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(54) **Dispersion method of spectral sensitizer and dispersion obtained thereby**

(57) A dispersion method of a spectral sensitizer by dissolving an inorganic salt of an amount of at least 0.5% by weight in water which does not substantially contain a surface active agent, an organic solvent, and a silver halide emulsion, adding a spectral sensitizer of an amount of at least 0.5% by weight in the solution, and dispersing the spectral sensitizer as fine solids. By the dispersion method, a dispersion of a spectral sensitizer having a high concentration is obtained.

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Description**FIELD OF THE INVENTION**

5 [0001] The present invention relates to a method of obtaining an aqueous dispersion of a spectral sensitizer used for silver halide photographic materials and to a dispersion obtained by the method.

BACKGROUND OF THE INVENTION

10 [0002] For the production of photographic light-sensitive materials, a spectral sensitizing technique, that is, the method of sufficiently sensitizing the light-sensitive materials up to the visible region is very important and, in particular, the sensitizing method is an indispensable technique for color photographic materials. Accordingly, about the addition method of a spectral sensitizer necessary for spectrally sensitizing silver halide emulsions, various methods have been developed.

15 [0003] Because the solubility of a spectral sensitizer to water is low, a method of adding a spectral sensitizer to a silver halide emulsion after dissolving it in an organic solvent having a water miscibility is disclosed, for example, in JP-B-49-46416 (the term "JP-B" as used herein means an "examined published Japanese patent application". Or a method of dissolving a spectral sensitizer in an organic solvent and after adding the solution to a silver halide emulsion, removing the organic solvent by heating is disclosed, for example, in JP-B-44-22948. However, in these methods, it is necessary
20 to use a large amount of an organic solvent, whereby troubles such as the aggregation of the emulsion, the abnormality of the coated surface form, etc., frequently occur. The removal of an organic solvent from the silver halide emulsion is a very complicated process as well as it is very difficult to completely remove the organic solvent, and it is generally known in the persons skilled in the field that even a slight amount of the remaining solvent causes the above-described troubles.

25 [0004] Also, the technique of dispersing a spectral sensitizer in an aqueous solution of a surface active agent and then adding the solution to a silver halide emulsion is disclosed, for example, in JP-B-49-44895 and U.S. Patent No. 4,006,025. However, the use of a surface active agent has the possibility of causing the problems of damaging the emulsion existing in the silver halide emulsion, the reduction of the coating property, etc.

30 [0005] A technique of completely dissolving a certain kind of spectral sensitizer in water under an acidic condition and then adding the solution to a silver halide emulsion is disclosed, for example, in JP-B-44-23389 and JP-B-50-80826. However, the method is limited to the applicable spectral sensitizers and also there is a problem in the chemical stability of these spectral sensitizers used in these methods.

[0006] Also, a technique of dissolving a spectral sensitizer in water containing a water-soluble organic compound and then adding the solution to a silver halide emulsion is disclosed, for example, in JP-B-57-22094 and JP-B-2-135437.
35 However, in the method, it is required to use a water-soluble organic compound in an amount almost same as that of the spectral sensitizer, which gives a possibility of causing an inferior adsorption of the spectral sensitizer to a silver halide emulsion.

[0007] Furthermore, a technique of adding a sensitizing dye to a silver halide emulsion as a solid state without forming the solution or the dispersion of the sensitizing dye. For example, JP-B-53-16624 discloses a technique of melting a
40 spectral sensitizer in an organic compound and then adding the melt to a silver halide emulsion. Also, in each of JP-B-53-102732 and JP-B-53-102733, a technique of forming photographically inactive water-soluble fine solids and a spectral sensitizer into tablets or granules and adding the tablets or the granules to a silver halide emulsion is disclosed. However, in these methods, because after dispersing the spectral sensitizer in a liquid, the spectral sensitizer is taken out as a solid state, a complicated process is required.

45 [0008] As the purpose of solving these problems, a method of dispersing a spectral sensitizer in water containing gelatin only as the fine solids is disclosed, for example, in JP-B-61-45217 and WO 93/23792. These methods are very excellent as a dispersion method of a spectral sensitizer because the methods do not use unnecessary additives such as an organic solvent and a dispersing agent and also the operation of the method is simple. However, it is described in JP-A-4-125031 and JP-A-5-297496 (the term "JP-A" as used herein means an "unexamined published Japanese
50 patent application") that in the above methods, in the case of preparing the high-concentrate dispersion of the spectral sensitizer, it sometimes happens that the viscosity is increased accompanied by the dispersion. Accordingly, it is disclosed that the problem can be solved by fluctuating a pressure in the former (JP-A-4-125631) or by using the spectral sensitizer having a limited solubility to water in the latter (JP-A-5-297496). However, the method of the former requires a complicated operation and the method of the latter cannot be applied to a spectral sensitizer having a high solubility.

