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(54) **Silver halide photographic materials.**

(57) A silver halide photographic material has at least one silver halide emulsion layer spectrally sensitized by spectral sensitizing dye(s), in which the silver halide emulsion layer contains in the hydrophilic dispersion medium a hydrophilic polymer having a cationic structure or a dispersion of the hydrophilic polymer and a luminous dye having a relatively weak adsorptive property to silver halide and simultaneously satisfying the conditions 1), 2), and 3), with the proviso that the light-collecting dye and the spectral sensitizing dye may be the same compound.

The conditions are:

1) the equilibrium adsorption amount of the dye in an aqueous 5% gelatin solution containing silver bromide the outer surface of which is substantially composed of a {III} plane is not more than 10^{-6} mole/m^2 per surface area of the silver bromide at a temperature of 40 °C, pH of 6.5 ±0.05, and a dye concentration in solution phase of 10^{-4} mole/liter;

2) the luminous quantum yield of the dye is at least 0.1 at room temperature and at a concentration in dry gelatin of 10^{-4} mole/dm^3; and

3) the dye has a luminous band at least partially overlapping the optical absorption band of the adsorptive spectral sensitizing dye on the silver halide.

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SILVER HALIDE PHOTOGRAPHIC MATERIALS

FIELD OF THE INVENTION

This invention relates to a novel technique for dye spectral sensitization of silver halide photographic materials. More specifically, the invention relates to a silver halide photographic material having greatly improved spectral sensitivity in the desired light-sensitive silver halide emulsion layer by incorporating a dye having a high luminousity and a relatively weak adsorptive property to silver halide in the dispersion medium of the spectrally sensitized light-sensitive silver halide emulsion and by co-existing a hydrophilic polymer having a mordanting power to the luminous dye or a dispersion of the hydrophilic polymer.

This invention is a fundamental technique of spectral sensitization on the whole silver halide photographic materials and the utilization field thereof includes all silver halide photographic materials such as negative, positive, and reversal black and white and color photographic light-sensitive materials.

BACKGROUND OF THE INVENTION

A method of spectrally sensitizing silver halide emulsions by dye(s) is a well-known technique and as the sensitizing dyes, methine series dyes such as cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, etc., are generally used. Also, as the case may be, a combination of two or more kinds of these dyes are used for expanding the color sensitizing wavelength region or giving a super color sensitizing effect. These sensitizing dyes are required to have a property of being adsorbed on the surfaces of silver halide grains as electron injection type sensitizing dyes. However, on the other hand, it is known that there is a limit in the adsorbing amount of sensitizing dyes onto the surfaces of silver halide grains and if sensitizing dyes are adsorbed in a saturated adsorption state or near the state, they frequently cause a severe desensitization (intrinsic desensitization) as described, e.g., in W.C. Lewis et al, Photographic Science and Engineering, Vol. 13, 54(1969). Also, at the same time, the surface coating of silver halide grains sometimes causes problems of development inhibition, etc. Accordingly, the percent absorption (utilization efficiency) of incident photons onto each silver halide grain in the spectral sensitizing region is very low at present. Thus, Bird et al disclose a method of adsorbing plural dyes onto silver halide grains in multilayer state in U.S. Patent 3,622,316 or adsorbing sensitizing dye molecules having plural cyanine chromophores onto silver halide grains in U.S. Patents 3,622,317 and 3,976,493 to increase the amount of absorbed light, whereby the silver halide grains are sensitized by the contribution of a Forster type excitation energy transfer. However, even by these methods, the limitation of the adsorbed area and the restriction by the intrinsic desensitization cannot be avoid and in fact, sufficient effects are not obtained by these methods.

On the other hand, Steiger et al disclose a sensitization method of chemically bonding fluorescent dyes such as cyanine dyes and xanthene dyes to colloid molecules which are a dispersion medium, such as gelatin, etc., and exciting the dyes adsorbed on the surface of silver halide grains or different kind of spectral sensitizing dyes by the Forster type energy transfer Th. Förster, Disc. Faraday Soc., Vol. 27, page 7, 1959) caused by the aforesaid dyes absorbing light energy or the optical absorption of the luminescence of the aforesaid dyes in Photographic Ecience Engineering, Vol. 27, 59(1983) and JP-A-51-117619. (The term "JP-A" as used herein means an "unexamined published Japanese Patent Application".) According to the method, dyes which are not directly adsorbed on silver halide grains also contribute to sensitization different from the Bird et al system.

However, since the aforesaid method is a means of dispersing spectral sensitizing dye having a strong adsorptive property in a medium, part of the dyes bonded to gelatin directly bond to silver halide grains. Accordingly, since the adsorbed dye acts as an energy acceptor, it is generally difficult to realize the optimum overlapping of the luminous band by a non-adsorbed dye and the absorption band of the adsorbed dye. This is a large restriction for attaining a high efficient energy transfer since the overlapping of a luminous band and an absorption band is principally necessary for the energy transfer in a Forster type energy transfer and the re-adsorption of luminescence. Furthermore, there is also a restriction that if dyes being used are of the type of causing desensitization when they are adsorbed on silver halide grains, the aforesaid method can not be used. Moreover, in the aforesaid method, complicated steps are required for the synthesis and purification of medium bonding type dyes being used, which greatly increases the production cost of the dyes.

Also, in the aforesaid method a light-collecting dye of high concentration is necessary but by practical restrictions that there is a limitation on the reactivity of the dye and the medium molecule and even if a high reactivity is realized, a sufficient hardening is reluctant to obtain since functional groups for the hardening treatment are lost, there is a limit on the amount of the dye being added.

Furthermore, the freedom of synthesizing and selecting such a medium bonding type luminous dye material is greatly restricted as compared to a method of simply dispersing an optional amount of a water-soluble luminous dye in a hydrophilic medium.

Finally, it is required to almost completely remove the lumonius dye in the processing steps for photographic light-sensitive materials, in the case of the dye fixed by chemical bonding, such a removal is impossible or requires a specific processing step.

For solving the aforesaid problems, a method of simply adding a water-soluble light-collecting dye having luminous property in a hydrophilic medium containing silver halide grains in JP-A-63-138341 and 63-138342.

However, in the case of using the method of simply adding a water-soluble luminous dye in a hydrophilic medium containing silver halide grains, since in, in particular, a photographic light-sensitive material having multilayer structure such as a color photographic material, the water-soluble light-collecting dye can freely diffuses into other layer(s), the light-collecting dye diffused into an upper layer on the light-sensitive emulsion layer being subjected to light-collecting sensitization has a prolonged transfer distance of a light-exiting energy, whereby the sensitization can not be expected as well as the dye has a fault of causing desensitization as a simple filter. This is true in black and white light-sensitive materials. That is, since a protective layer is generally formed on a light-sensitive emulsion layer in a black and white light-sensitive material, if the light-collecting dye diffuses into the protective layer, the occurrence of a sensitivity loss to some extent is unavoidable.

In this specification, the terms of "luminous dye" and "light-collecting dye" are used interchangeably.

SUMMARY OF THE INVENTION

An object of this invention is, therefore, to provide a silver halide photographic material wherein the light utilization is increased and the color sensitizing sensitivity is greatly improved by using light-collecting dye(s).

Other object of this invention is to provide a silver halide photographic material giving good photographic images without introducing desensitizing factors such as intrinsic desensitization and development inhibition by using light-collecting dye(s) having weak adsorptive property to silver halide grains.

A still other object of this invention is to provide a silver halide photographic material having plural layer structure, in which a light-collecting dye is fixed in a desired light-sensitive emulsion layer, functions the light-collecting sensitizing effect at light exposure, and is almost completely washed out at processing to give substantially no color residue.

As the result of various investigations, the inventors have succeeded in solving the aforesaid various problems by greatly increasing the utilization efficiency of light energy by a light-collecting sensitization method of utilizing the light absorption by a luminous dye dispersed in a hydrophilic medium and the subsequent light-exiting energy transfer, and also co-existing a cationic polymer in the medium, whereby the light-collecting dye is fixed in the desired light-sensitive emulsion layer to prevent the reduction of sensitivity by the diffusion of the light-collecting dye into other layer(s).

The aforesaid various objects of this invention have been attained by using a silver halide photographic material having at least one silver halide emulsion layer spectrally sensitized by spectral sensitizing dye(s), wherein the silver halide emulsion layer or other hydrophilic colloid contains in the hydrophilic dispersion medium a hydrophilic polymer having a cationic structure or a dispersion of the polymer and a luminous dye (light-collecting dye) which has a relatively weak adsorptive property to silver halide grains, is easily removed by photographic processing, and simultaneously meets the following conditions 1) to 3), with the proviso that the light-collecting dye and the spectral sensitizing dye may be the same compounnd;

1) the equilibrium adsorption amount thereof in an aqueous 5 wt.% gelatin solution containing 5% by weight silver bromide the outer surface of which is substantially composed of a {111} plane is not more than 10^{-6} mole/m^2 per area of silver bromide at a temperature of 40 °C, pH of 6.5 ± 0.05, and a dye concentration in liquid phase of 10^{-4} mole/liter,

2) the luminous quantum yield thereof is at least 0.1 at a concentration of 10^{-4} mole/dm^2 in dry gelatin at room temperature, and

3) the dye has a luminous band in the optical absorption band of a spectral sensitizing dye on silver halide grains, said luminous band, at least partially overlapping the optical absorption band.

DETAILED DESCRIPTION OF THE INVENTION

The luminous dye (light-collecting dye) for use in this invention is a dye having a high water solubility and a relatively weak adsorptive property to silver halide grains. The term "relatively weak adsorptive property" in this invention is defined as that the adsorptive power thereof is lower than 10^{-6} mole/m^2 to the outer surface of the {111} plane of silver bromide grain under the equilibrium concentration of 10^{-4} mole/liter in an aqueous 5 wt.% gelatin solution at a temperature of 40° C and pH of 6.5 ± 0.05. The adsorption amount is preferably less than 5×10^{-7} mole/m^2, and more preferably less than 10^{-7} mole/m^2.

The adsorption amount of a dye can be determined by a method of adding the dye to an emulsion containing 5% by weight gelatin, after stirring the emulsion for 18 hours at 40° C under safelight, separating the silver halide grains by centrifugal separation, and measuring the concentration of the dye in the supernatant liquid.

The adsorption amount of the light-collecting dye for use in this invention is as defined above for silver bromide but the adsorption amount is also preferably low as above for silver halide grains containing iodine or chlorine.

It is preferred that the luminous dye (light-collecting dye) for use in this invention has a sufficiently high water solubility, and preferably has a solubility of higher than 10^{-2} mole/liter for water at 25° C and pH 7.0. Also, it is preferred that when the luminous dye molecule in this invention is dissociated in water medium, the total static charges are negative. As a water-solubilizing group, a sulfonic acid group and a carboxylic acid group are particularly preferred and when the dye has at least 4 such anionic hydrophilic groups, the dye is imparted with a particularly high water solubility and at the same time becomes substantially non-adsorptive to silver halide. Furthermore, in this case the dye can be dissolved in a hydrophilic colloid of a silver halide emulsion layer at a high concentration as well as can be quickly and completely removed therefrom by water washing. The light-collecting dyes for use in this invention having a high water solubility and being substantially non-adsorptive to silver halide grains are not always limited to the molecule having the aforesaid structure but as the kind of the dyes, cyanine series dyes are particularly preferred in the points that water-solubilizing groups are easily introduced in the case of synthesizing the dyes and the dyes are excellent in luminous efficiency.

The quantum yield of the luminescence of the light-collecting dye for use in this invention is required to be higher than 0.1, preferably higher than 0.8, and more preferably higher than 0.5 at a concentration of 10^{-4} mole/dm^2 in dry gelatin medium at room temperature.

The luminous quantum yield of the light-collecting dye in dry layer can be fundamentally measured by the same method for measuring the luminous quantum yield in a solution and usually by referring to a standard sample (e.g., rhodamine B, quinine sulfate, and 9,10-diphenylanthracene) having a known absolute quantum yield, the luminous quantum yield of the dye can be obtained by a relative measurement of comparing the intensity of incident light, the light absorption coefficient of the sample, and the luminous intensity of the sample. The relative measurement method is described, for example, in C.A. Parker and W.T. Rees, Analyst, Vol. 85, 587(1960).

Accordingly, the luminous quantum yield of the light-collecting dye in dry gelatin defined in this invention can be easily obtained by performing the aforesaid relative measuring method by referring to a dry gelatin film (sheet form sample) having a known absolute quantum yield, in which a standard luminous dye is dispersed at an optional concentration. The inventors measured the luminous absolute quantum yield on a dry film of a standard sample by the following method.

Measurement Method of Absolute Luminous Quantum Yield of Standard Sample:

As a standard dye, fluorescent N-phenyl-1-naphthylamine-8-sulfonic acid having no contribution of re-absorption by overlapping of the absorption band and the luminous band was selected and gelatin containing the compound was uniformly coated on a transparent support followed by drying to provide a standard sample having a dye concentration in the dry layer of 10^{-2} mole/dm^2 and a gelatin coverage of 6 g/m^2. Thereafter, the sample was set in the inside of an integrating sphere the inside wall of which was coated with white powder ($BaSO_4$), the sample was irradiation with monochromatic excited light of 380 n.m., and the intensities of the excited light and fluorescence were detected by a photomultiplier equipped to the window of the integrating sphere. In this case the light absorption coefficient A of the sample was measured by mounting a fluorescent cutting filter on the photomultiplier and comparing the intensity of the excited light between the case of setting the sample and the case of not setting the sample. On the other hand, about the fluorescent component from the sample, the fluorescent integrating intensity F' was measured by mounting an excited light cutting filter in place of the aforesaid filter. Also, after converting the fluorescent integrating intensity F' and an incident monochromatic light intensity I' measured in the same measurement system as above without the sample and filter into the forms of the true relative photon numbers F and I, respectively based on the spectral transmittance of the excited light cutting filter, the effective spectral relfectance of the integrating sphere, the spectral sensitivity of the photomultiplier, etc, the absolute fluorescent quantum yield was calculated from $F/(I \bullet A)$.

From the relative measurement of the luminous quantum yield based on the standard sample having the known absolute luminous quantum yield thus obtained, the luminous quantum yield of water-soluble cyanine series dyes which were typical light-collecting dyes in this invention in dry gelatin layer was measured.

In the dyes having high luminous property for use in this invention, it is preferred that a so-called stoke shift, i.e., the distance between the wavelength of the absorption peak and the wavelength of the luminous peak is sufficiently small from the purpose of increasing the overlapping of the absorption band and the luminous band and also increasing the energy transfer efficiency. The stoke shift for increasing the energy transfer efficiency is preferably within 40 n.m., and more preferably within 20 n.m. at a concentration in dry gelatin layer of 10^{-4} mole/dm^2 at room temperature. The stoke shift having sufficiently small value within 20 n.m. can be found in many cyanine dyes.

Since the light-collecting dye for use in this invention gives a luminous band sufficiently overlapping the absorption band given by the adsorption seeds of blue, orthomatic, or panchromatic sensitizing dyes which are generally used for black and white and silver halide color photographic light-sensitive materials, and further it is preferred for effective purpose that the stokes shift is relatively short as described above, the maximum adsorption wavelength of the light-collecting dye is preferably longer than 400 n.m., more preferably longer than 420 n.m., and particularly preferably from 420 n.m. to 740 n.m.

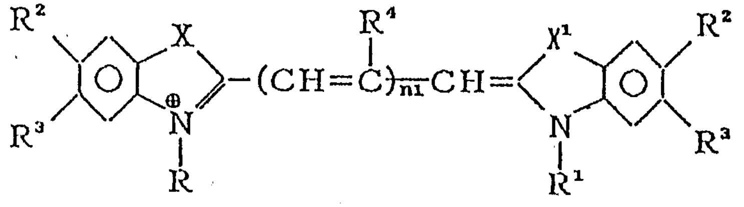
As the kind of the light-collecting dyes for use in this invention, cyanine series dyes are particularly preferred in the points of the luminous quantum yield and the stokes shift as described above. In regard to cyanine series dyes, D.F. O'Brien et al reported the fluorescent yields of the dyes in solution or other materials in Photographic Science Engineering, Vol. 18, 76(1974) and about oxacarbocyanine derivatives, the value of 0.75 was obtained in gelatin. Furthermore, as other kind of dyes having a high luminous quantum yield, there are typical dyes having a skeleton structure of dyes which are used for dye laser. Examples of these dyes are described, for example, in Mitsuo Maeda, Laser Kenkyo (Research), Vol. 8, pages 694, 803, and 958(1980), ibid., Vol. 9, page 85(1981), and F.P. Schaefer, Dye Lasers, Springer (1973). Many of these dyes are originally poor in water solubility but by introducing plural sulfonic groups or carboxylic groups as in this invention into the molecular structures thereof, they are imparted with water solubility and relatively weak adsorptive property and they can be suitably used as the light-collecting sensitizing dyes in this invention.

