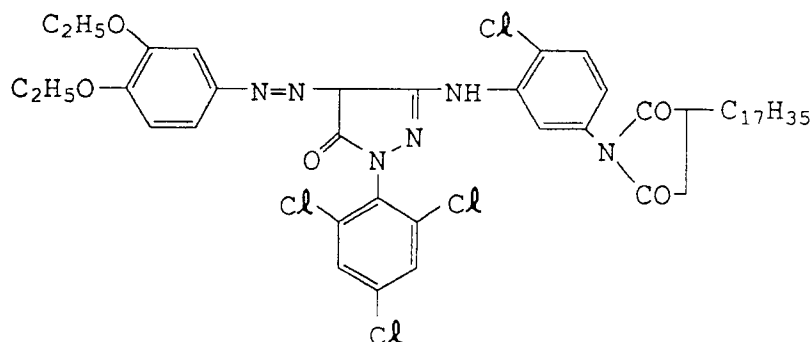
Sensitizing Dye II



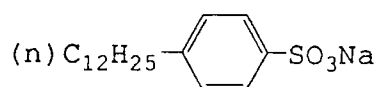
M-1



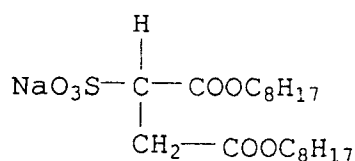
CM-1



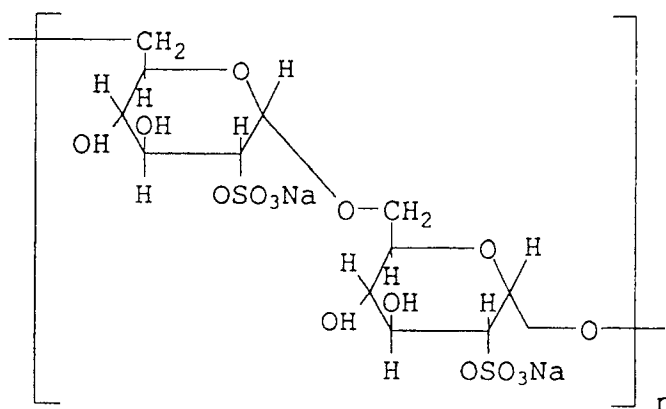
Su-1



Su-2



V-1

**Example 3**

A coating solution was prepared in the same manner as in Example 2 except that the emulsion without preservation was used.

A portion of the obtained coating solution was coated on a subbed triacetate film base and dried to prepare a control sample. The remainder of the emulsion was put under a reduced pressure, boiled, and rapidly cooled so that it could become a gel; then it was divided into several portions so that each portion was preserved in a refrigerator for 6 months at the temperature shown in Table 3. After the preservation,

each sample was taken out from the refrigerator, and melted and coated on a support and dried in the same manner as in the control sample.

The freezing point of the coating solution was -5.1°C . The coating solution preserved at a temperature of -5.5°C was frozen and separated ice particles were observed. On the other hand, the coating solution
5 preserved at a temperature of -4.5°C was not frozen and maintained the state of a resilient gel.

The above-described photosensitive material samples were exposed to light through an optical wedge by a sensitometer and processed so that the sensitivity and fogging were measured. The processing conditions were as follows.

10 Processing Solution and Conditions

Process (38°C)

15	Color development	3min. 15sec.
	Bleaching	6min. 30sec.
	Washing	3min. 15sec.
20	Fixing	6min. 30sec.
	Washing	3min. 15sec.
25	Stabilizing	1min. 30sec.
	Drying	

30 The composition of processing solution used in each process is shown as follows.

Color developer

35	4-amino-3-methyl-N-ethyl-N-(β -hydroxyethyl) aniline	
	sulfate	4.75g
	Sodium sulfite anhydride	4.25g
40	Hydroxylamine 1/2 sulfate	2.0g
	Potassium carbonate anhydride	37.5g
45	Potassium bromide	1.3g
	Trisodium nitrilotriacetate	
	monohydrate	2.5g
50	Potassium hydroxide	1.0g
	Water to make	1l
55		pH = 10.02

Bleaching solution

5	Ferric ammonium ethylenediaminetetraacetate	100.0g
10	Diammonium ethylenediaminetetraacetate	10.0g
	Ammonium bromide	150.0g
15	Glacial acetic acid	10.0g
	Water make to	1l

pH of the solution was adjusted to 6.0 by ammonia water.