55 [0009] Convention methods of adding a spectral sensitizer to a silver halide emulsion have the following problems;

- (1) the use of an organic solvent requiring an environmental counterplan,
- (2) the use of a surface active agent giving bad influences on the photographic property and the coating property,

- (3) the isolation of a spectral sensitizer in a solid state requiring a very complicated operation,
 (4) the use of a dispersion formed by dispersing a spectral sensitizer in an aqueous gelatin solution in which a highly concentrated dispersion is impossible, etc.

5 SUMMARY OF THE INVENTION

[0010] Accordingly, an object of the present invention is to provide a method of obtaining a highly concentrated dispersion of a spectral sensitizer solving the above-described problems.

[0011] It has now been discovered that the above-described object can be achieved by the present invention described below.

[0012] That is, according to a 1st aspect of the present invention, there is provided a dispersion method of a spectral sensitizer which comprising after dissolving an inorganic salt in an amount of at least 0.5% by weight in water which does not substantially contain a surface active agent, an organic solvent, and a silver halide emulsion, adding to the solution a spectral sensitizer in an amount of at least 0.5% by weight and dispersing the spectral sensitizer as the fine solids thereof.

[0013] According to a 2nd aspect of the present invention, there is provided a dispersion method of a spectral sensitizer of the 1st aspect, wherein the spectral sensitizer is added to the dissolved solution in an amount of from 2% by weight to 30% by weight.

[0014] According to a 3rd aspect of the present invention, there is provided a dispersion method of a spectral sensitizer of the 1st aspect, wherein the pH in the case of dissolving the inorganic salt in an amount of at least 0.5% by weight in water which does not substantially contain a surface active agent, an organic solvent, and a silver halide emulsion is in the range of from 4 to 10.

[0015] According to a 4th aspect of the present invention, there is provided a dispersion method of a spectral sensitizer of the 3rd aspect, wherein the dissolved solution obtained by dissolving the inorganic salt in an amount of at least 0.5% by weight in water which does not substantially contain a surface active agent, an organic solvent and a silver halide emulsion has a pH of 6 to 8.

[0016] According to a 5th aspect of the present invention, there is provided a dispersion method of a spectral sensitizer of any one of the aspects 1 to 4, wherein the weight ratio of the inorganic salt to the spectral sensitizer is at least 0.5.

[0017] According to a 6th aspect of the present invention, there is provided a dispersion method of a spectral sensitizer of any one of the aspects 1 to 5, wherein the spectral sensitizer is a cyanine dye.

[0018] According to a 7th aspect of the present invention, there is provided a dispersion method of a spectral sensitizer of any one of the aspects 1 to 6, wherein the dispersion obtained is mixed with a water-soluble polymer.

[0019] According to an 8th aspect of the present invention, there is provided a dispersion method of a spectral sensitizer of the aspect 7, wherein the concentration of the water-soluble polymer in water is at least 0.5% by weight.

[0020] According to a 9th aspect of the present invention, there is provided a dispersion method of a spectral sensitizer of the aspect 7 or 8, wherein the water-soluble polymer is gelatin.

[0021] According to a 10th aspect of the present invention, there is provided a dispersion obtained by the dispersion method of the aspect 1 to 9.

40 BRIEF DESCRIPTION OF THE DRAWINGS

[0022]

45 Fig. 1 is an SEM image (about 5,000 magnification) showing the three-dimensional network structure of Sample 4 of Example 1, and

Fig. 2 is a graph showing the viscosities of Samples 1 to 4 in Example 1 at 20°C.

50 DETAILED DESCRIPTION OF THE INVENTION

[0023] As the result of various investigations, the present inventor has discovered that a spectral sensitizer forms a fibrous associated material in an aqueous dispersion of the spectral sensitizer having a high viscosity and the fibrous associated material forms a three-dimensional network structure. The fibrous associated material is caused by that the spectral sensitizer once dissolved in water is fibrously recrystallized in water. That is, it is considered that the existent state of the spectral sensitizer molecule in water is shown by the following equilibrium;



[0024] From the above-described matter, the present inventor has considered that it is not effective to increase the solubility of a spectral sensitizer in a solvent, which is hitherto been believed to be effective, and it is effective to lower the solubility of the spectral sensitizer to restrain the increase of the viscosity of the dispersion. That is, the inventor set up a hypothesis that the prevention of a spectral sensitizer from dissolving as a monomer in water restrains the formation of the fibrous associated material, that is, is effective for restraining the increase of the viscosity of the dispersion. As the result of dispersing a spectral sensitizer in water containing an inorganic salt for lowering the solubility of the spectral sensitizer in water based on the hypothesis, a high-concentration dispersion of the spectral sensitizer could be obtained.

[0025] This is practically a dispersion method wherein after dissolving an inorganic salt in an amount of at least 0.5% by weight in water which does not substantially contain a surface active agent, an organic solvent, and a silver halide emulsion, a specific sensitizer of at least 0.5% by weight is added to the solution to disperse therein as the fine solids.