Then, the typical kinds of the light-collecting dyes for use in this invention are illustrated below but the invention is not limited to them.

I Water-soluble cyanine dyes, water-soluble merocyanine dyes
II Xanthene series dyes
III Acridine series dyes
IV Oxazine series dyes
V Thiazine series dyes
VI Riboflavin series dyes
VII Triarylmethane series dyes
VIII Aminonaphthalene series dyes
IX Pyrene series dyes
X Coumarine series dyes
XI Porphyrin series dyes

XII Phthalocyanine series dyes

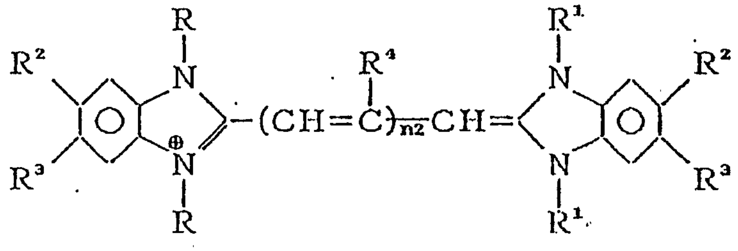
Then, specific examples of the non-adsorptive luminous dyes particularly preferred in this invention are illustrated below but the skeletone structures and substituents are not limited to them.



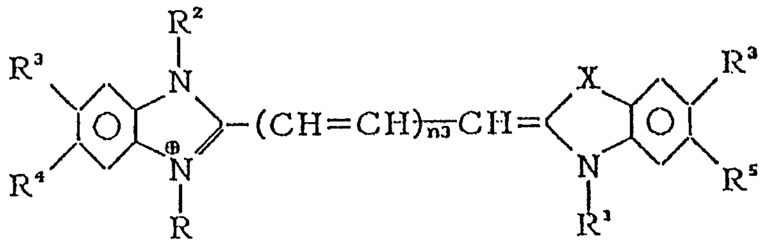
	X	X1	R	R1	R2	R3	R4	n1
A-1	0	0	$(CH_2)_4SO_3^{\ominus}$	$(CH_2)_4SO_3Na$	CO_2Na	H	H	1
A-2	0	0	"	"	SO_3Na	H	H	1
A-3	0	0	"	$(CH_2)_4SO_3K$	H	SO_3K	-	0
A-4	0	0	$(CH_2)_4SO_3^{\ominus}$	$(CH_2)_2SO_3Na$	$SO_2(CH_2)_2SO_3Na$	H	H	1
A-5	0	0	"	"	$SO_2NH(CH_2)_2SO_3Na$	H	H	1
A-6	0	0	$(CH_2)_3CO_2^{\ominus}$	$(CH_2)_3CO_2H$	$O(CH_2)_3SO_3H$	SO_3H	CH_3	1
A-7	0	0	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3Na$	$CONH(CH_2)_2SO_3Na$	H	H	1
A-8	0	0	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3K$	$N(CH_2CH_2SO_3K)_2$	H	H	1
A-9	0	0	C_2H_5	C_2H_5	SO_3Na	SO_3Na	H	1

	X	X^1	R	R^1	R^2	R^3	R^4	n_1
A-10	0	0	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3Na$	CH_2CO_2Na	Cl	H	1
A-11	0	0	$(CH_2)_4SO_3^{\ominus}$	$(CH_2)_4SO_3H$	CO_2H	H	–	0
A-12	0	0	"	"	H	SO_3H	H	2
A-13	0	0	"	$(CH_2)_4SO_3K$	$SO_2(CH_2)_2SO_3K$	H	H	3
A-14	S	S	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3Na$	H	CH_2Na	H	1
A-15	S	S	"	"	SO_3Na	H	CH_3	1
A-16	S	S	$(CH_2)_2SO_3^{\ominus}$	$(CH_2)_2SO_3Na$	$SO_2(CH_2)_2SO_3Na$	Cl	H	1
A-17	S	S	"	"	$CONH(CH_2)_2SO_3Na$	H	H	1
A-18	S	S	$(CH_2)_3CO_2^{\ominus}$	$(CH_2)_3CO_2H$	$O(CH_2)_3SO_3H$	H	H	1
A-19	S	S	CH_3	CH_3	CH_2SO_3K	SO_3K	H	1
A-20	S	S	$(CH_2)_4SO_3^{\ominus}$	$(CH_2)_4SO_3Na$	H	CO_2Na	–	0
A-21	S	S	"	"	SO_3Na	H	–	0
A-22	S	S	$(CH_2)_2SO_3^{\ominus}$	$(CH_2)_2SO_3Na$	SO_3Na	SO_3Na	H	2

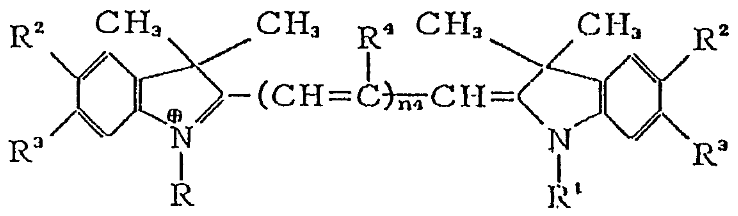
	X	X^1	R	R^1	R^2	R^3	R^4	n_1
A-23	S	S	$(CH_2)_2SO_3^{\ominus}$	$(CH_2)_2SO_3Na$	SO_3Na	H	H	2
A-24	0	S	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3H$	CO_2H	H	–	0
A-25	0	S	"	"	SO_3Na	H	H	1
A-26	0	S	"	"	SO_3Na	Cl	H	1
A-27	0	S	"	$(CH_2)_4SO_3Na$	H	$O(CH_2)_2SO_3Na$	H	1
A-28	0	S	"	"	H	SO_3Na	H	2
A-29	0	S	"	"	SO_3Na	H	CH_3	2



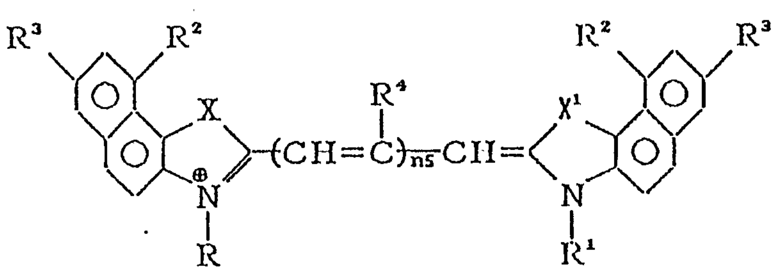
	R	R1	R2	R3	R4	n2
A-30	$(CH_2)_3SO_3^{\ominus}$	CH_2SO_3Na	CF_3	H	H	1
A-31	"	"	H	Cl	H	1
A-32	"	"	$(CH_2)_4SO_3Na$	H	H	1
A-33	"	CH_2CO_2K	$(CH_2)_4SO_3K$	$(CH_2)_4SO_3K$	CH_3	1
A-34	"	$(CH_2)_3SO_3K$	CF_3	H	H	1
A-35	"	"	CO_2K	Cl	H	2
A-36	"	CH_2CO_2K	H	Cl	H	2
A-37	"	CH_2SO_3H	$(CH_2)_4SO_3H$	H	H	3



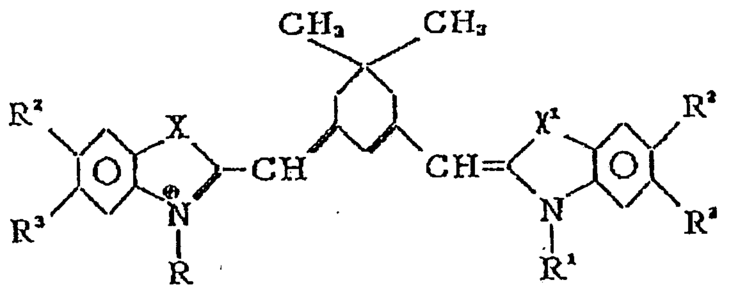
	X	R	R1	R2	R3	R4	R5	n3
A-38	S	$(CH_2)_4SO_3^{\ominus}$	$(CH_2)_4SO_3K$	CH_2CO_2K	H	CF_3	CO_2K	1
A-39	S	"	"	$(CH_2)_4SO_3K$	CO_2K	H	CO_2K	1
A-40	S	"	"	"	H	$(CH_2)_4SO_3K$	$O(CH_2)_2SO_3K$	1
A-41	S	"	C_2H_5	"	H	CH_2CO_2K	CH_2CO_2K	1
A-42	S	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3Na$	CH_2CO_2Na	H	CF_3	SO_3Na	2
A-43	S	"	"	"	H	Cl	"	0
A-44	0	"	"	CH_2CO_2Na	H	Cl	CO_2Na	1
A-45	0	$(CH_2)_2SO_3^{\ominus}$	$(CH_2)_2SO_3Na$	CH_2SO_3Na	H	Cl	"	2
A-46	0	"	"	"	H	Cl	"	3



	R	R1	R2	R3	R4	n_4
A-47	$(CH_2)_4SO_3^{\ominus}$	$(CH_2)_4SO_3K$	SO_3K	H	H	1
A-48	"	$(CH_2)_4SO_3H$	SO_3H	H	H	1
A-49	"	"	CH_2CO_2K	Cl	H	1
A-50	$(CH_2)_2O(CH_2)_3SO_3^{\ominus}$	$(CH_2)_2O(CH_2)_3SO_3K$	SO_3K	H	H	1
A-51	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3Na$	$(CH_2)_2CO_2Na$	H	H	1
A-52	"	"	SO_3Na	H	Cl	1
A-53	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3Na$	CH_2CO_2Na	H	–	0
A-54	$(CH_2)_2CO_2^{\ominus}$	$(CH_2)_2CO_2Na$	SO_3Na	H	–	0
A-55	C_2H_5	C_2H_5	SO_3Na	SO_2Na	H	2
A-56	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3Na$	CO_2Na	H	H	2

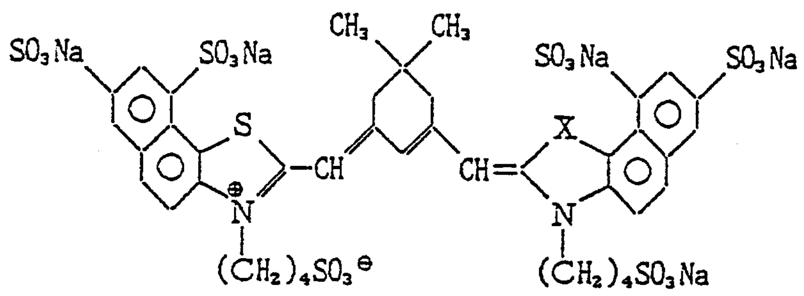


	X	X1	R	R1	R2	R3	R4	n_5
A-57	0	0	$(CH_2)_3SO_3^{\ominus}$	$(CH_2)_3SO_3Na$	SO_3Na	SO_3Na	–	0
A-58	0	0	"	"	"	"	CH_3	1
A-59	0	0	"	"	CO_2Na	CO_2Na	H	2
A-60	S	S	C_2H_5	C_2H_5	SO_3Na	SO_3Na	H	1
A-61	S	S	$CH_2CO_2^{\ominus}$	CH_2CO_2K	"	"	–	0
A-62	0	S	$(CH_2)_4SO_3^{\ominus}$	$(CH_2)_4SO_3K$	"	"	H	1
A-63	0	S	"	"	"	"	H	2
A-64	NCH_3	NCH_3	"	"	"	"	H	1
A-65	NCH_3	S	"	"	"	"	H	1
A-66	NCH_3	0	"	"	"	"	H	1



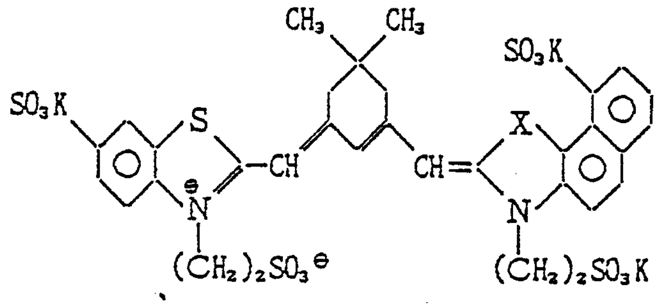
	X	X1	R	R1	R2	R3
A-67	S	S	$(CH_2)_3SO_3^\ominus$	$(CH_2)_3SO_3Na$	SO_3Na	H
A-68	S	S	〃	$(CH_2)_3SO_3^-K$	CO_2K	H
A-69	S	O	〃	〃	H	SO_3K
A-70	S	O	〃	〃	OCH_2SO_3K	H

A-71



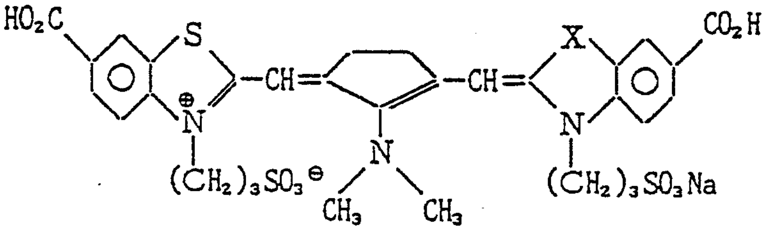
X=S, O

A-72



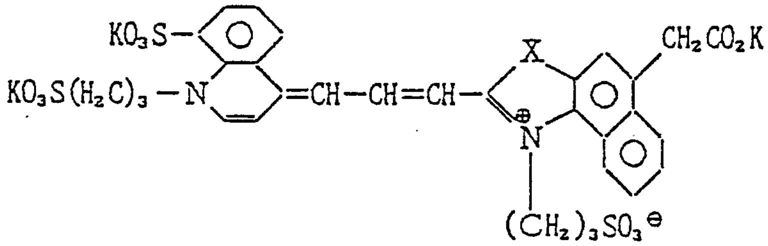
X=S, O

A-73



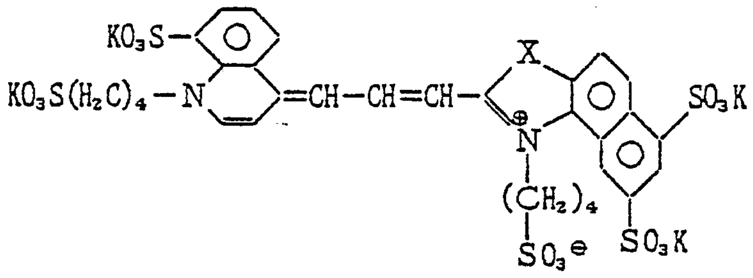
X=S, O

A-74



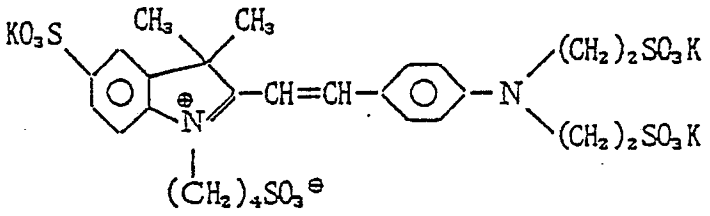
X=S, O

A-75



X=S, O

A-76



The adsorption amounts of the aforesaid light-collecting dyes A-1 to A-76 to silver bromide measured by a centrifugal separation method under the conditions described in the claim of this invention were all less than 10^{-6} mole/m^2 and the luminous quantum yields thereof measured under the conditions described in the claim were all above 0.1. In particular, the luminous quantum yields of the dyes A-1 to A-11 and A-47 to A-54 were all high as above 0.7.

The aforesaid cyanine dyes for use in this invention can be synthesized based on the various methods described, e.g., in F.M. Hamer, The Cyanine Dyes and Related Compounds, Interscience, New York (1964). Typical Synthesis methods are shown below.

Synthesis of Compound A-1:

In a 100 ml flask equipped with a stirrer were placed 6.3 g of 4-(6-carboxy-2-methylbenzoxazolio-3)-butane sulfonate, 12 g of ethyl o-formate, 18 ml of pyridine, and 7 ml of acetic acid and the mixture was stirred in an oil bath pre-heated to 140° C for 1.5 hours. Thereafter, the mixture was allowed to cool and crystals precipiated were collected by filtration. The crystals were washed with acetone and then methanol, and thereafter dissolved in methanol added with triethylamine. After removing insoluble matters by filtration, a methanol solution of sodium iodide was added to the solution and crystals precipiated were collected by filtration and washed with methanol under heating. By drying the crystals thus obtained under reduced pressure, the desired product was obtained.