20

Fixing solution

25	Ammonium thiosulfate	175.0g
	Ammonium sulfite anhydride	8.6g
	Sodium metasulfite	2.3g
30	Water to make	1l

pH of the solution was adjusted to 6.0 with acetic acid.

35

Stabilizing solution

	Formalin (37% aqueous solution)	1.5ml
40	Koniducks (Konica Corporation)	7.5ml
	Water to make	1l

45 The thus obtained results are shown in Tables 3. In the table, sensitivity and fogging of each sample are shown by the relative values to the reference sample in which the coating solution was not preserved for a long period of time. After development, Each processed sample was observed with a magnifying glass in order to count the number of pinholes. The number of pinholes is expressed in terms of number per square meter.

50

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Table 3

Preserving temperature (°C)	(Reference)	7	0	-4.5	-5.5	-20
Relative sensitivity	100	92	97	98	98	99
Relative fog value	100	120	102	101	129	138
Pinhole number/m ²	1	5	2	1	30	23

The lower the preserving temperature was, the less the sensitivity was decreased. When the preserving temperature was not higher than 0 °C, the decrease in sensitivity was kept to be within 3%. On the other hand, the preserving temperature was -5.5 °C or lower, in other words when the solution was frozen, fog was remarkably increased and at the same time the number of pinholes was considerably increased. The experimental results show that the emulsion can be preserved for a long period of time when it is preserved at a temperature of 0 to -5 °C. When an emulsion is preserved under the condition very close to the freezing temperature, the change of characteristics can be minimized.

EXAMPLE 4

Bacterium belonging to the genus of *Pseudomonas* were implanted to 1 liter of prepared coating solution which was made in Example 3. The solution was divided to five portion and preserved for 6 months under the conditions shown in Table 4, the number of bacterium per ml was measured. The results are shown in Table 4.

Table 4

Preserving temperature (°C)	7	0	-4.5	-5.5	-20
Number of bacterium	10 ²⁰	10 ¹²	10 ²	10 ²	70

As shown in the above table, breeding of bacterium was inhibited when the preserving temperature was lowered.

EXAMPLE 5

The viscosity of the prepared coating solution obtained in Example 3 and that of the coating solution preserved for 6 months were measured by a Brook Field viscometer. The results are shown in Table 5.

Table 5

Preserving temperature (°C)	(Reference)	7	0	-4.5	-5.5	-20
Viscosity (cp)	32	30	32	32	10	21

When the temperature was lowered to -4.5 °C, the viscosity decreasing could be avoided. However,

when the temperature was lowered below -5.5°C at which the solution was frozen, the viscosity was extremely decreased.

Example 6

5

An emulsion of cubic silver bromide chloride having the average particle size is $0.85\mu\text{m}$, which was prepared by the double jet method, was chemically sensitized with sodium thiosulfate and chlorauric acid so that the most adequate sensitivity could be obtained. Color sensitizing dyes (III) and (IV) were added to 1 mol of silver of the emulsion described above by $4 \times 10^{-4}\text{mol}$ and $1 \times 10^{-4}\text{mol}$ respectively for spectral sensitization.

10

A coating solution was prepared in such a manner that the following coupler dispersion was mixed with the emulsion by the ratio of, Y-1 3.08g, ST-1 1.15g and ST-2 0.77g per grain of the emulsion.

The freezing point of this coating solution was -4.8°C . After this coating solution was preserved at a temperature shown in Table 6 for 6 months, coated samples were made from the coating solution. The samples were exposed and processed in the manner after-mention to evaluate the characteristics of them.