[0026] The inorganic salt in the present invention is a salt of an acid without containing carbon, such as hydrochloric acid, sulfuric acid, nitric acid, etc., and an alkali metal, an alkaline earth metal, or ammonium and practically includes lithium chloride, sodium chloride, potassium chloride, rubidium chloride, cesium chloride, magnesium chloride, calcium chloride, lithium bromide, sodium bromide, potassium bromide, rubidium bromide, cesium bromide, magnesium bromide, calcium bromide, lithium iodide, sodium iodide, potassium iodide, rubidium iodide, cesium iodide, magnesium iodide, calcium iodide, lithium sulfate, sodium sulfate, potassium sulfate, magnesium sulfate, calcium sulfate, ammonium sulfate, lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, calcium nitrate, ammonium nitrate, etc. In these inorganic salts, preferable salts are sodium nitrate, sodium sulfate, ammonium nitrate, and ammonium sulfate each containing no halogen atom which is worried about making an interaction with a silver halide emulsion, and sodium nitrate and sodium sulfate are more preferred.

[0027] In the present invention, the inorganic salts may be used singly or as a combination of them.

[0028] The concentration of the inorganic salt in water is at least 5% by weight, preferably from 1% by weight to 50% by weight, and more preferably from 2% by weight to 30% by weight.

[0029] It is generally known that when the pH of an aqueous solution in the case of dispersing a spectral sensitizer is not within a neutral region, the chemical stability of the spectral sensitizer is reduced and it is disclosed, for example, in JP-B-61-45217 that it is effective to disperse the spectral sensitizer in the neutral region. Accordingly, in the present invention, the above-described inorganic salt that the pH of water at dissolving the above-described inorganic salt is in the range of from 4 to 10, preferably in the range of from 5 to 9, and more preferably from 6 to 8 is used.

[0030] The spectral sensitizer in the present invention means a compound which causes a photoinductive electron transfer to a silver halide emulsion when the compound adsorbs on the silver halide emulsion and does not include organic dyestuffs not having the above function (photoinductive electron transfer).

[0031] The spectral sensitizer used in the present invention includes methine dyes such as cyanine dyes, merocyanine dyes, hemicyanine dyes, rhodacyanine dyes, oxonol dyes, hemioxonol dyes, etc., and styryl dyes. In these spectral sensitizers, cyanine dyes are particularly preferred. More preferably, an anionic cyanine dye having one or two hydrophilic group (for example, a sulfo group, a sulfoalkyl group, and a carboxyl group) is effective.

[0032] The concentration of the spectral sensitizer in water is at least 0.5% by weight, preferably in the range of from 1 to 30% by weight, and more preferably in the range of from 2 to 20% by weight.

[0033] The weight ratio of the inorganic salt and the spectral sensitizer has a large meaning to the viscosity of the dispersion. To restrain the viscosity of dispersion of the spectral sensitizer, it is effective to disperse the spectral sensitizer in water having dissolved therein the inorganic salt in an amount of preferably at least 1/2, and more preferably at least an equivalent amount to the addition amount of the spectral sensitizer.

[0034] In the present invention, for mechanically grinding and dispersing the spectral sensitizer in water, various dispersing means can be effectively used. Practically, a high-speed stirring means, a ball mill, a sand mill, an attritor, a ultrasonic dispersing means, etc., can be used.

[0035] In the present invention, the temperature in the case of dispersing the spectral sensitizer in water is in the range of from 0°C to 100°C, preferably in the range of from 20°C to 80°C, and more preferably from 50°C to 80°C.

[0036] The dispersion of the spectral sensitizer obtained by the present invention is mixed with a water-soluble polymer for having a precipitation preventing property and can be stored for long period of time at a temperature of 30°C or lower or can be refrigerated.

[0037] The water-soluble polymer used in the present invention is a linear high-molecular compound having a molecular weight of at least 1,000 and can be dissolved in water at room temperature in an amount of 0.5% by weight and practically includes gelatin, carboxymethyl cellulose, hydroxyethyl cellulose, a cellulose sulfuric acid ester, chondroitin sulfuric acid, sodium alginate, chitin, chitosan, polyvinyl alcohol, polyethylene glycol, polypropylene glycol, sodium polyacrylate, polyvinyl pyrrolidone, etc., and the copolymers of them.

[0038] In the present invention, the water-soluble polymers may be used singly or as a combination of the plural water-soluble polymers.

[0039] The water-soluble polymer may be added to a silver halide emulsion as the aqueous solution thereof or as

solids thereof. Also, in the case of adding the water-soluble polymer, if necessary, a known antiseptic may be used.

[0040] The concentration of the water-soluble polymer used in the present invention is preferably at least 0.5% by weight, more preferably from 1% by weight to 50% by weight, and far more preferably from 2% by weight to 10% by weight.

[0041] By the dispersion method of the present invention, the high-concentration dispersion of a spectral sensitizer, which has never been obtained by conventional methods, can be prepared without increasing the viscosity thereof.

[0042] Furthermore, because in the dispersion method of the present invention, the mixed composition is prepared using the water-soluble polymer, the dispersion of the spectral sensitizer prepared can be stably stored for a long period of time by simply cooling the composition without carrying out drying, etc.