Amount 4.11 g (yield 58.5%), melting point above 300C,

λ^{MeOH}_{Max} = 496 n.m. (ϵ = 1.32 x 10^5).

Synthesis of Compound A-47:

In a one liter flask equipped with a stirrer were placed 69 g of 4-(2,3,3-trimethyl-5-sulfo-3H-indolio-3)-butane sulfonate, 55 ml of ethyl o-formate, 69 ml of acetic acid, and 150 ml of pyridine and the mixture was stirred in an oil bath pre-heated to 140° C for one hour. After allowing to stand the reaction mixture, 400 ml of acetone was added and after removing the supernatant liquid by decantation, the residue thus formed was dissolved in 500 ml of methanol. Then, a methanol solution of potassium acetate and the mixture was refluxed for 10 minutes. Crystals precipitated were collected by filtration and washed with isopropanol. Then, by releasing the re-crystallization from water and isopropanol and drying the crystals obtained under reduced pressure, the desired product was obtained.

Yield 41.2 g (yield 52.3%), melting point above 300° C,

λ^{MeOH}_{Max} = 555 n.m. (ϵ = 1.33 x 10^5).

The light-sensitive silver halide grains for the silver halide photographic materials of this invention are a dispersion of fine grains, have an adsorbed layer of a spectral sensitizing dye on the surface thereof, and have been spectrally sensitized by the spectral sensitizing dye. Furthermore, outside of the adsorbed layer of spectral sensitizing dye, there exists a hydrophilic colloid medium in which the water-soluble light-collecting dye molecule in this invention is uniformly dispersed and the medium is in a body with the aforesaid light-sensitive silver halide grains to form a light-sensitive element. In this case the light-collecting dye dispersed in a hydrophilic colloid medium exists in a state that the chromophores thereof are not directly adsorbed on the light-sensitive silver halide grains.

In this invention the light-collecting dye is preferably added to a silver halide emulsion layer containing an adsorptive spectral sensitizing dye.

In the photographic light-sensitive materials of this invention the addition amount of the light-collecting dye in a dispersion medium is preferably at least 2 x 10^{-3} mole/dm^2 and more preferably at least 10^{-2} mole/dm^2 as concentration. In this case the term "concentration" is a concentration per dry amount of the dispersion medium exclusive of silver halide grains and adsorption seeds on the surface of the grains. Also, if the addition concentration is too high, the sensitizing efficiency sometimes is saturated or reduced, the concentrations is preferably less than 10^{-1} mole/dm^2 in this meaning.

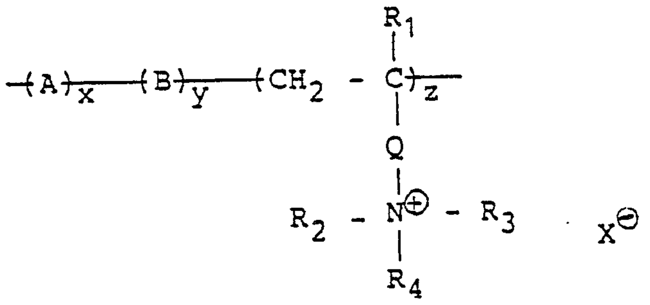
The light-collecting dyes in this invention can be also used as a mixture of plural dyes and in this case it is required that at least a part of the luminous wavelength bands of these dyes overlaps the optical absorption band of the at least one kind of sensitizing dye adsorbing on silver halide grains. Substantially, the maximum luminous wavelength of the light-collecting dye giving the maximum luminescence to the longest wavelength in these dyes is preferably disposed near the maximum absorption wavelength of the adsorbed sensitizing dye receiving energy transfer, and, in particular, is preferably disposed within 60 n.m., more preferably within 30 n.m. from the maximum absorption wavelength to a shorter wavelength side. In particular, when plural adsorption dyes are co-adosrobed on the silver halide, the wavelength giving the luminous maximum of the luminous dye is preferably not over the wavelength of the maximum absorption of the dye having absorption at the longest wavelength region in the dyes adsorbedd on the silver halide. Also, it is preferred for the Forster type energy transfer that the overlap of the absorption band and the luminous band given by the light-collecting dyes in a medium is large, and the so-called stroke shift, e.i., the difference between the maximum absorption wavelength and the maximum luminous wavelength is preferably within 40 n.m., and particularly preferably within 20 n.m.

The light-collecting dyes for use in this invention can be used together with a proper surface active agent and organic additives such as a solubilizing agent and an association preventing agent.

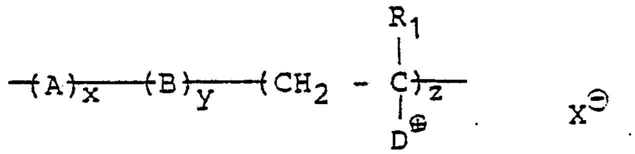
It is preferred that the light-collecting dyes for use in this invention are quickly removed from the photographic light-sensitive materials by photographic processing or washing or are decomposed and bleached during processing. In this case it is more preferred that the light-collecting dyes are of the type of being discolored by hydrolysis, etc., in an alkaline aqueous solution after removed from the light-sensitive materials.

In this invention, it is preferred that the reduction potential of the light-collecting dyes for use in this invention is baser than 0.10 volt to a standard calomel reference electrode in a mixture of water and methanol (1 : 1). The reduction portential of dyes can be measured according to the description of Tadaaki Tani et al, Denski Kagaku (Electrochemistry), Vol. 34, 149(1966).

The polymers having a cationic structure, which are preferably used in this invention, are shown by following formula (I), (II), or (III);

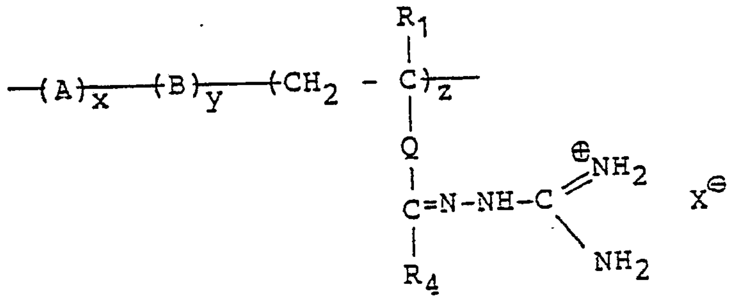


(I)



(II)

$$-(A)_x-(B)_y-(CH_2-\underset{D^{\oplus}}{\overset{R_1}{C}})_z- \quad X^{\ominus}$$

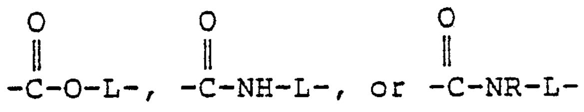


(III)

In the above formulae, A represents a monomer unit having at least two copolymerizable ethylenically unsaturated groups and copolymerized with a copolymerizable monomer having at least one of the aforesaid ethylenically unsaturated groups at the side chain thereof; B represents a monomer unit copolymerized with a copolymerizable ethylenically unsaturated monomer; R_1 represents a hydrogen atom, a lower alkyl group, or an aralkyl group; and R_2, R_3, and R_4, which may be the same or different, each represents a hydrogen atom, an alkyl group, or an aralkyl group.

In formula (I), optional two or three groups of R_2, R_3, and R_4 may form a 5-membered or 6-membered ring or such a heterocyclic ring together with nitrogen atom.

In the aforesaid formulae, Q represents an alkylene group, a phenylene group, an aralkylene group,



$$-\overset{\overset{O}{\|}}{C}-O-L-,\quad -\overset{\overset{O}{\|}}{C}-NH-L-,\ \text{or}\ -\overset{\overset{O}{\|}}{C}-NR-L-$$

(wherein L represents an alkyl group, an arylene group, or an aralkylene group and R represents an alkyl group).

In formula (III), Q may be a single bond.

In the aforesaid formulae, $X^{\ominus}$ represents an anion; $D^{\oplus}$ represents a 5-membered or 6-membered heterocyclic ring having 1 or 2 nitrogen atoms, wherein the nitrogen atom is positively charged; $D^{\oplus}$ may have substituent; x, y, and z represent mole percentage, and x is from 0 to 60 mole%, y is from 0 to 60 mole%, and z is from 30 to 100 mole%.

Then, preferred embodiments of the polymers shown by formulae (I), (II), and (III) described above are explained in detail.

In the aforesaid formulae, examples of the monomer shown by A are divinylbenzene, ethylene glycol methacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, 1,6-hexanediol diacrylate, meopentyl glycol dimethacrylate, and tetramethylene glycol dimethacrylate. In these monomers, divinylbenzene and ethylene glycol dimethacrylate are particularly preferred.

Examples of the ethylenically unsaturated monomer shown by B are ethylene, propylene, 1-vinyltoluene, monoethylenically unsaturated esters of alipathic acids (e.g., vinyl acetate and allyl acetate), amides of ethylenically unsaturated monocarboxylic acid or dicarboxylic acid (e.g., acrylamide, methacrylamide, N-methylacrylamide, and N-tert-butylacrylamide), esters if ethylenically unsaturated monocarboxylic acid or dicarboxylic acid (e.g., methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, n-hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, n-butyl acrylate, n-hexyl acrylate, and 2-ethylhexyl acrylate), monoethylenically unsaturated compounds (e.g., acrylonitrile), and dienes (e.g., butadiene and isoprene). In these monomers styrene, n-butyl methacrylate and cyclohexyl methacrylate and particularly preferred.

B may contain two or more kinds of the aforesaid monomers.

In the aforesaid formulae R_1 preferably represents a hydrogen or a lower alkyl group having from 1 to 6 carbon atoms (e.g., methyl, ethyl, n-propyl, n-butyl, n-amyl, and n-hexyl) and is particularly preferably a hydrogen atom or a methyl group.

R_2, R_3, and R_4, which may be the same or different, each is preferably a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms. The alkyl group and the aralkyl group include substituted alkyl groups and substituted aralkyl groups, respectively.

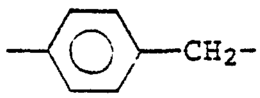
Also, optional two or three groups of R_2, R_3, and R_4 may combine with each other to form a 5-membered or 6-membered ring structure or such a heterocyclic structure together with nitrogen atom.

Examples of the aforesaid alkyl group are unsubstituted alkyl groups (e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-amyl, isoamyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, and n-dodecyl), the carbon atom number of said alkyl group being preferably from 1 to 6, and substituted alkyl groups such as alkoxyalkyl groups (e.g., methoxymethyl, methoxyethyl, methoxybutyl, butoxyethyl, butoxypropyl, butoxybutyl, and vinyloxyethyl), cyanoalkyl groups (e.g., 2-cyanoethyl, 3-cyanopropyl, and 4-cyanobutyl), halogenated alkyl groups (e.g., 2-fluoroethyl, 2-chloroethyl, and 3-fluoropropyl), alkoxycarbonylalkyl groups (e.g., ethoxycarbonylmethyl), an allyl group, 2-butenyl group, and a propargyl group.

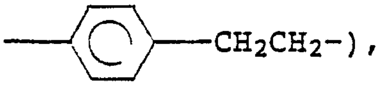
Examples of the aforesaid aralkyl group are unsubstituted aralkyl groups (e.g., benzyl, phenetyl, diphenylmethyl, and naphthylmethyl) and substituted aralkyl groups such as alkylaralkyl groups (e.g., 4-methylbenzyl, 2,5-dimethylbenzyl, and 4-isopropylbenzyl), alkoxyaralkyl groups (e.g., 4-methoxybenzyl, 4-ethoxybenzyl, and 4-(4-methoxyphenyl)benzyl), cyanoaralkyl groups (e.g., 4-cyanobenzyl and 4-(4-cyanophenyl)benzyl), perfluoroaralkyl groups (e.g., 4-pentafluoropropoxybenzyl and 4-undecanefluorohexylbenzyl), and halogenated aralkyl groups (e.g., 4-chlorobenzyl, 4-bromobenzyl, 3-chlorobenzyl, 4-(4-chlorophenyl)benzyl, and 4-(4-bromophenyl)benzyl). The carbon atom number of the aralkyl group is preferably from 7 to 14. In the aforesaid groups, a benzyl group is particularly preferred.

Examples of the ring structure formed by the combination of optional two or three groups of R_2, R_3, and R_4 together with nitrogen atom are a pyrrolidine ring, a piperidine ring, a morpholine ring, and quinuclidine ring.

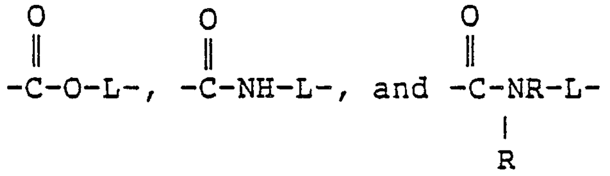
In the aforesaid formulae, Q is preferably a divalent alkylene group having from 1 to 12 carbon atoms (e.g., methylene or a group shown by $-(CH_2)_6$), a phenylene group, or an aralkyl group having from 7 to 12 carbon atoms (e.g., a group shown by



or



and also the groups shown by the following formulae are preferred as Q;



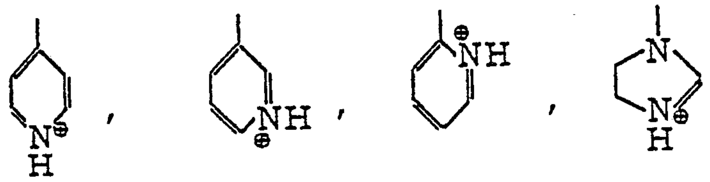
$$-\overset{\overset{O}{\|}}{C}-O-L-,\quad -\overset{\overset{O}{\|}}{C}-NH-L-,\quad \text{and}\quad -\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{N}-L-$$

(wherein L is preferably an alkylene group having from 1 to 6 carbon atoms, an arylene group, or an aralkylene group having from 7 to 12 carbon atoms and R is preferably an alkyl group having from 1 to 6 carbon atoms).

In formula (III), Q is also preferably a single bond.

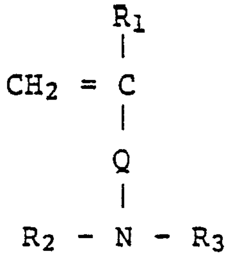
In the aforesaid formulae, $X^{\ominus}$ represents an anion and examples of the anion are halogen ions (e.g., chloride ions and bromide ions), alkylsulfonate ions or arylsulfonate ions (e.g., methanesulfonate ions, ethanesulfonate ions, benzenesulfonate ions, and p-toluenesulfonate ions), acetate ions, sulfate ions, and nitrate ions and in these anions, chloride ions, acetate ions, sulfate ions, and nitrate ions are particularly preferred.

Examples $D^{\oplus}$ are preferably as follows;



Also, in the aforesaid formulae, X is from 0 to 60 mole%, preferably from 0 to 40 mole%, and more preferably from 0 to 20 mole%; y is from 0 to 60 mole%, preferably from 0 to 40 mole%, and more preferably from 0 to 20 mole%; and z is from 30 to 100 mole%, preferably from 40 to 90 mole%, and more preferably from 50 to 90 mole%.

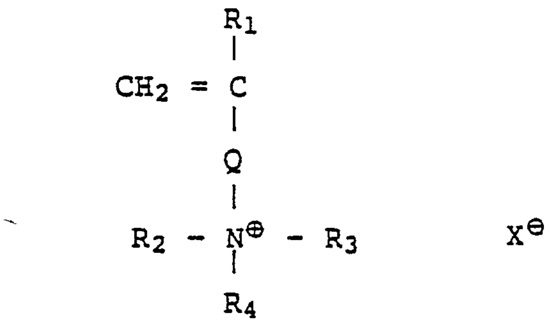
The polymer mordant shown by formula (I) described above for use in this invention can be generally obtained by polymerizing the copolymerizable monomer (A) having at least two ethylenically unsaturated groups described above, the ethylenically unsaturated monomer (B), and an unsaturated monomer shown by the following formula



$$CH_2=\underset{\underset{\underset{\underset{\underset{R_2-N-R_3}{|}}{Q}}{|}}{}}{\overset{\overset{R_1}{|}}{C}}$$

(wherein R_1, R_2, R_3, and Q have the same significance as described above), such as N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, N-(N,N-dimethylaminopropyl)acrylamide, N-(N,N-dihexylaminomethyl)-acrylamide, 3-(4-pyridyl)propyl acrylate, N,N-diethylaminomethylstyrene, 2-vinylpyridine, or 4-vinylpyridine, and particularly preferably N,N-diethylaminoethyl methacrylate or N,N-diethylaminomethylstyrene, and then converting the product into an ammonium salt thereof by a compound having a structure of R_4-X (wherein R_4 and X are same as defied above), such as hydrochloric acid, nitric acid, sulfuric acid, p-toluenesulfonic acid, acetic acid, methyl chloride, ethyl chloride, isopropyl chloride, benzyl chloride, etc.