15

Coupler dispersion recipe

20

Y-1 26.7g

ST-1 10.0g

ST-2 6.67g

25

Dinonyl phthalate 6.67g

10% Gel solution 220ml

30

Dispersion assistant (Su-3) 20% solution 7ml

Table 6

35

Preserving temperature ($^{\circ}\text{C}$)	(Reference)	7	0	-4.5	-5.5	-20
Specific sensitivity	100	85	92	97	97	99
Specific fog value	100	121	102	101	128	145
Pinhole	1	6	2	1	28	20

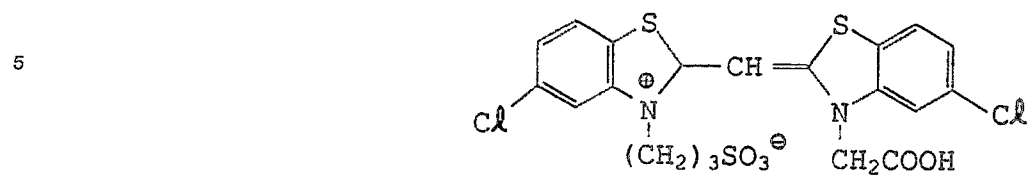
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In the same manner as Example 3, the occurrence of pinholes and fogging could be inhibited by preserving the coating solution in the temperature range of 1 to -5°C , so that the coating solution can be preserved for a long period of time without deteriorating its performance.

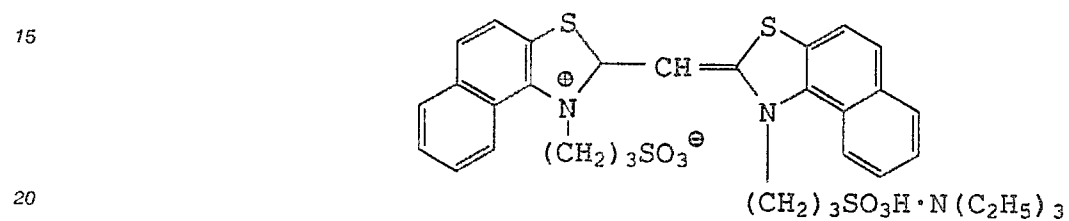
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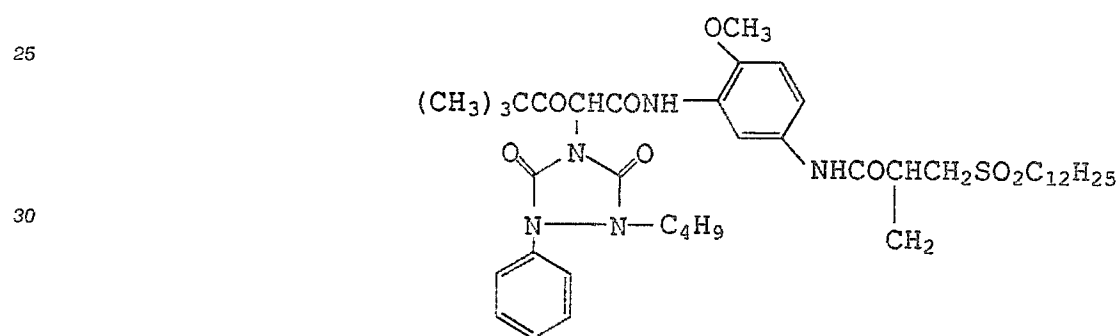
Sensitizing dye III