[0043] To the silver halide emulsion spectrally sensitized using the dispersion prepared by the dispersion method of the spectral sensitizer of the present invention or before applying the spectral sensitization, various additives according to the purposes may be added. Also, for the photographic light-sensitive materials prepared by such silver halide emulsions, various additives can be used.

[0044] More specifically these additives are described in Research Disclosure (RD), No. 17643 (December 1978), ibid., No. 18716 (November 1979), and ibid., No. 308119 (December, 1989) and the described portions are summarized below.

	<u>Kind of additives</u>	<u>RD 17643</u>	<u>RD 18716</u>	<u>RD 308119</u>
20	1. Chemical Sensitizer	p. 23	p. 648 right col.	p. 996
25	2. Sensitivity increasing agent	-	p. 648 right col.	-
30	3. Spectral sensitizer & Super sensitizer	pp. 23 to 24	p. 648 right col. to p. 649 right col.	p. 996 right to p. 998 right
35	4. Whitening agent	p. 24	-	p. 998 right
40	5. Anti-foggant & stabilizer	pp. 24 to 25	p. 649 right col.	p. 998 right to p. 1000 left

5	6. Light absorber, filter dye, & UV absorber	pp. 25 to 26	p. 649 right col. to p. 650 left col.	p.1003 left yo p.1003 right
10	7. Anti-stain agent	p. 25 right col.	p. 650 left to right col.	p.1002 right
	8. Dye image stabilizer	p. 25	-	p.1002 right
15	9. Hardener	p.26	p. 561 left col.	p.1004 right to p.1005 left
20	10. Binder	p.26	p. 561 left col.	p.1003 right to p.1004 right
25	11. Plasticizer & lubricant	p.27	p. 650 right col.	p.1006 left to right
30	12. Coating aid & surface active agent	pp. 26 to 27	p. 650 right col.	p.1005 left to p.1006 right
35	13. Anti-static agent	p.27	p. 659 right col,	p.1006 right to p.1007 left
40	14. Matting agent	-	p. 659 right col.	p.1008 left to p.1009 right

45

[0045] The techniques for the layer disposition, etc., silver halide emulsion, functional couplers such as dye-forming couplers, DIR couplers, etc., various additives, and photographic processings, which can be used for the silver halide emulsions spectrally sensitized using the dispersion prepared by the dispersion method of a spectral sensitizer of this invention and also for the photographic light-sensitive materials using the silver halide emulsions are described in European Patent No. 0565096A1 [published (unexamined) October 13, 1993] and the patents cited therein. Each term and the described portion of the term are described below.

55 1. Layer structure: Page 61, lines 23 to 35 and page 61, lines 41 to page 62, line 14.

2. Inter layer: Page 61, lines 36 to 40.

3. Double layer effect-imparting Layer: Page 62, lines 15 to 18.

4. Silver halide composition: Page 62, lines 21 to 25.

5. Silver halide grain crystal habit: Page 62, lines 26 to 30.
6. Silver halide grain sizes: Page 62, lines 31 to 34.
7. Emulsion production method: Page 62, lines 35 to 40.
8. Silver halide grain distribution: Page 62, lines 41 to 42.
9. Tabular grains: Page 62, lines 43 to 46.
10. Inside structure of grains: Page 62, lines 47 to 53.
11. Latent image-forming type of emulsion: Page 62, line 54 to page 63, line 5.
12. Physical ripening and chemical ripening of emulsion: Page 63, lines 6 to 9.
13. Mixed use of emulsions: Page 63, lines 10 to 13.
14. Fogged emulsion: Page 63, lines 14 to 31.
15. Light-insensitive emulsion: Page 63, lines 32 to 43.
16. Coated silver amount: Page 63, lines 49 to 50.
17. Photographic additives: Shown before.
18. Formaldehyde scavenger: Page 64, lines 54 to 57.
19. Mercapto series antifoggant: Page 65, lines 1 to 2.
20. Releasing agents such as fogging agent, etc.: Page 65, lines 3 to 7.
21. Dyes; Page 65, lines 7 to 10.
22. Color coupler general: Page 65, lines 11 to 13.
23. Yellow, Magenta and cyan couplers: Page 65 to 28.
24. Polymer coupler: Page 65, lines 26 to 28.
25. Diffusible dye-forming coupler: Page 65, lines 29 to 31.
26. Colored coupler: Page 65, lines 32 to 38.
27. Functional coupler general: Page 65, lines 39 to 44.
28. Bleach accelerator-releasing coupler: Page 65, lines 45 to 48.
29. Development accelerator-releasing coupler: Page 65, lines 49 to 53.
30. Other DIR coupler: Page 65, line 64 to page 66, line 4.
31. Coupler dispersing method: Page 66, lines 5 to 29.
32. Antiseptics and antifungal agent: Page 66, lines 29 to 33.
33. Kind of light-sensitive materials: Page 66, lines 34 to 36.
34. Thickness and Swelling speed of light-sensitive layers: Page 66, line 40 to page 67, line 1.
35. Back layer: Page 67, lines 3 to 8.
36. Photographic processing general: Page 67, lines 9 to 11.
37. Developer and developing agent: Page 67, lines 12 to 30.
38. Additives to developer: Page 67, lines 31 to 44.
39. Reversal processing: Page 67, lines 45 to 56.
40. Opening ratio of processing liquid: Page 67, line 57 to page 68, line 12.
41. Processing time: Page 68, lines 13 to 15.
42. Bleach-fix, bleach, and fix: Page 68, line 16 to page 69, line 31.
43. Automatic processing apparatus: Page 69, lines 32 to 40.
44. Water washing, rinse, and stabilization: Page 69, line 41 to page 70, line 18.
45. Processing liquid replenishing: Page 70, lines 19 to 23.
46. Developer-containing light-sensitive material: Page 70, lines 24 to 33.
47. Processing temperature: Page 70, lines 34 to 38.
48. Utilization to lens-attached film: Page 70, lines 39 to 41.