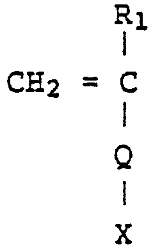
Also, the polymer mordant shown by formula (I) for use in this invention can be obtained by polymerizing the copolymerizable monomer (A) having at least two ethylenically unsaturated groups, the ethylenically unsaturated monomer (B) described above, and an unsaturated monomer shown by the formula;



$$CH_2=\underset{\substack{|\\ Q\\ |\\ R_2-\underset{\substack{|\\ R_4}}{N^{\oplus}}-R_3}}{\overset{\substack{R_1\\ |}}{C}}\qquad X^{\ominus}$$

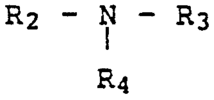
(wherein R_1, R_2, R_3, R_4, X and Q are same as defined above), such as N,N-dimethylaminoethyl methacrylate hydrochloride, N,N-diethylaminoethyl methacrylate sulfate, N,N-dimethylaminoethyl acrylate hydrochloride, N,N-diethylaminoethyl acrylate acetate, N-(N,N,N-trimethylaminopropyl)acrylamide chloride, N-(N,N,N-trihexylaminomethyl)acrylamide chloride, 3-(4-N-methylpyridyl)propyl acrylate-p-toluenesulfonate, N,N-diethylaminomethylstyrene sulfate, 2-vinylpyridine hydrochloride, 4-vinylpyridine hydrochloride, and particularly preferably N,N-diethylaminoethyl methacrylate acetate or N,N-diethylaminomethylstyrene sulfate.

Furthermore, the polymer mordant shown by formula (I) for use in this invention can be obtained by polymerizing the copolymerizable monomer (A) having at least two ethylenically unsaturated groups, the ethylenically unsaturated monomer (B), and an unsaturated monomer shown by the formula



$$CH_2=\underset{\substack{|\\ Q\\ |\\ X}}{\overset{\substack{R_1\\ |}}{C}}$$

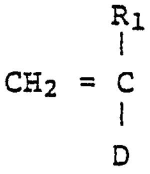
(wherein R_1, Q, and X are same as defined above), such as β-chloroethyl methacrylate, β-p-toluenesulfonylethyl methacrylate, and chloromethylstyrene and then converting the product into an ammonium salt by an amine having the structure



$$R_2-\underset{\substack{|\\ R_4}}{N}-R_3$$

(wherein R_2, R_3, and R_4 are same as defined above), such as dimethylamine, diethylamine, diisopropylamine, morphiline piperazine trimethylamine, methylmorpholine, and trihexylamine.

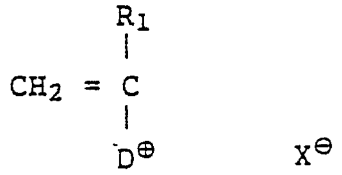
Also, the polymer mordant shown by formula (II) for use in this invention can be obtained by polymerizing the copolymerizable monomer (A) having at least two ethylenically unsaturated groups, the ethylenically unsaturated monomer (B), and an unsaturated monomer shown by the formula



$$CH_2=\underset{\substack{|\\ D}}{\overset{\substack{R_1\\ |}}{C}}$$

(wherein R_1 is same as defined above and D represents a 5-membered or 6-membered heterocyclic ring having 1 or 2 carbon atoms, and D may have substituent), such as 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, 1-vinyl-imidazole, and 2-methyl-4-vinylpyridine, and then converting the product into an ammonium salt by a compound shown by the formula R_4 - X (wherein x is same as defined above).

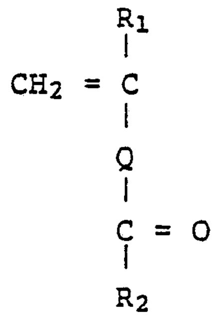
Furthermore, the polymer mordant shown by formula (II) for use in this invention can be obtained by polymerizing the copolymerizable monomer (A) having at least two ethylenically unsaturated groups, the ethylenically unsaturated monomer (B), and an unsaturated monomer shown by the formula



$$CH_2 = C(R_1)-D^{\oplus} \quad X^{\ominus}$$

(wherein R_1, $D^{\oplus}$, and $X^{\ominus}$ are same as defined above), such as 2-vinylpyridine hydrochloride, 1-methyl-3-vinylpyridine chloride, 4-vinylpyridine sulfate, 1-vinylimidazole hydrochloride, and 2-methyl-4-vinylpyridine sulfate.

The polymer mordant shown by formula (III) for use in this invention can be obtained by polymerizing the copolymerizable monomer (A) having at least two ethylenically unsaturated groups, the ethylenically unsaturated monomer (B), and an unsaturated monomer shown by the formula



$$CH_2 = C(R_1)-Q-C(=O)-R_2$$

(wherein R_1, R_2, and Q are same as defined above), such as vinyl methyl ketone and diacetone acrylamide) and then converting the product into a guanidine salt by aminoguanidine bicarbonate and an acid shown by the formula H-X (wherein X is same as defined above).

The aforesaid polymerization reaction may be performed by a solution polymerization, an emulsion polymerization, a suspension polymerization a precipitation polymerization, or a dispersion polymerization. In particular, a solution polymerization and an emulsion polymerization are preferred.

The aforesaid solution polymerization is generally performed in the existence of a radical polymerization initiator (e.g., the co-use of potassium persulfate and sodium hydrogensulfite, the initiators commercially available as V-50 and V-65 from Wako Junyaku K.K.) at temperature of from 30 °C to 120 °C, and preferably from 40 °C to 100 °C.

The aforesaid emulsion polymerization is generally performed in the existence of at least one emulsifier selected from anionic active agents (e.g., sodium dodecylsulfate and Triton 770 (trade name, made by Rhom & Haas Co.), cationic surface active agents (e.g., octadecyltrimethyl ammonium chloride), nonionic surface active agents (e.g., Emulex NP-20 (trade name, made by Nippon Emulsion K.K.)), gelatin, polyvinyl alcohol, etc., and a radical polymerization initiator (e.g., the co-use of potassium persulfate and sodium hydrogensulfite, and V-50 commercially available from Wako Junyaku K.K.) at temperature of from 30 °C to 100 °C, and preferably from 40 °C to 80 °C.

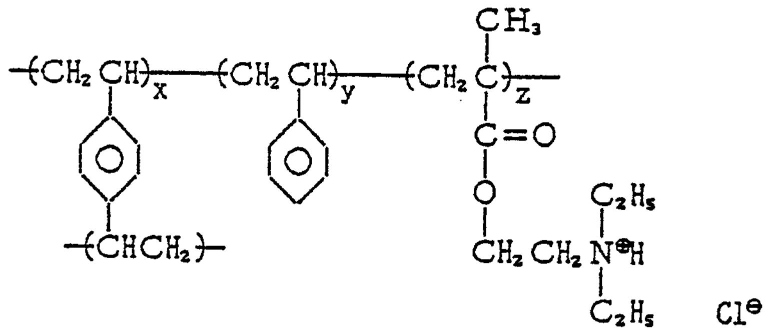
The aforesaid reaction for converting into an ammonium salt or a guanidium salt is performed at temperature of from -10 °C to 40 °C, and preferably from 0 °C to 30 °C.

The polymer dispersion mordant for use in this invention can be very easily produced in one reaction vessel.

Then, specific examples of the polymer mordant for use in this invention are illustrated below together with the synthesis methods thereof but the invention is not limited to them.

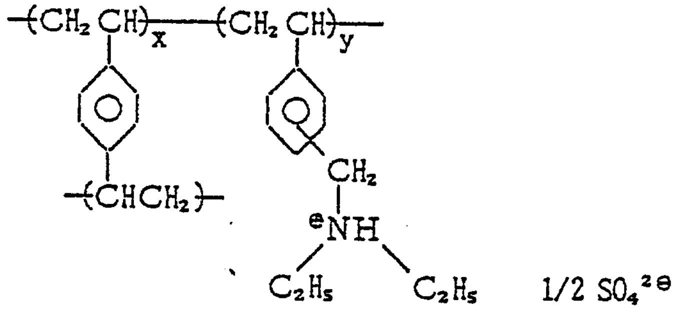
Polymer mordant

(1)



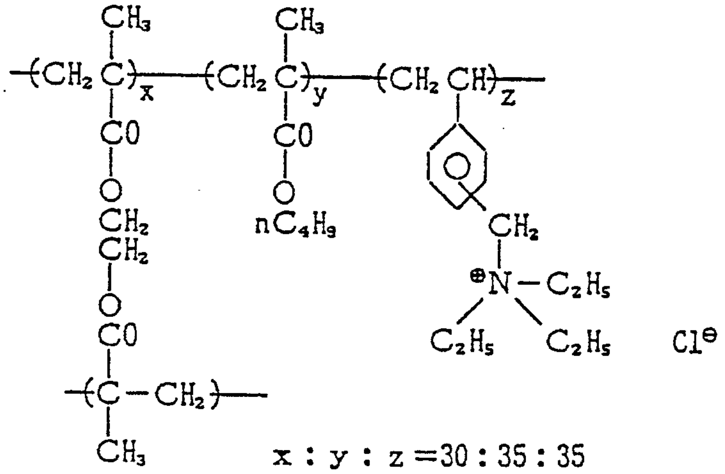
x : y : z =15 : 5 : 80

(2)



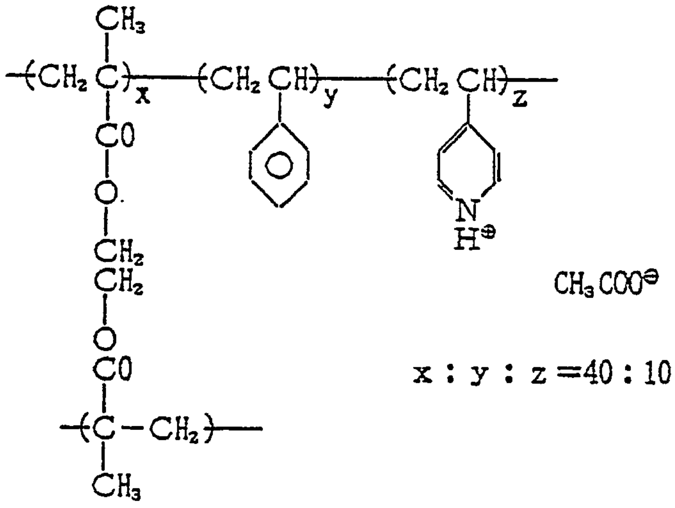
x : y =25 : 75

(3)



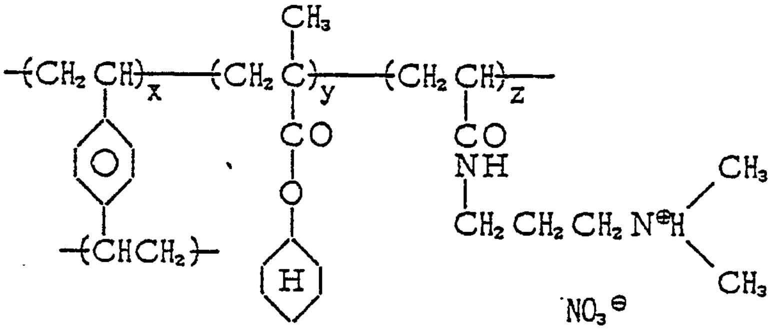
x : y : z =30 : 35 : 35

(4)



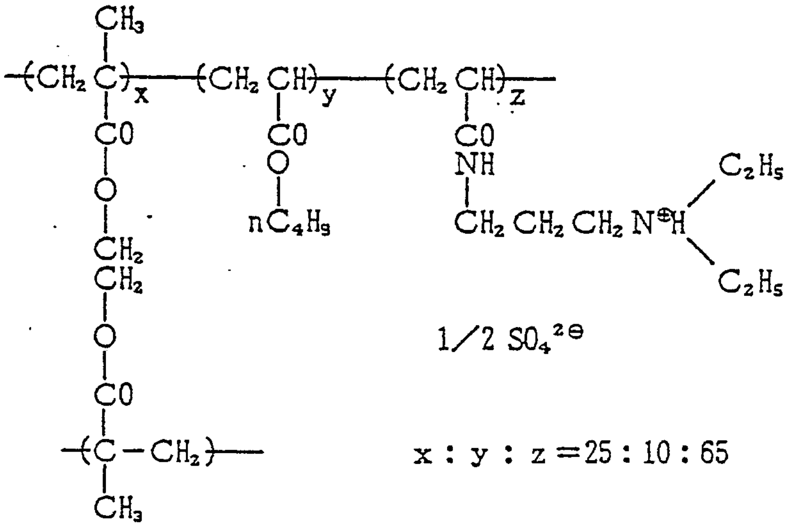
x : y : z = 40 : 10 : 50

(5)



x : y : z = 25 : 15 : 60

(6)



x : y : z = 25 : 10 : 65

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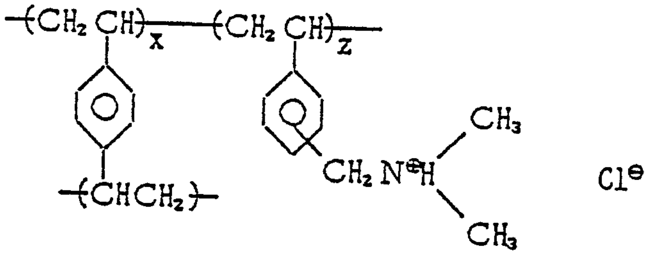

x : z =20 : 80

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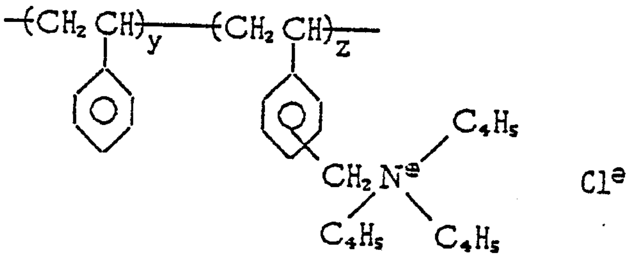
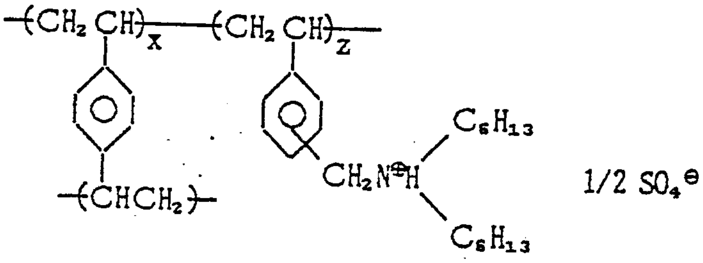


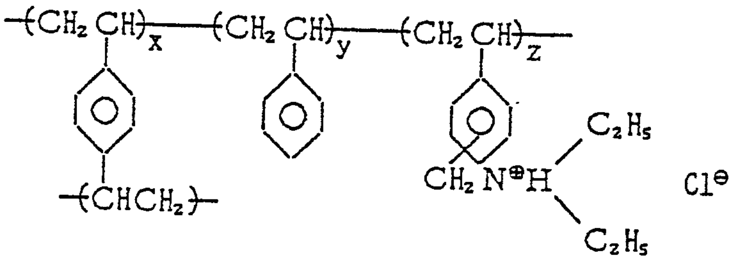
y : z =30 : 70

(9)



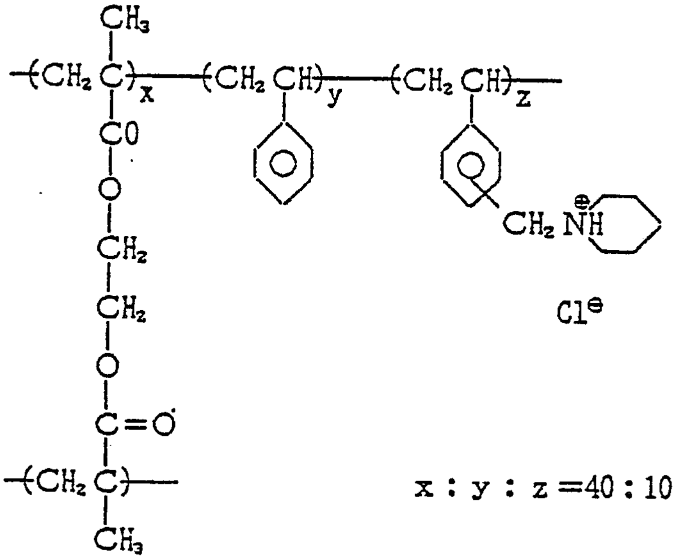
x : z =30 : 70

(10)