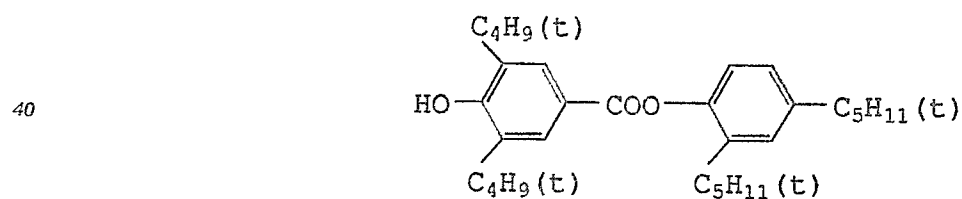
Sensitizing dye IV



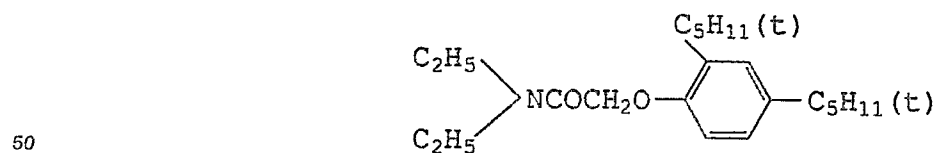
Y-1



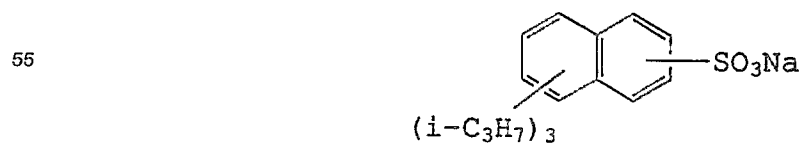
ST-1



ST-2



SU-3



	Process	Temperature	Time
5	Coloring development	35.0 $\pm$ 0.3°C	45sec
	Bleaching and fixing	35.0 $\pm$ 0.5°C	45sec
	Stabilization	30 to 34°C	90sec
10	Drying	60 to 80°C	60sec

Color developer

15	Pure water	800ml
	Triethanol amine	10g
20	N,N diethyl hydroxylamine	5g
	Potassium bromide	0.02g
	Potassium chloride	2g
25	Potassium sulfite	0.3g
	1-hydroxyl ethylidene-1,1-diphosphonic acid	1.0g
30	Ethylenediaminetetraacetic acid	1.0g
	Disodium catechol-3,5-diphosphonate	1.0g
	N-ethyl-N- β methanesulfonamide	
35	ethyl-3-butyl-4-amino aniline sulfate	4.5g
	Whitening agent (4,4'-diamino stilbene	
40	sulfonic acid derivative)	1.0g
	Potassium carbonate	27g
45	Water to make 1l in order to adjust pH = 10,10	

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Bleach-fixer

5 Ferric ammonium ethylenediaminetetraacetic
acid dihydride 60g

Ethylenediaminetetraacetic acid 3g

10 Thioammonium sulfite (70% aqueous solution) 100ml

Ammonium sulfite (40% aqueous solution) 27.5ml

15 Water to make 1ℓ, and pH is adjusted with potassium
carbonate or glacial acetic acid so that pH = 5.7.

20 Stabilizer

5-chloro-2-methyl-4-isothiazoline-3-one 1.0g

Ethylene glycol 1.0g

25 1-hydroxyl ethylidene-1,1-diphosphonic acid 2.0g

Ethylenediaminetetraacetic acid 1.0g

30 Ammonium hydroxide (20% aqueous solution) 3.0g

Whitening agent (4,4'-diamino stilbene
sulfonic acid derivative) 1.5g

35 Water to make 1ℓ, and pH is adjusted with sulfuric acid or
potassium hydroxide so that pH = 7.0.

40

Claims

- 45 1. A method for preserving a composition for silver halide photographic light-sensitive material wherein a composition for silver halide photographic light-sensitive material is preserved at a temperature within the range of from 0° C to the freezing point of said composition.
2. The method of claim 1, wherein said composition is an oil-in-water type dispersion.
- 50 3. The method of claim 2, wherein said dispersion comprises dispersed drops of an organic high-boiling solvent in which a color forming coupler is dissolved.
4. The method of claim 1, wherein said composition is a silver halide emulsion essentially consisting of silver halide grains, a binder and water.
- 55 5. The method of claim 4, wherein said silver halide emulsion is chemically or optically sensitized.

6. The method of claim 1, wherein said composition is a coating solution of emulsion prepared to be coated in the photographic and physical properties thereof.
7. The method of claim 6, wherein said coating solution contains an oil-in-water type dispersion.
8. The method of claim 7, wherein said dispersion comprises dispersed drops of an organic high-boiling solvent in which a color forming coupler is dissolved.

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