[0046] The following examples are intended to illustrate the present invention in more detail but not to limit the invention in any way.

Example 1

[0047] This example shows that in the dispersion method of the present invention, various inorganic salts having a very large effect for restraining the increase of viscosity at dispersing a spectral sensitizer at a high concentration as shown in Table 1 below.

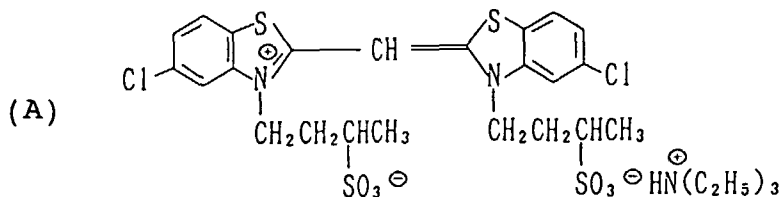
Table 1

Sample No.	Inorganic Sale	Water	Spectral Sensitizer 1	Property of Dispersion
1	none	99 g	1 g	Fluid liquid
2	none	98 g	2 g	Viscous liquid
3	none	97 g	3 g	"
4	none	96 g	4 g	"
5	none	90 g	10 g	gelled
6	LiCl 10g	80 g	10 g	Fluid liquid
7	KCl 10g	80 g	10 g	"
8	NaCl 10g	80 g	10 g	"
9	CaCl ₂ 10g	80 g	10 g	"
10	NaBr 10g	80 g	10 g	"
11	NaNO ₃ 10g	80 g	10 g	"
12	Na ₂ SO ₄ 10g	80 g	10 g	"
13	(NH ₄) ₂ SO ₄ 10 g	80 g	10 g	"

[0048] In the above table, Sample Nos. 1 to 5 are samples of comparative example and Sample Nos. 6 to 13 are samples of this invention.

[0049] Also, the spectral sensitizer used in this example is shown below.

Spectral sensitizer 1:



[0050] In the cases of Sample Nos. 1 to 5, a definite amount of the spectral sensitizer 1 was added to ion-exchanged water and was dispersed under the condition of 60°C using a dissolver blade at 2,000 r.p.m. over a period of about one hour. In the cases of Sample Nos. 6 to 14, after completely dissolving 10 g of each inorganic salt in ion-exchanged water, 10 g of the spectral sensitizer 1 was added to the solution, and dispersed under the condition of 60°C using a dissolver blade at 2,000 r.p.m. over a period of about one hour.

[0051] In the case of the comparative examples, when the concentration of the spectral sensitizer 1 was 1% by weight or lower, the dispersion had a fluidity but when the concentration was 2% by weight or higher, the viscosity increased with the progress of the dispersion and the dispersion could not be carried out. Also, when the concentration of the spectral sensitizer 1 was 10% by weight, at the time of adding the spectral sensitizer 1 to water, the system was gelled and thus the dispersion became impossible. As described above, in the cases of the comparative examples, it was very difficult to obtain the dispersion of a high concentration (see Table 2, measured by an E-type viscometer, VISCONIC EHD, trade name, manufactured by Tokyo Keiki K.K., under the condition of 1 r.p.m.).

[0052] On the other hand, in Sample Nos. 6 to 13 of the present invention, in spite of that the concentration of the spectral sensitizer 1 was as high as 10% by weight, about all the samples, the dispersion was completed without increasing the viscosity of the dispersions.

[0053] Also, Sample No. 4 having increased viscosity was lyophilized, and after vapor-depositing platinum thereto, observation by SEM (scanning type electron microscope) was carried out. As the result, a three-dimensional structure of intertwined fibrous associated material was observed as shown in Fig. 1.

Example 2

[0054] This example shows that the dispersion method of the present invention can be applied to the high-concentration dispersions of various spectral sensitizers (see, Table 2 below).