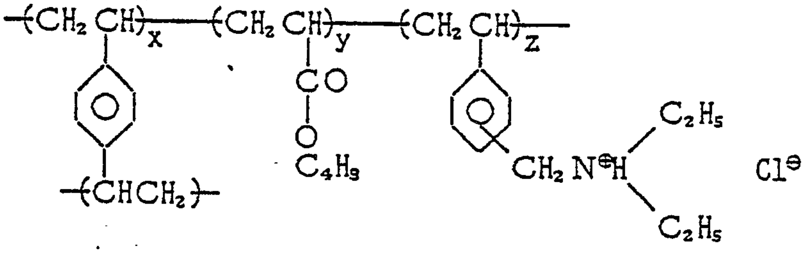
x : y : z =15 : 30 : 55

(11)



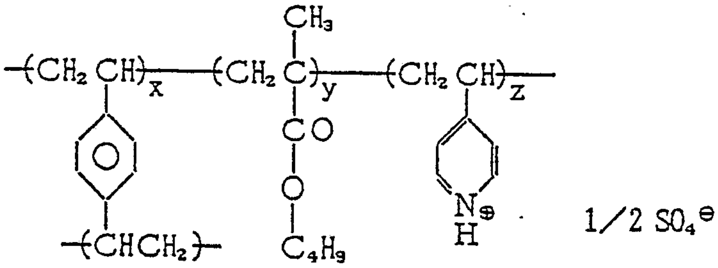
x : y : z =40 : 10 : 50

(12)



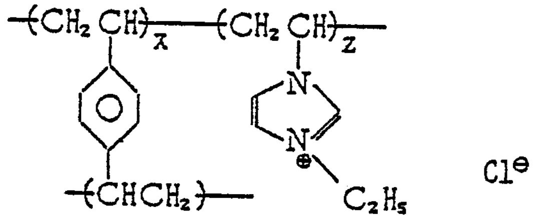
x : y : z =50 : 10 : 40

(13)



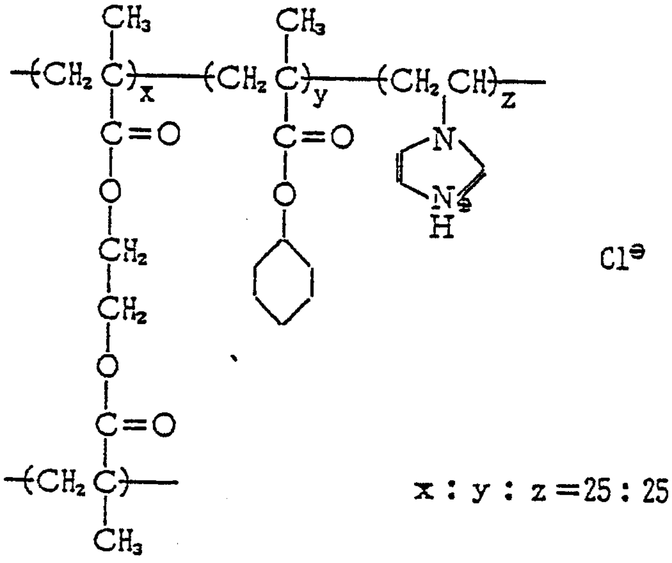
x : y : z =20 : 10 : 70

(14)



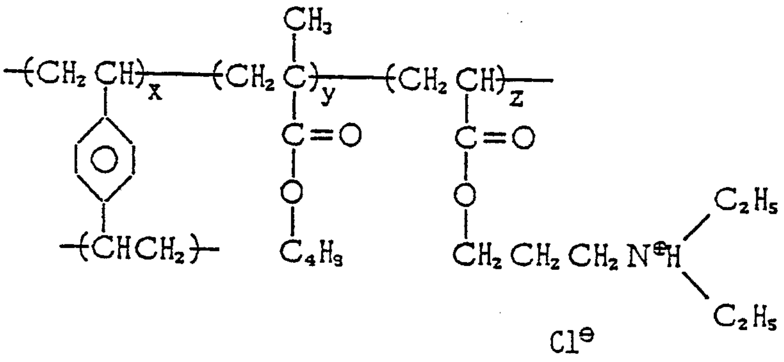
x : z = 50 : 50

(15)



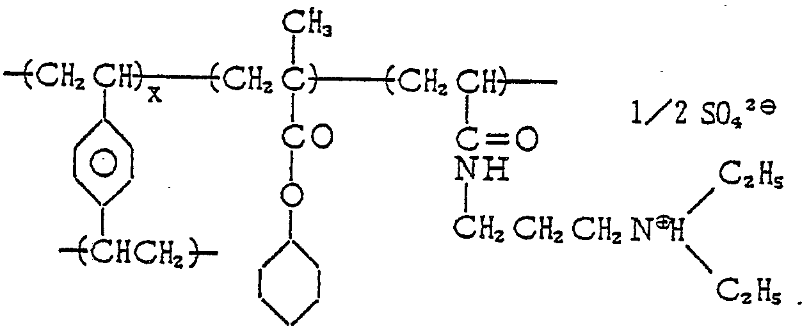
x : y : z = 25 : 25 : 50

(16)



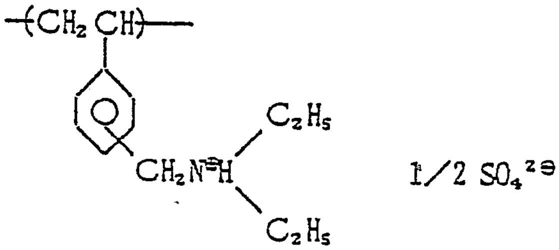
x : y : z = 15 : 15 : 70

(17)



x : y : z =35 : 5 : 60

(18)



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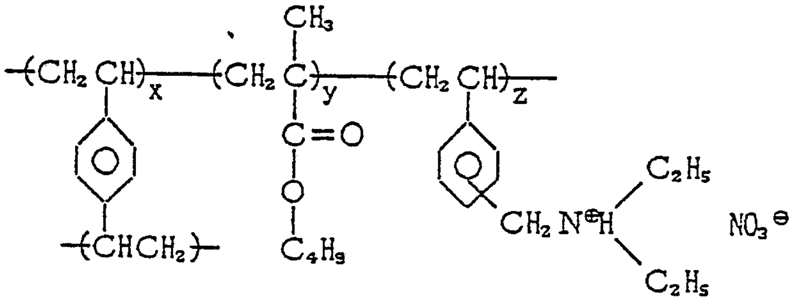
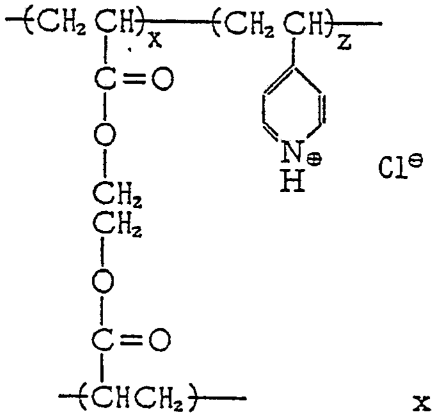


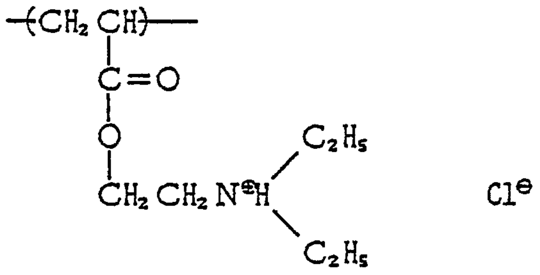
x : y : z =45 : 5 : 50

(20)



x : z =15 : 85

(21)



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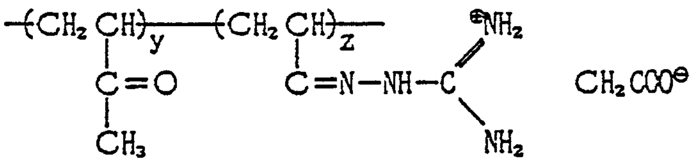
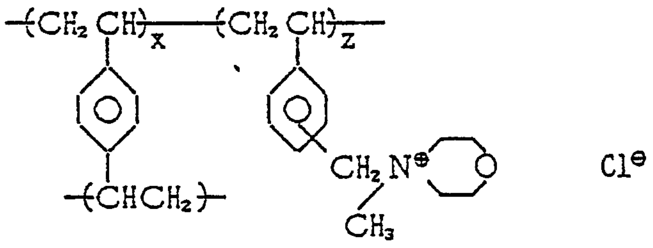


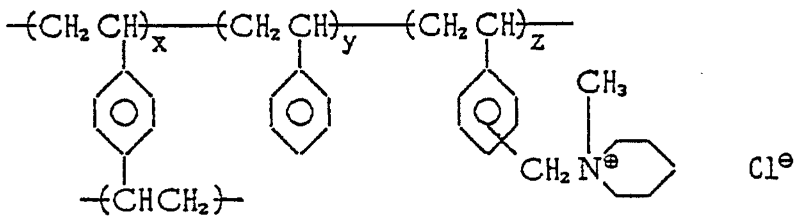
$y : z = 30 : 70$

(23)



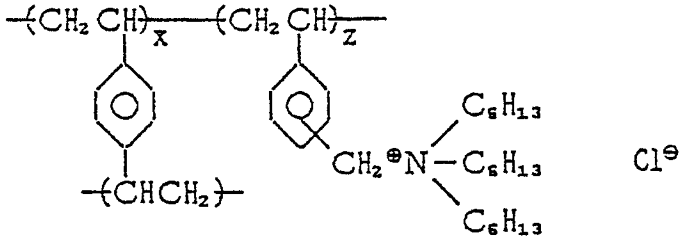
$x : z = 10 : 90$

(24)



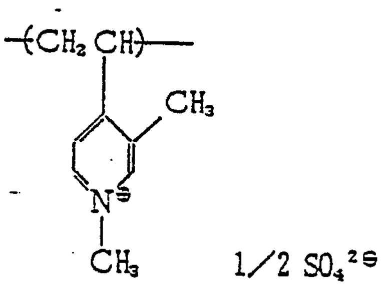
$x : y : z = 5 : 47 : 48$

(25)



$x : z = 33 : 67$

(26)



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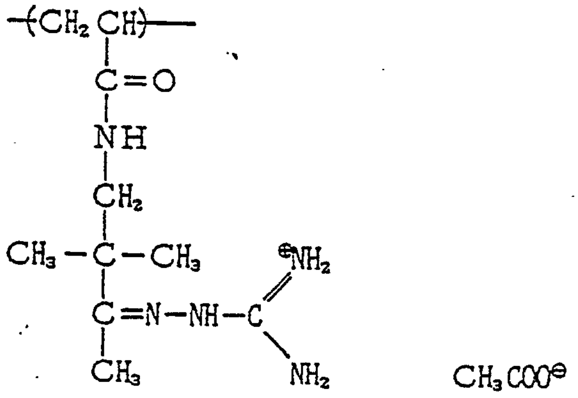

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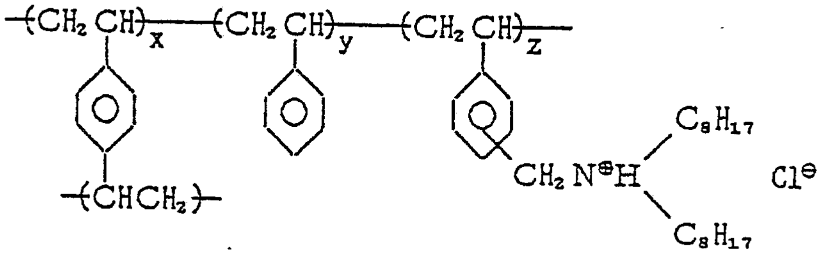
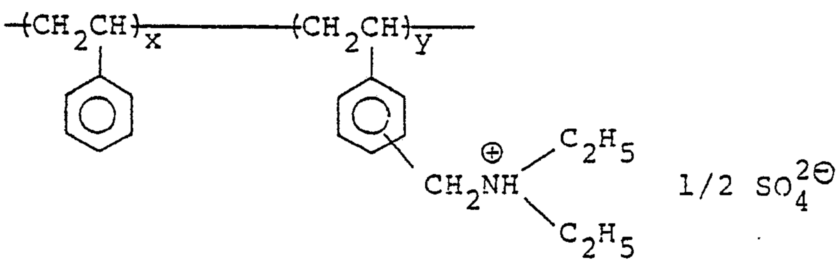


x : y : z =17.5 : 2.5 : 80

(29)



x:y = 30:70

Synthesis Example 1

Synthesis of poly(divinylbenzene-co-styrene-co-N,N-diethyl-N-methylacryloxyethyl ammonium chloride) polymer dispersion (Mordant 1):

In a reaction vessel was placed 108 g of water and the water was degassed with nitrogen gas and heated to 60°C under nitrogen gas stream. Then, after adding thereto 7.9 g of octadecyltrimethyl ammonium chloride (23%), 0.04 g of polyvinyl alcohol (saponification degree of 95%), 0.78 g of styrene, 2.94 g of divinylbenzene, and 20.63 g of N,N-diethylaminoethyl methacrylate, the mixture was stirred. Thereafter, a solution of 0.44 g of potassium persulfate and 0.14 g of sodium hydrogensulfite dissolved in 10.8 g distilled water degassed by nitrogen gas was added to the mixture and the resultant mixture was stirred for 5 hours. Then, after cooling the reaction mixture to room temperature, a solution of 10.6 g of concentrated hydrochloric acid dissolved in 100 g of distilled water was added to the mixture followed by filtration to provide the polymer dispersion having a solid component concentration of 14.0 wt.% and an amine content of 4.5 g x 10^{-4} egv/g.

Synthesis Example 2

Synthesis of poly(divinylbenzene-co-diethylaminomethylstyrene sulfate) polymer dispersion (Mordant 2):

In a reaction vessel was placed 1100 g of distilled water and the water was degassed with nitrogen gas. Then, after adding thereto 16.6 g of sodium dodecyl sulfate, 1.9 g of sodium hydroxide, 1.4 g of sodium sulfite, 33.6 g of divinylbenzene, and 195.7 g of diethyleneaminomethylstyrene, the mixture was stirred.

After heating the mixture to 60°C, a solution of 0.9 g of potassium persulfate dissolved in 60 g of distilled water was added every one hour total 4 times and then mixture was stirred for 2 hours. Then, after allowing to cool the reaction mixture to room temperature, a solution of 48.9 g of concentrated sulfuric acid dissolved in 313 g of distilled water was added thereto followed by filtration to provide the polymer dispersion having a solid component concentration of 15.4 wt.% and an amine content of 5.29 x 10^{-4} eqv/g.

Synthesis Example 3

Synthesis of poly(ethylene glycol dimethacrylate-co-butyl methacrylate-co-triethylaminomethylstyrene chloride) polymer dispersion (Mordant 1):

In a reaction vessel was placed 2.8 g of an emulsifier commercially available as Nissan Trux H-45 (trade name, made by Nippon Oil and Fats Co., Ltd.), 75 g of distilled water, 5.95 g of ethylene glycol dimethacrylate, 4.98 g of butyl methacrylate, and 5.3 g of chloromethylstyrene and the mixture was stirred. Then, after heating the mixture to 60°C, 0.2 g of a polymerization initiator commercially available as V-40 (trade name, made by Wako Junyaku K.K.) was added to the mixture and the resultant mixture was stirred for 3 hours. Thereafter, the mixture was cooled to 40°C, 108 g of distilled water and 62 g of isopropyl alcohol were added thereto, and after further adding dropwise 3.4 g of triethylamine to the mixture over a period of 15 minutes, the resultant mixture was stirred for 2 hours and 40 minutes followed by filtration to provide the polymer dispersion having a solid component concentration of 8.46 wt.%.

Other polymers than the above illustrated polymers can be also synthesized by similar manners to the aforesaid methods.

The aforesaid cationic polymers may be used singly or as a mixture thereof.

The amount of the cationic polymer being used is preferably from 0.5 to 100, and more preferably from 1 to 40 in gram equivalent as the cation of the cationic polymer per mole of the light-harvesting dye being used.