Table 2

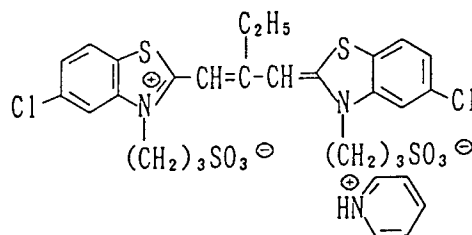
Sample No.	Inorganic Sale	Water	Spectral Sensitizer	Property of Dispersion
14	none	90 g	2 = 10 g	gelation
15	none	90 g	3 = 10 g	"
16	none	90 g	4 = 10 g	"
17	none	90 g	5 = 10 g	"
18	NaNO ₃ 10g	80 g	2 = 10 g	Fluid liquid
19	NaNO ₃ 10g	80 g	3 = 10 g	"
20	NaNO ₃ 10g	80 g	4 = 10 g	"
21	NaNO ₃ 10g	80 g	5 = 10 g	"
22	NaNO ₃ 10g	80 g	6 = 10 g	"
23	NaNO ₃ 10g	80 g	7 = 10 g	"

[0055] In the above table, Sample Nos. 14 to 17 are comparative samples and Sample Nos. 18 to 23 are samples of this invention.

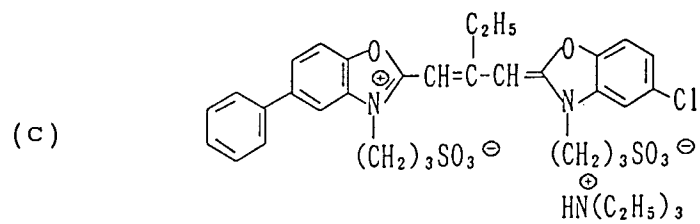
[0056] Also, the spectral sensitizers used in the example are shown below.

Spectral Sensitizer 2

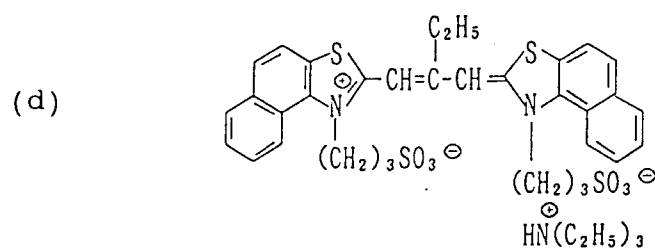
(B)



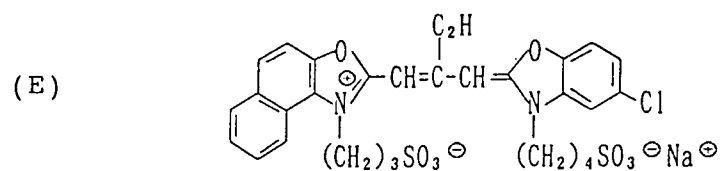
Spectral Sensitive 3



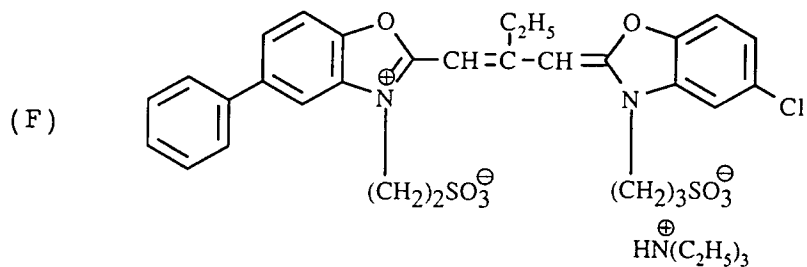
Spectral Sensitizer 4



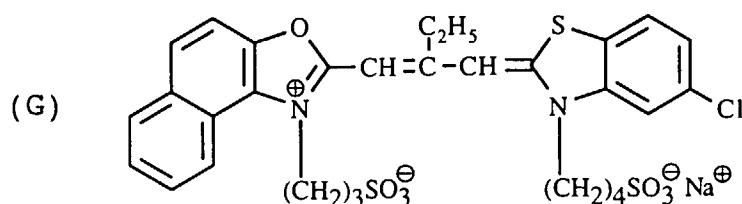
Spectral Sensitizer 5



Spectral Sensitizer 6



Spectral Sensitizer 7



[0057] In the cases of Sample Nos. 14 to 17, each of the spectral sensitizers 2 to 5 was added to 90 g of water. In the cases of Sample Nos. 18 to 23, after completely dissolving 10 g of sodium nitrate in 80 g of ion-exchanged water, 10 g of each of spectral sensitizers 2 to 7 was added and dispersed under the condition of 60°C, using a dissolver blade at 2,000 r.p.m. over a period of about one hour.

[0058] In the comparative examples, at the time of adding the spectral sensitizer to water, the system was gelled and the dispersion could not be carried out as in Sample No. 5. As described above, in the comparative examples, it was very difficult to obtain the high-concentration dispersion.