As the hydrophilic dispersion medium which can be used for the emulsion layers or other layers of the photographic light-sensitive materials of this invention, gelatin is advantageously used but other hydrophilic colloids can be used. For example, there are proteins such as gelatin derivatives, graft polymers of gelatin and other polymers, albumin, casein, etc.; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfuric acid esters, etc.; saccharose derivatives such as sodium alginate, starch derivatives, etc.; and various synthetic hydrophilic polymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinyl-pyrrolidone, polyacrylic acid, polymethacrylic acid polyacrylamide, polyvinyl imidazole, polyvinyl pyrazole, etc.

As gelatin, limed gelatin as well as acid-treated gelatin and enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, No. 16, 30(1966) can be used. Also, hydrolyzed products of gelatin can be used.

The composition of the light-sensitive silver halide for use in this invention includes ordinary silver halides such as silver bromide, silver iodioromide, silver chloride, silver chlorobromide, silver chloroiodobromide, etc. The form of the light-sensitive silver halide grains may be spherical, tabular, octahedral, cubic, tetradecahedral, amorphous, etc., but tabular silver halide grains having a large area for adsorbing dyes and capable of attaining high spectral sensitization are particularly preferred in this invention, with particularly preferred the tabular silver halide grains, the tabular grains having an aspect ratio of at least 5, and particularly at least 8 account for at least 50% of the total projected area of the whole grains. For example, the tabular grains described, e.g., in Research Disclosure, No. 22534 (1983), JP-A-58-127921 and 59-99433, and U.S. Patent 4,585,729 can be preferably used in this invention.

Also, the composition of the silver halide grains may be either homogeneous throughout the grain or heterogenous. As the heterogenous silver halide grains, the double structure grains having different composition between the central portion and the surface portion as described in JP-A-58-113926, 58-113927, and 59-99433 can be preferably used.

Furthermore, silver halide grains formed by epitaxial glowing of fine silver halide crystals each having a different halide composition as described in U.S. Patents 4,094,684, 4,459,343, and 4,463,087 and JP-A-58-108526, silver halide grains having therein spectral sensitizing dye(s) described in Phot. Sci. Eng., Vol. 8, 102(1968), silver halide grains having a high order index of plane described in JP-A-62-123446, troglodyte nuclei type silver halide grains described in JP-B-58-1409 (the term "JP-B" as used herein means an "examined Japanese patent publication"), and silver halide grains having sensitive specks in the side thereof near the surface.

There is no particular restriction on the mean grain of silver halide grains for silver halide emulsions but the equivalent sphere diameter thereof is preferably less than 3 µm, and more preferably less than 1.8 µm. The grain size distribution may be narrow or broad.

The silver halide grains may be of the type of forming latent images mainly on the surface thereof or of the type of forming latent images mainly in the inside thereof.

During the formation of physical ripening of the silver halide grains, a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, or an iron salt or a complex salt hereof may exist in the system.

The silver halide emulsion may be used as a so-called primitive emulsion without being chemically sensitized but is usually chemically sensitized by well-known methods. For the chemical sensitization, for example, the method described in H. Frieser, Die Grundlagen der Photographischen Prozessemit Silber-Halogeniden, pages 675 - 734 (Akademische Verladgsgesellschaft, 1968) can be used.

That is a sulfur sensitizing method using active gelatin or a sulfur-containing compound capable of reacting with silver (e.g., thisulfates, thioureas, mercapto compounds, rhodanines); a reduction sensitizing method using a reducing agent (e.g., stannous salts, amines, hydrazine derivatives, formamidinesulfinic acid, and silane compounds); and a noble metal sensitizing method using a noble metal compound (e.g., gold complexes as well as complex salts of metals belonging to group VIII of the Periodic Table, such as Pt, Ir, Pd, etc.). In this invention, the sulfur sensitization and a combination of the sulfur sensitization and gold sensitization are particularly preferred.

The silver halide photographic emulsions for use in this invention can contain various compounds for preventing the occurrence of fog during the production, storage, and/or photographic processing of the photographic light-sensitive materials containing the emulsions or stabilizing the photographic performance thereof. For example, there are many compounds known as antifoggants or stabilizers. Examples of those compounds are azoles such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazole, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiazoles, aminotriazoles, benztriazoles, nitrobenzotriazoles, mercaptotetrazole (in particular, 1-phenyl-5-mercaptotetrazole), etc.; mercaptopyrimidines; mercatptriazines; thioketo compounds such as oxazolinethione, etc.; azaindenes such as triazaindenes, tetraazaindenes (in particular, 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes), pentaazaindenes, etc.; benzenethiosulfonic acid; benzenesulfinic acid; and benzenesulfonic acid amide.

Furthermore, the silver halide emulsions for use in this invention may contain polyalkylene oxide or their derivatives thereof, such as the ethers, esters, amines, etc., thioether compounds, thiomorpholines, quarternary ammonium salt compounds, urethane derivatives, urea derivatives, imidazole derivatives, 3-pyrazolidones, etc., for increasing sensitivity and contrast and for further increasing the development acceleration.

The light-sensitive silver halide is spectrally sensitized by adsorptive spectral sensitizing dye(s). In this case, the surface coating ratio of the adsorbed dye is preferably at least 20%, and more preferably at least 40% of the saturated adsorption amount of monomolecular layer.

In the case of surface latent image type negative light-sensitive materials and inside latent image forming type direct positive light-sensitive materials, sensitizing dye(s) are used as spectral sensitizing dye.

As positive type photographic light-sensitive materials, there are light-sensitive materials of the type of obtaining positive images by the rupture of surface fog nucleus under light exposure using, for example, electron acceptive dyes. Also, adsorptive super color sensitizing agents and various kinds of additives (antifogging agents, etc.) may be used together with adsorptive dyes for the purpose of specially sensitizing in an optimum sate according to the purpose of the photographic light-sensitive materials.

The adsorptive dyes which are used for the spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, hemioxonole dyes, xanthene dyes, triarylmethane dyes, phenothizine dyes, acryzine dyes, metal chelating compounds, etc. To these dyes can be applied nuclei which are usually utilized for cyanine dyes as basic heterocyclic nuclei. Examples of these nuclei are pyrroline nuclei, oxazoline nuclei, thiazoline nuclei, pyrrole nuclei, imidazole nuclei, tetrazole nuclei, pyridine nuclei, etc;.; the nuclei formed by fusing an alicyclic hydrocarbon ring to the aforesaid nuclei or the nuclei formed by fusing an aromatic hydrocarbon ring to the aforesaid nuclei, i.e., indolenine nuclei, benzindolenine nuclei, indole nuclei, benzoxazole nuclei, naphthoxazole nuclei, benzothiazole nuclei, nephthothiazole nuclei, benzoselenazole nuclei, benzimidazole nuclei, quinone nuclei, etc. The nuclei may have a substituent on the carbon atom thereof.

In these cyanine dyes, the dyes which give particularly higher sensitizing efficiency by the use with super color sensitizing dyes than the case of single use thereof are preferred. For example, cyanine dyes having at least one of thiazole nuclei, selenazole nuclei, quinoline nuclei, and indolenine nuclei in the molecule or cyanine dyes having at least two of oxazole nuclei or at least two of imidazole nuclei in the molecule are preferably used in this invention. As a matter of course, however, the nuclei formed by fusing an aliphatic hydrocarbon ring and/or an aromatic hydrocarbon ring to these basic heterocyclic nuclei are particularly preferably used.

For the merocyanine dyes or complex merocyanine dyes can be applied 5- or 6-membered heterocyclic nuclei such as pyrazololin-5-one nuclei, thiohydantoin nuclei, 1-thio-oxazolidin-2,4-dione nuclei, thiazolidine-2,4-dione nuclei, rhodanine nuclei, thiobarbituric acid nuclei, etc., as nuclei having a ketomethylene structure.

Specific examples of the useful sensitizing dyes for use in this invention are described in German Patent 929,080, U.S. Patents 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 2,656,959, 3,672,897, 3,694,217, 4,025,349, and 4,046,572, British Patent 1,242,588, JP-B-44-14030 and 52-24844. The term "JP-B" as used herein means an "examined Japanese patent application".

These sensitizing dyes may be used singly or as a combination thereof. A combination of sensitizing dyes is frequently used for the purpose of super color sensitization. Typical examples thereof are described in U.S. Patents 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, and 4,026,707, British Patents 1,344,281 and 1,507,803, JP-B-43-4936 and 53-12375, and JP-A-52-110618 and 52-109925.

The silver halide emulsions for use in this invention may contain, together with the sensitizing dyes, a dye having no spectral sensitizing action by itself or a material which does not substantially absorb visible light and shows super color sensitization. Examples of such compounds are aminostyilbene compounds substituted by a nitrogen-containing heterocyclic group (described, e.g., in U.S. Patents 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensation products (described, e.g., in U.S. Patent 3,743,510), cadmium salts, and azaindene compounds. The combinations of the compounds described in U.S. Patents 3,615,613, 3.615,641, 3,617,295, and 3,635,721 are particularly useful in this invention.

In the case of applying the present invention to color photographic light-sensitive materials, various kinds of color couplers can be used. The term "color coupler" in this invention means a compound capable of forming a dye by causing coupling reaction with the oxidation product of an aromatic primary amine developing agent.

Typical examples of the useful color couplers are naphtholic or phenolic compounds, pyrazoline or pyrazoloazole series compounds, and open chain or heterocyclic ketomethylene compounds. Specific examples of these cyan, magenta, and yellow couplers which can be used in this invention are described in the patents cited in Research Disclosure, No. 17643 (December, 1978), Paragraph VII-D and ibid., No. 18717 (November, 1979).

In this invention two or more kinds of couplers can be used in a same light-sensitive emulsion layer for meeting the characteristics required for the color photographic materials or a same kind of coupler may be used for two or more different emulsion layers for the purpose as described above.

For correcting unnecessary absorptions at short wavelength region shown by the dyes formed by magenta couplers and cyan couplers, it is preferred to use colored couplers together with the aforesaid color couplers in color negative photographic materials for camera use. Examples of such colored couplers are the yellow-colored magenta couplers described in U.S. Patent 4,163,670 and JP-B-57-39413 and the magenta-colored cyan couplers described in U.S. Patents 4,004,929 and 4,138,258 and British Patent 1,146,368.

Furthermore, in this invention the graininess of color images formed can be improved by using a coupler giving a colored dye having a proper diffusibility together with the aforesaid couplers. Specific examples of such properly controlled smearing are described in U.S. Patent 4,366,237 and British Patent 2,125,570 for magenta couplers and in European Patent 96,570 and West German Patent Application (OLS) No. 3,234,533 for yellow, magenta, and cyan couplers.

The dye-forming couplers and specific couplers described above for use in this invention may form dimers or more polymers. Typical examples of the polymerized couplers are described in U.S. Patents 3,451,820 and 4,080,211. Also, examples of polymerized magenta couplers are described in British Patent 2,102,173, U.S. Patent 4,367,282, and JP-A-62-54260 and Japanese Patent Application 60-113596.

Couplers releasing photographically useful residue with coupling can be also used in this invention. DIR couplers releasing a development inhibitor with coupling are described in Research Disclosure, No. 17643, Paragraph VII-F.

For the color photographic materials of this invention can be also used couplers imagewise releasing a nucleating agent or a development accelerator, or a precursor therefor at development. Specific examples of such couplers are described in British Patents 2,097,140 and 2,131,188. Also, couplers releasing a nucleating agent having an adsorptive action to silver halide are particularly preferable and typical examples thereof are described in JP-A-59-157638 and 59-170840.

The photographic light-sensitive materials of this invention may contain an inorganic or organic hardener in hydrophilic colloid layers forming the photographic emulsion layers, etc., and back layer. Typical examples thereof are chromium salts, aldehydes (e.g., formaldehyde, glyoxale, and glutar aldehyde), and N-methylol series compounds (e.g., dimethylolurea). Active halogen compounds (e.g., 2,4-dichloro-6-hydroxy-1,3,5-triazine) and active vinyl compounds (e.g., 1,3-bis-vinylsulfonyl-2-propanol, 1,2-bis-vinylsulfonyl acetamide ethane and vinylic polymers having a vinylsulfonyl group at the side chain thereof) are preferred since they quickly harden hydrophilic colloids such as gelatin to give stable photographic characteristics. Also, N-carbamoylpyridinium salts and haloamidinium salts are excellent in the point of giving quick hardening.

The silver halide emulsions for use in this invention can further contain various additives such as surface active agents, tackifiers, dyes, ultraviolet absorbents, antistatic agents, whitening agents, desensitizers, developing agents, fading preventors, etc.

Practical examples of these additives are described, for example, in Research Disclosure, No. 17643, Vol. 176, pages 22-31 and T.H. James, The Theory of the Photographic Process, 4th Ed., published by Macmillan Publishing Co., Inc., 1977.

For producing the photographic light-sensitive materials, photographic emulsion layer(s) and other layer(s) are formed on a flexible support such as plastic films, papers, cloths, etc., or a solid support such as glass plates, ceramics, metals, etc. Useful flexible supports are films of semisynthetic or synthetic polymers such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate, etc., and papers having a baryta layer or a layer of an α-olefin polymer (e.g., polyethylene, polypropylene, and ethylene/butene copolymer). The support may be colored by dyes or pigments. The support may, as the case may be, blacked for light-shielding.

The surface of the support is generally subjected to a subbing treatment for improving the adhesion for a photographic emulsion layer, etc. Before or after subbing treatment, the surface of the support may be subjected to a glow discharging treatment, corona discharging treatment, ultraviolet irradiation, a flame treatment, etc.

The light exposure for obtaining photographic images may be performed by an ordinary manner. That is, various light sources such as natural light (sunlight), a tungsten lamp, a fluorescent lamp, a mercury lamp, a xenon arc lamp, a carbon arc lamp, a xenon flash lamp, a cathode ray tube, a flying spot, etc., can be used. The exposure time is as a matter of course from 1/1000 sec. to one second which are usually used for camera as well as may be shorter than 1/1000 sec., for example from $1/10^4$ to $1/10^9$ sec. in the case of using a xenon flash lamp, a cathode ray tube, or a laser light or may be longer than one second.

Also, if necessary, the spectral composition of light for use the exposure can be controlled using color filters. Also, the exposure may be performed by light emitted from a fluorescent substance excited by electron beam, X-rays, γ-rays, α-rays, etc.

The photographic light-sensitive materials of this invention can be processed by any known processed using known processing solutions as described, e.g., in Research Disclosure, No. 17643, Vol. 176, pages

28-30. The photographic process may be a photographic process of forming silver images (black and white processing) or a photographic process of forming dye images (color photographic processing) according to the purpose.

The processing temperature is usually selected between 18°C to 50°C but, as the case may be, may be lower than 18°C or higher than 50°C.

As a specific system of photographic processing, a process of processing photographic light-sensitive materials containing a developing agent in, for example, the photographic emulsion layers thereof in an alkaline aqueous solution may be used. A hydrophobic developing agent can be incorporated in the emulsion layer by various methods as described in Research Disclosure, Vol. 169, No. 16928, U.S. Patent 2,739,890, British Patent 813,253, and West German Patent 1,547,763. Such a development process may be combined with a silver salt stabilization process by a thiocyanate.

As a fix solution for use in this invention, an ordinary composition can be used. As the fixing agent, thiosulfates, thiocyanates as well as organic sulfur compounds which are known to have an effect as fixing agent can be used. The fix solution may contain a water-soluble aluminum salt as a hardener.

A color developer which is used for developing the color photographic materials of this invention is generally composed of an alkaline aqueous solution containing a color developing agent. As the color developing agent, there are primary aromatic amine developing agents such as phenylenediamines (e.g., 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfoamidoethylaniline, and 4-amino-3-methyl-N-ethyl-N-β-methoxyethylaniline).

Other color developing agents which can be also used in this invention are described in L.F.A. Mason, Photographic Processing Chemistry, pages 226-229 (Focal Press, 1966), U.S. Patents 2,193,015 and 2,592,364, JP-A-48-64933.

The color developer may further contain a pH buffer, a development inhibitor or an antifoggant. Also, if necessary, the color developers may contain a water softener, a preservative, an organic solvent, a development accelerator, a dye-forming coupler, a competing coupler, a fogging agent, an auxiliary developing agent, a tackifier, a polycarboxylic chelating agent, an antioxidant, etc.

Specific examples of these additives are described in Research Disclosure, No. 17643, U.S. Patent 4,083,723, and West German Patent Application (OLS) 2,622,950.

After color development, the color photographic materials are usually bleached. The bleach process may be performed simultaneously with or separately from a fix process.

As the bleaching agent, there are compounds of multivalent metals such as iron(III), cobalt(III), chromium(VI), copper(II), etc., peracids, quinones, nitroso compounds, etc.