[0059] On the other hand, in the cases of Sample Nos. 18 to 23 of the present invention, in spite of that the concentration of each spectral sensitizer was as high as 10% by weight, the dispersion was completed about all the samples without increasing the viscosity of the dispersion.

Example 3

[0060] This example shows the influence of the ratio of the addition amount of a spectral sensitizer and the addition amount of an inorganic salt in the dispersion method of the present invention to the viscosity of the dispersion (see Table 3).

Table 3

Sample No.	Inorganic Salt	Water	Spectral Sensitizer	Property of Dispersion
24	NaNO ₃ = 2g	88 g	10 g	Gelation
25	NaNO ₃ = 4g	86 g	10 g	Viscous liquid
26	NaNO ₃ = 6g	84 g	10 g	Low-viscous liquid
27	NaNO ₃ = 8g	82 g	10 g	Fluid liquid
28	NaNO ₃ = 10g	80 g	10 g	"

[0061] In the cases of Sample Nos. 24 to 28, after completely dissolving the definite amount of sodium nitrate in ion-exchanged water to form 90 g of the solution, 10 g of the spectral sensitizer 1 described above was added to the solu-

tion and dispersed under the condition of 60°C using a dissolver blade at 2,000 r.p.m. over a period of about one hour.

[0062] To the concentration of the spectral sensitizer 1 was 10% by weight, in Sample Nos. 24 to 28 wherein the addition amount of sodium nitrate was small, the viscosity restraining effect of the dispersion was insufficient, while in Sample Nos. 27 and 28 wherein the addition amount of the spectral sensitizer 1 was almost same as that of sodium nitrate, the restraining effect of the viscosity of the dispersion was confirmed.

[0063] As described above, in the present invention, it is very effective for restraining the increase of the viscosity of the dispersion to disperse a spectral sensitizer in water containing an inorganic salt in an amount of almost same as the amount of the spectral sensitizer.

Example 4

[0064] This example shows that when gelatin is added to the dispersion of this invention and the dispersion is stored in a cold dark place, the physical and chemical stabilities of the dispersion are high (see, Table 4),

Table 4

Sample No.	Sample 14	12% Gelatin	Storing Condition	Property of Dispersion
29	100 g	none	Direct after dispersion	Fluid liquid
30	50 g	50 g	Direct after dispersion	Fluid liquid (50°C)
31	100 g	none	Light-shield 10°C 4 weeks	Dispersion precipitated
32	50 g	50 g	Light-shield 10°C 4 weeks	Gelation

[0065] Sample No. 29 was same as Sample No. 11 described above. That is, after dissolving 10 g of sodium nitrate in 80 g of ion-exchanged water, 10 g of the spectral sensitizer was added and dispersed under the condition of 60°C using a dissolver blade at 2,000 r.p.m. over a period of about one hour. Sample No. 30 was prepared by adding 50 g of an aqueous solution of 12% by weight gelatin to 50 g of the dispersion obtained by the manner as preparing Sample No. 29. Sample Nos. 31 and 32 were prepared by light-shielding Sample Nos. 29 and 30 respectively and stored in a refrigerator of 10°C for 4 weeks.

[0066] In Sample No. 31 stored in a refrigerator for 4 weeks, it was confirmed that the particles of the dispersion were precipitated. However, the precipitates could be re-dispersed by lightly stirring. Sample No. 32 was completely set and no precipitation of the dispersion was observed.

[0067] Sample Nos. 29 and 31 were diluted to 20,000 times with water/methanol (volume ratio 1/1), Sample Nos. 30 and 32 were diluted to 10,000 times with water/methanol (volume ratio 1/1), the ultraviolet and visible absorption spectra were measured about these diluted samples, and the absorption of each solution obtained from each dispersion showed the same spectrum. It was also confirmed that at mixing with gelatin and during storing in the cold dark place, the chemical decomposition of the spectral sensitizer in each dispersion did not occur.

[0068] As described above, by the dispersion method of the present invention, the high-concentrate dispersion of a spectral sensitizer, which has never been obtained by conventional methods, can be prepared without increasing the viscosity thereof.

[0069] Furthermore, because the mixed composition was prepared using a water-soluble polymer by the dispersion method of the present invention, the dispersion of the spectral sensitizer prepared can be stably stored for long period of time as 1 month or longer by simply cooling it without need of drying, etc.

5 Claims

1. A dispersion method of a spectral sensitizer, which comprises:

dissolving an inorganic salt in an amount of at least 0.5% by weight in water which does not substantially contain any of a surface active agent, an organic solvent and a silver halide emulsion to prepare a dissolved solution;

adding to the dissolved solution a spectral sensitizer in an amount of at least 0.5% by weight; and dispersing the spectral sensitizer as fine solids to prepare a water dispersion of the spectral sensitizer.

2. A dispersion method of a spectral sensitizer according to claim 1, which comprises:

dissolving an inorganic salt in an amount of at least 0.5% by weight in water which does not substantially contain any of a surface active agent, an organic solvent and a silver halide emulsion to prepare a dissolved solution;

adding to the dissolved solution a spectral sensitizer in an amount of from 2% by weight to 30% by weight; and dispersing the spectral sensitizer as fine solids to prepare a water dispersion of the spectral sensitizer.