Specific examples thereof are ferricyanides; bichromates; organic complex salts of iron(III) or cobalt(III), e.g., complex salts thereof and aminopolycarboxylic acids (e.g., ethylenediaminetetraacetic acid, nitrilotriacetic acid, and 1,3-diamino-2-propanoltetraacetic acid) or other organic- acids (e.g., citric acid, tartaric acid, and malic acid); persulfates; permanganates; and nitrosophenol. In these materials, potassium ferricyanide, ethylenediaminetetraacetic acid iron(III) sodium and ethylenediaminetetraacetic acid iron(III) ammonium are particularly useful. Ethylenediaminetetraacetic acid iron(III) complex salts are useful for both a bleach solution and a bleach-fix (blix) solution.

For the bleach solution or blix solution for use in this invention, various additives such as the bleach accelerators described in U.S. Patents 3,042,520, 3,241,966, JP-B-45-8506 and 45-8836 and the thiol compounds described in JP-A-54-65732 can be used.

In processing of the photographic light-sensitive materials of this invention, additives causing reaction with the light-collecting dyes can be added to the processing solutions such as developer, blix solution, etc., for the purpose of decomposing and disclosing the light-collecting dyes existing in the light-sensitive materials.

This invention can be applied to various kinds of color photographic materials and black and white photographic materials, such as general or cinne color negative films, color reversal films for slide or television, color photographic papers, color positive films, color reversal photographic papers, color diffusion transfer type photographic materials, heat development type color photographic material, etc. This invention can be also applied to radiographic black and white photographic materials utilizing a mixture of three color couplers described in Research Disclosure, No. 17123 (July, 1978) and utilizing black coloring couplers described in U.S. Patent 4,126,461 and British Patent 2,102,136.

This invention can be further applied to process films such as lith films or scanner films, direct or indirect medical and industrial radiographic films, negative black and white photographic films for camera use, black and white photographic papers, computer output microfilms (COM), ordinary microfilms, silver salt diffusion transfer type photographic materials and printout type photographic materials.

The most preferred utilization of this invention is as a matter of course in the point of further improving the spectrally sensitized sensitivity of a silver halide photographic material spectrally sensitized by dye(s) according to the use of the light-collecting dye(s) together with the aforesaid spectrally sensitizing dye(s) but among them, examples of the particularly preferred utilization method are, in the case of a black and white photographic material, the improvement of the sensitivity at the region having relatively low sensitized degree corresponding to the valley between the intrinsic sensitivity and the spectral. sensitivity, e.g., the blue region (450 to 520 n.m.) by the addition of the light-collecting dye and, in the case of a color photographic material, the reinforcement of each spectral sensitivity of blue, green and red regions by the addition of the proper light-collecting dyes.

The technique of this invention is effective as a means for improving the spectrally sensitized sensitivity as well as is expected to improve the sharpness of images of the photographic light-sensitive materials in addition to the sensitization by an irradiation preventing effect or antihalation effect of the light-collecting dyes since the light-collecting dyes, which are sensitizers, in a dispersion medium are also light absorbers.

In other words, the use of an irradiation preventing dye or an antihalation dye is generally accompanied by a desensitization by a light filter effect but the use of the light-collecting dyes in this invention can improve the sharpness of images formed without substantially reducing the sensitivity or rather with increasing the sensitivity.

For example, in a direct medical X-ray photographic film having each emulsion layer on both surfaces of a support, it is known that the sharpness of images is greatly reduced by crossover light, that is, the fluorescence from a fluorescent intensifying screen transmitting into the light-sensitive emulsion layer at the said opposite to the light incident side but according to the present invention, it is expected that the sharpness can be greatly improved by greatly increasing the light absorption amount at the light incident side to increase the sensitivity and at the sale time intercept the crossover light.

Then, the invention is described in more practically by the following examples but the invention is not limited to them.

Example 1

A multilayer color photographic material having the layers of the compositions shown below on a cellulose triacetate film support having subbing layer was prepared as a base sample. Also, a comparison sample was prepared by simply adding the light-collecting dye A-47 to the 1st to 3rd green-sensitive emulsion layer of the base sample and furthermore, samples of this invention were also prepared by further adding various polymer mordants to these green-sensitive emulsion layers.

In this case, the quantum yield of the luminescence of the light-collecting dye A-47 at a concentration of 10^{-4} mole/dm^3 in dry gelatin was 0.74.

Composition of the Layers of Base Sample

In the following composition the coating amounts were silver halide, shown by the g/m^2 unit of silver for silver halide, emulsions and colloid silver, the g/m^2 unit for coupers, additives and gelatin, and the mole number per mole of silver halide in the same layer for a sensitizing dye.

Layer 1 (Antihalation layer)

Black Colloid Silver	0.2
Gelatin	1.3
ExM-8	0.06
UV-1	0.1
UV-2	0.2
Solv-1	0.01
Solv-2	0.01

Layer 2 (Interlayer)

Fine Grain Silver Bromide (mean grain size 0.07μm)	0.10
Grain	1.5
UV-1	0.06
UV-2	0.03
ExC-2	0.02
ExF-1	0.004
Solv-1	0.1
Solv-2	0.09

Layer 3 (1st Red-Sensitive Emulsion Layer)

Silver Iodobromide Emuslion (AgI 2 mole%, inside high-AgI type, sphere-corresponding diameter 0.3 μm, coeff. of variation of sphere-corresponding diameters 29%, normal crystal, twin-mixed grains, aspect ratio 2.5)	0.4
Gelatin	0.6
ExS-1	1.0×10^{-4}
ExS-2	3.0×10^{-4}
ExS-3	1×10^{-5}
ExC-3	0.06
ExC-4	0.06
ExC-7	0.04
ExC-2	0.03
Solv-1	0.03
Solv-3	0.012

Layer 4 (2nd Red-Sensitive Emulsion Layer)

Silver Iodobromide Emuslion (AgI 5 mole%, inside high-AgI type, sphere-corresponding diameter 0.7 μm, coeff. of variation of sphere-corresponding diameters 25%, normal crystal, twin-mixed grains, aspect ratio 4)	0.7
Gelatin	0.5
ExS-1	1×10^{-4}
ExS-2	3×10^{-4}
ExS-3	1×10^{-5}
ExC-3	0.24
ExC-4	0.24
ExC-7	0.04
ExC-2	0.04
Solv-1	0.15
Solv-3	0.02

Layer 5 (3rd Red-Sensitive Emulsion Layer)

Silver Iodobromide Emuslion (AgI 10 mole%, inside high-AgI type, sphere-corresponding diameter 0.8 μm, coeff. of variation of sphere-corresponding diameters 16%, normal crystal, twin-mixed grains, aspect ratio)	1.0
Gelatin	1.0
ExS-1	1×10^{-4}
ExS-2	3×10^{-4}
ExS-3	1×10^{-5}
ExC-5	0.05
ExC-6	0.1
Solv-1	0.01
Solv-2	0.05

Layer 6 (InterLayer)

Gelatin	1.0
Cpd-1	0.03
Solv-1	0.05

Layer 7 (1st Green-Sensitive Emulsion Layer)

Silver Iodobromide Emuslion (AgI 2 mole%, inside high-AgI type, sphere-corresponding diameter 0.3 µm, coeff. of variation of sphere-corresponding diameters 28%, normal crystal, twin-mixed grains, aspect ratio 2.5)	0.30
ExS-4	5×10^{-4}
ExS-6	0.3×10^{-4}
ExS-5	2×10^{-4}
Gelatin	1.0
ExM-9	0.2
ExY-14	0.03
ExM-8	0.03
Solv-1	0.5

Layer 8 (2nd Green-Sensitive Emulsion Layer)

Silver Iodobromide Emuslion (AgI 4 mole%, inside high-AgI type, sphere-corresponding diameter 0.6 µm, coeff. of variation of sphere-corresponding diameters 38%, normal crystal, twin-mixed grains, aspect ratio 4)	0.4
Gelatin	0.5
ExS-4	5×10^{-4}
ExS-5	2×10^{-4}
ExS-6	0.3×10^{-4}
ExM-9	0.25
ExM-8	0.03
ExM-10	0.015
ExY-14	0.01
Solv-1	0.2

Layer 9 (3rd Green-Sensitive Emulsion Layer)

Silver Iodobromide Emuslion (AgI 6 mole%, inside high-AgI type, sphere-corresponding diameter 1.0 µm, coeff. of variation of sphere-corresponding diameters 80%, normal crystal, twin-mixed grains, aspect ratio 1.2)	0.85
Gelatin	1.0
ExS-7	3.5×10^{-4}
ExS-8	1.4×10^{-4}
ExM-11	0.01
ExM-12	0.03
ExM-13	0.20
ExM-8	0.02
ExY-15	0.02
Solv-1	0.20
Solv-2	0.05

Layer 10 (Yellow Filter Layer)

Gelatin	1.2

Yellow Colloid silver	0.08
Cpd-2	0.1
Solv-1	0.3

Layer 11 (1st Blue-Sensitive Emulsion Layer)

Silver Iodobromide Emuslion (AgI 4 mole%, inside high-AgI type, sphere-corresponding diameter 0.5 μm, coeff. of variation of sphere-corresponding diameters 15%, octahedral grains)	0.4
Gelatin	1.0
ExS-9	2×10^{-4}
ExY-16	0.9
ExY-14	0.07
Solv-1	0.2

Layer 12 (2nd Blue-Sensitive Emulsion Layer)

Silver Iodobromide Emuslion (AgI 10 mole%, inside high-AgI type, sphere-corresponding diameter 1.3 μm, coeff. of variation of sphere-corresponding diameters 25%, normal crystal, twin-mixed grains, aspect ratio 4.5)	0.5
Gelatin	0.6
ExS-9	1×10^{-4}
ExY-16	0.25
Solv-1	0.07

Layer 13 (1st Protective Layer)

Gelatin	0.8
UV-1	0.1
UV-2	0.2
Solv-1	0.01
Solv-2	0.01

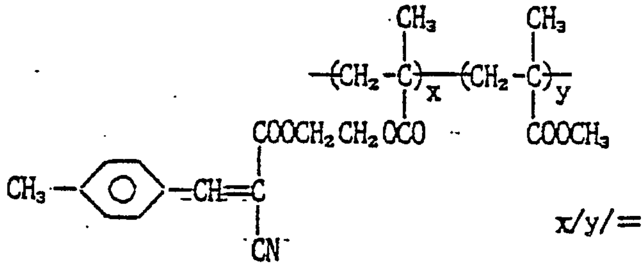
Layer 14 (2nd Protective Layer)

Fine Grain Silver Bromide (mean grain size 0.07 μm)	0.5
Gelatin	0.45
Polymethyl Methacrylate Particles (diameter 1.5 μm)	0.2
H-1	0.4
Cpd-3	0.5
cpd-4	0.5

In addition, each layer further contained a surface active agent as a coating aid in addition to the aforesaid components. The sample as obtained was used as the base sample.

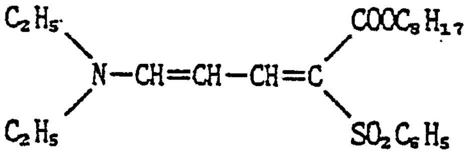
The chemical structures or chemical names of the compounds used above are shown below.

UV-1



x/y/=7/3(weight ratio)