3. A dispersion method of a spectral sensitizer accordingly to claim 1, wherein the dissolved solution obtained by dissolving the inorganic salt in an amount of at least 0.5% by weight in water which does not substantially contain a surface active agent, an organic solvent and a silver halide emulsion has a pH of 4 to 10.

4. A dispersion method of a spectral sensitizer accordingly to claim 3, wherein the dissolved solution obtained by dissolving the inorganic salt in an amount of at least 0.5% by weight in water which does not substantially contain a surface active agent, an organic solvent and a silver halide emulsion has a pH of 6 to 8.

5. A dispersion method of a spectral sensitizer according to any one of claims 1 to 4, wherein the weight ratio of the inorganic salt to the spectral sensitizer is at least 0.5.

6. A dispersion method of a spectral sensitizer of according to any one of claims 1 to 5, wherein the spectral sensitizer is a cyanine dye.

7. A dispersion method of a spectral sensitizer according to any one of claims 1 to 6, wherein the water dispersion of the spectral sensitizer is further mixed with a water-soluble polymer.

8. A dispersion method of a spectral sensitizer according to claim 7, wherein the concentration of the water-soluble polymer in water is at least 0.5% by weight.

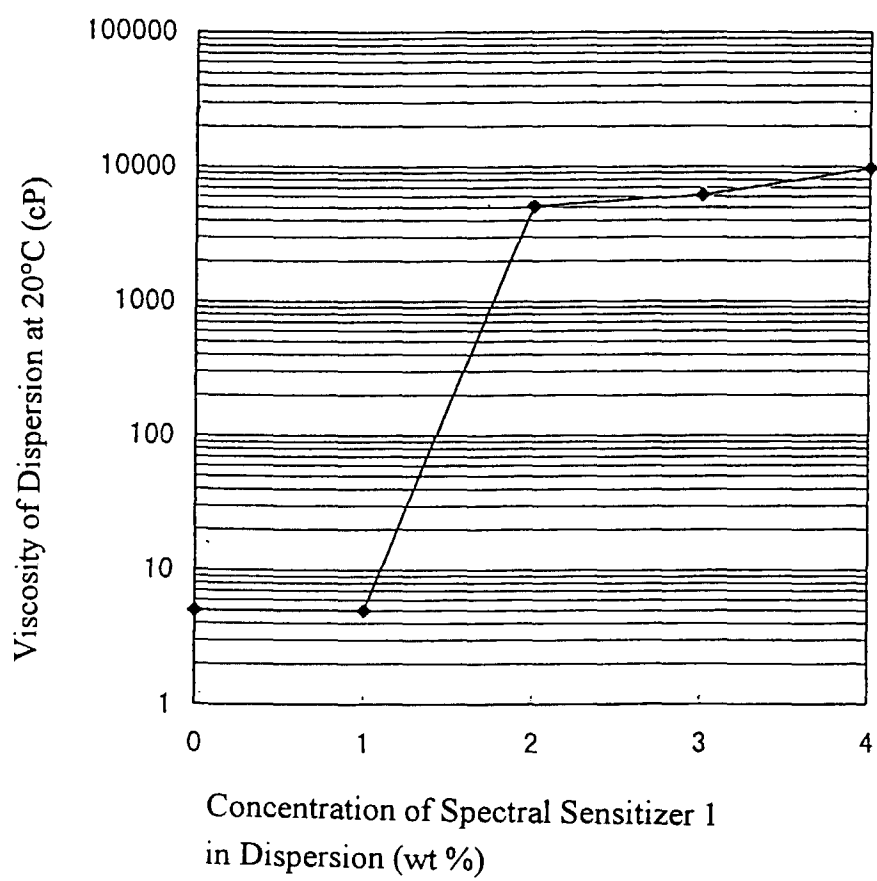
9. A dispersion method of a spectral sensitizer according to claim 7 or 8, wherein the water-soluble polymer is gelatin.

10. A dispersion which is obtained by the dispersion method according to claims 1 to 9.

Fig. 1



Fig. 2





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EUROPEAN SEARCH REPORT

Application Number
EP 98 11 4460

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.6)
Y	US 4 683 193 A (IHAMA ET AL.) 28 July 1987 * column 2, line 30 - line 50 * * column 2, line 63 - column 3, line 3 * * column 4, line 18 - line 24 * * column 8, line 55 - line 57 * * column 11, line 33 - line 52 * ---	1-4,6-10	G03C1/005
D,Y	US 4 006 025 A (SWANK ET AL.) 1 February 1977	1-4,6-10	
A	* column 1, line 67 - column 2, line 19 * * column 5, line 64 - column 6, line 10 * * column 6, line 19 - line 25 * * column 7, line 23 - line 37 * -----	5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 November 1998	Examiner Magrizos, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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