UV-2

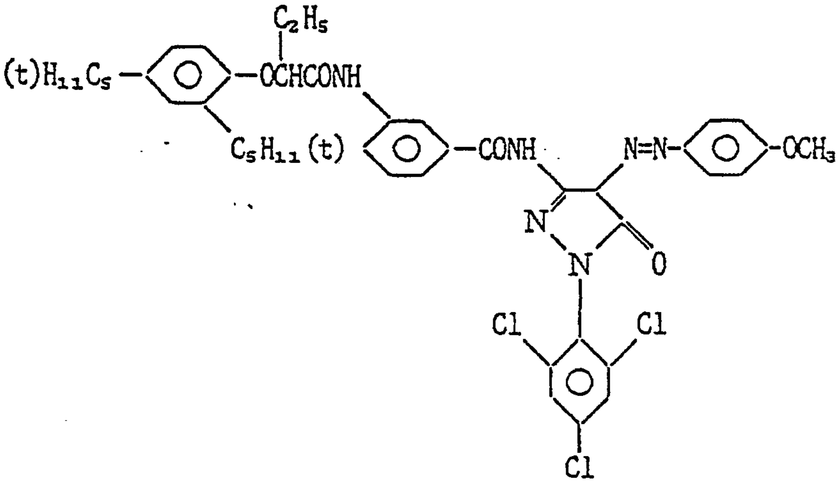


Solv-1 Tricrisyl Phosphate

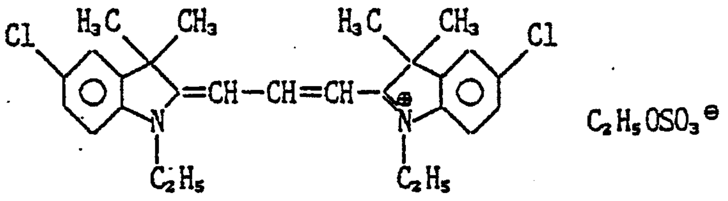
Solv-2 Dibutyl Phthalate

Solv-3 Bis(2-ethyl hexyl) Phthalate

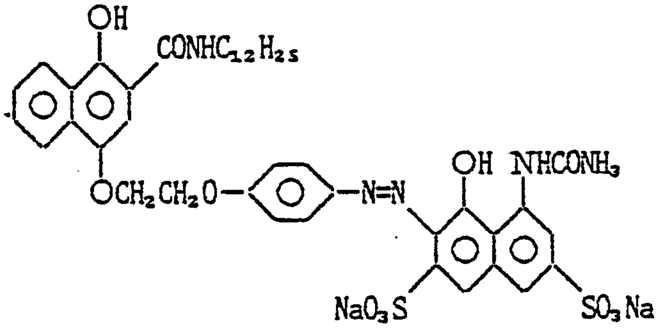
ExM-8



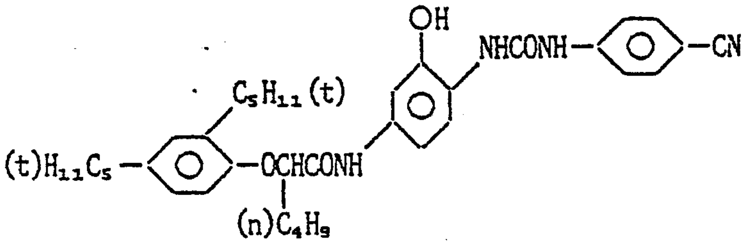
ExF-1



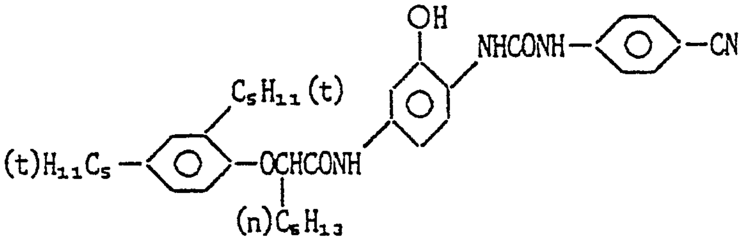
ExC-2



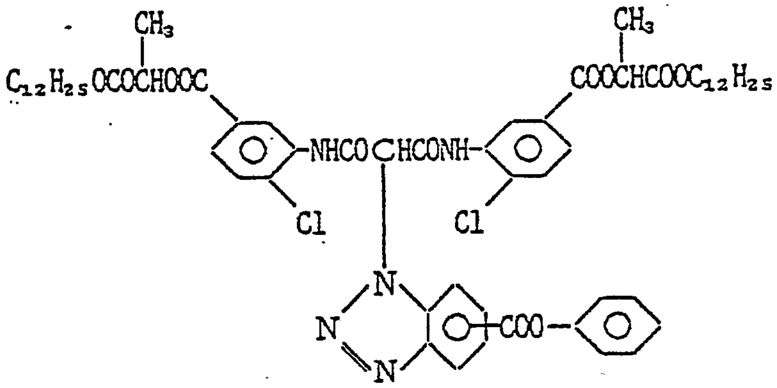
ExC-3



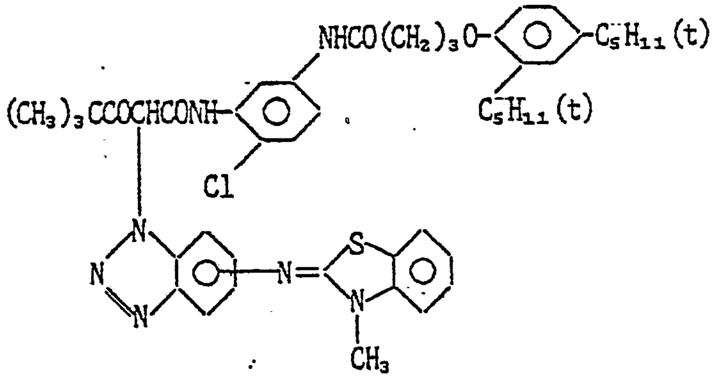
ExC-4



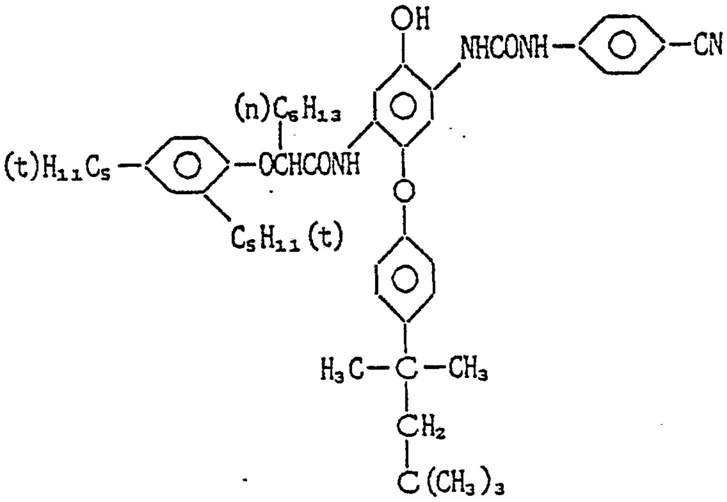
ExY-14



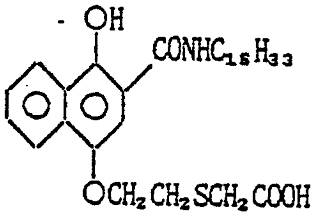
ExY-15



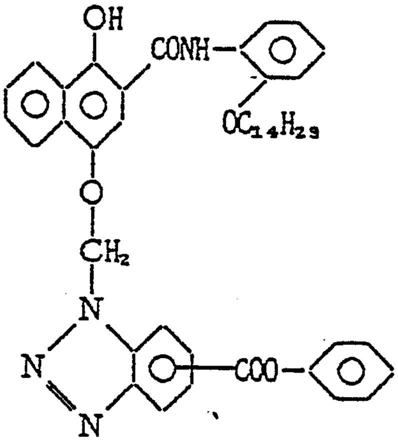
ExC-5



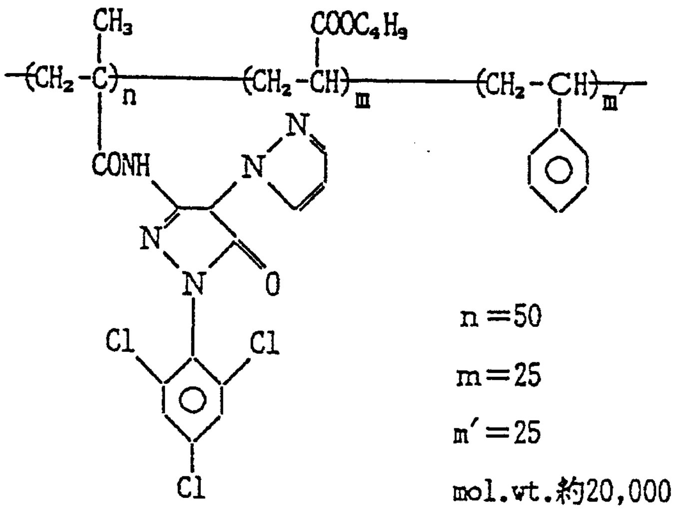
ExC-6



ExC-7



ExM-9



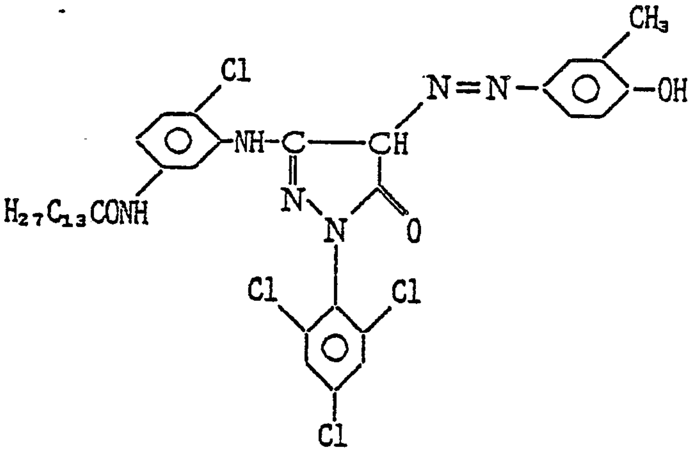
n=50

m=25

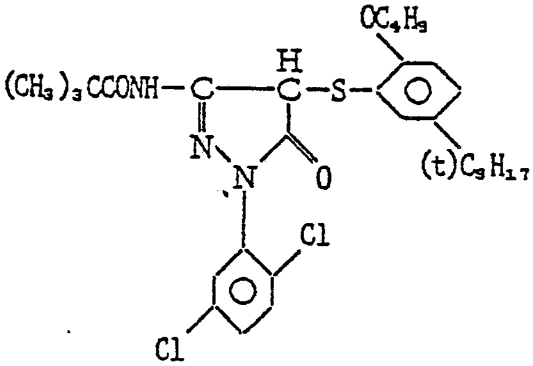
m′=25

mol.vt.約20,000

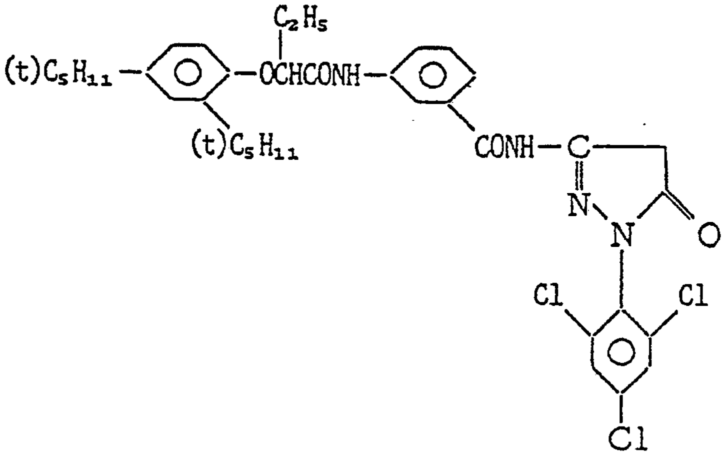
ExM-10



ExM-11



ExM-12



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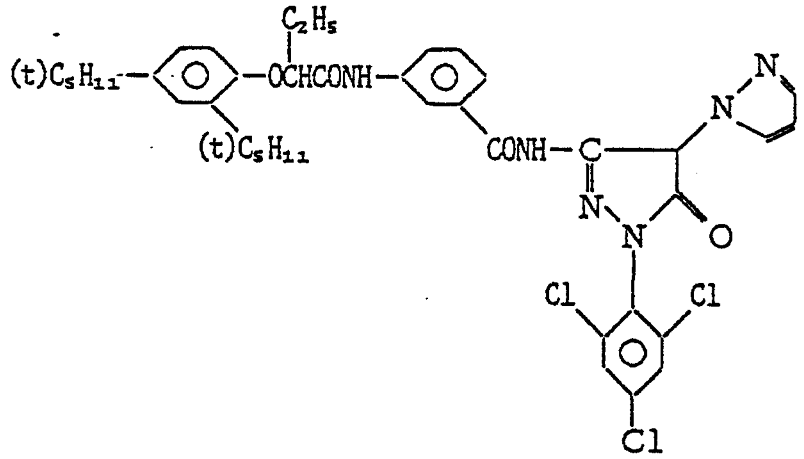
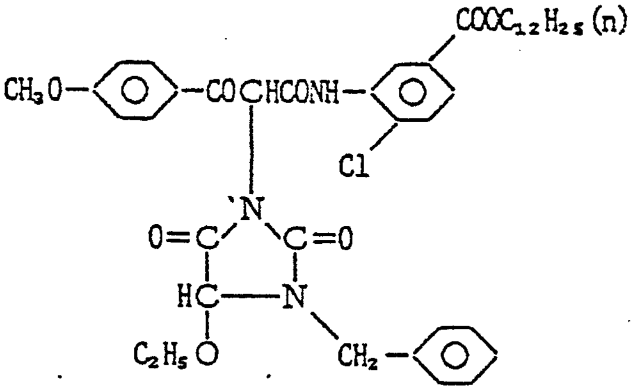
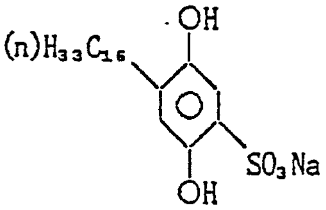


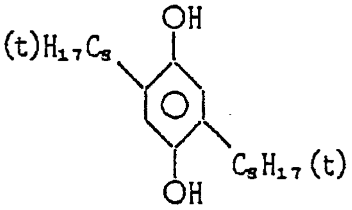
ExY-16



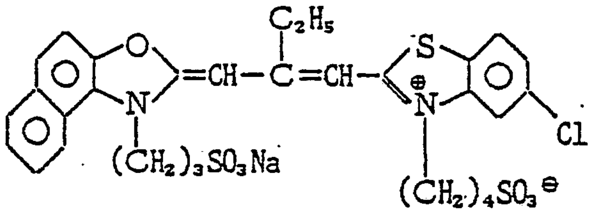
Cpd-1



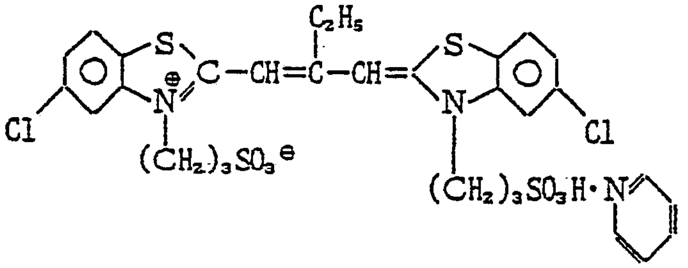
Cpd-2



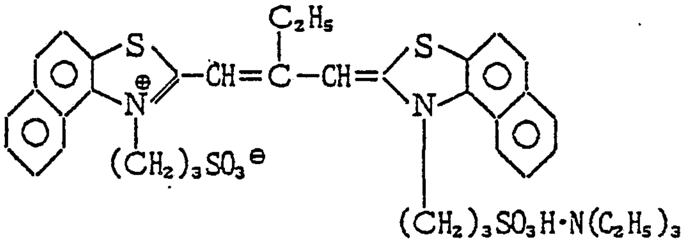
ExS-1



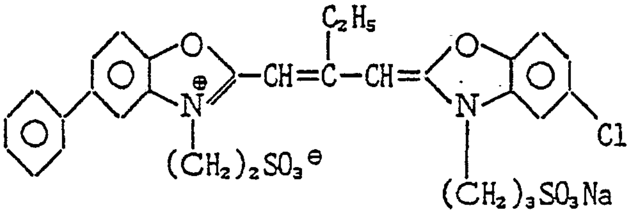
ExS-2



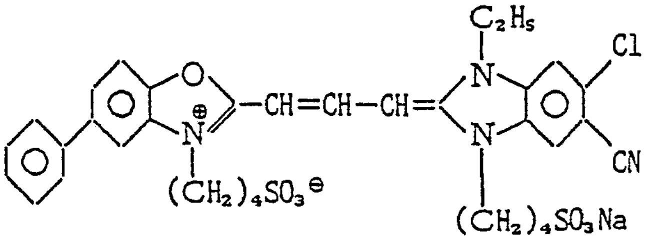
ExS-3



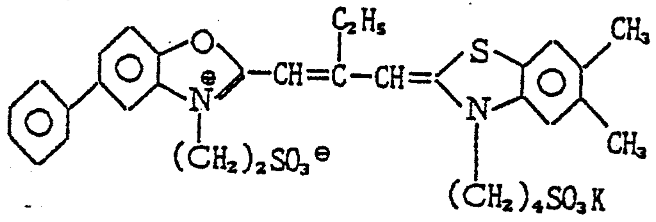
ExS-4



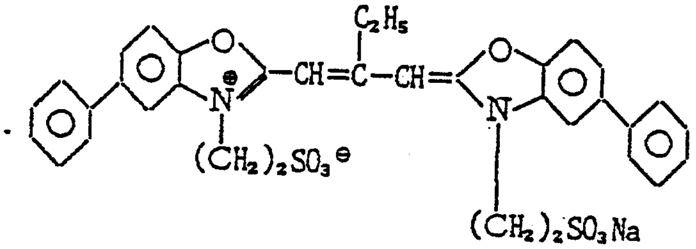
ExS-5



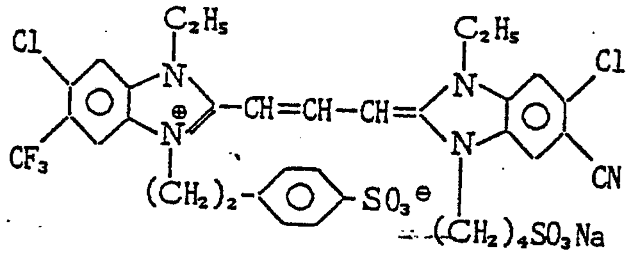
ExS-6



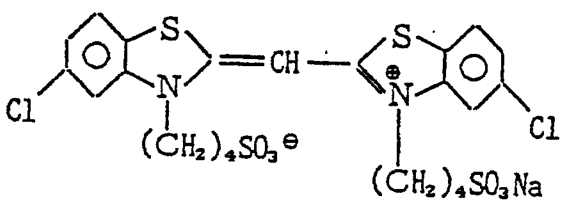
ExS-7



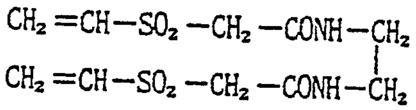
ExS-8



ExS-9

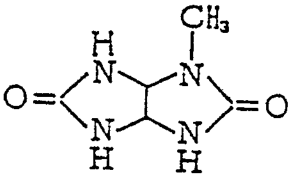


H-1

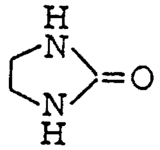


$$\begin{array}{l} CH_2=CH-SO_2-CH_2-CONH-CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2=CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

Cpd-3



Cpd-4

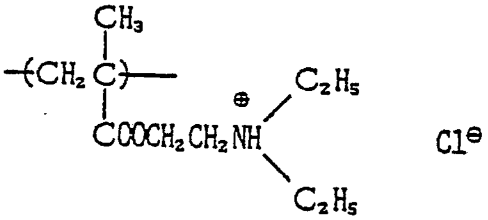


Then, comparison sample I-1 was prepared by adding light-collecting dye A-47 to the base sample and samples I-2, I-3, I-4 and I-5 of this invention were also prepared by further adding each polymer mordant to the sample I-1.

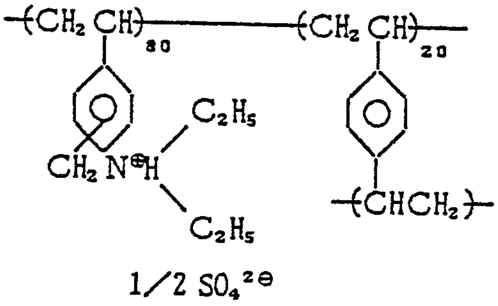
That is, in comparison sample I-1, light-collecting dye A-47 was added to the 1st, 2nd, and 3rd green-sensitive emulsion layers of the base sample in a total amount of 28 moles per dm^3 of gelation and/in samples I-2, I-3, I-4 and I-5 of this invention, each of polymer mordants B-1, B-2, B-3 and B-4 was added to the green-sensitive emulsion layers of the comparison sample I-1. The addition amount of each polymer mordant was shown by the ratio of the grain equivalent number as the cation thereof to the mole number of the dye A-47 and shown in Table 1 below. each addition amount was the amount necessary for having a mordanting power as each mordant.

The polymer mordants B-1 to B-4 are shown below.

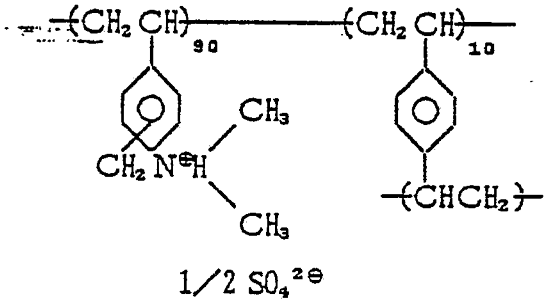
B-1



B-2



B-3



B-4

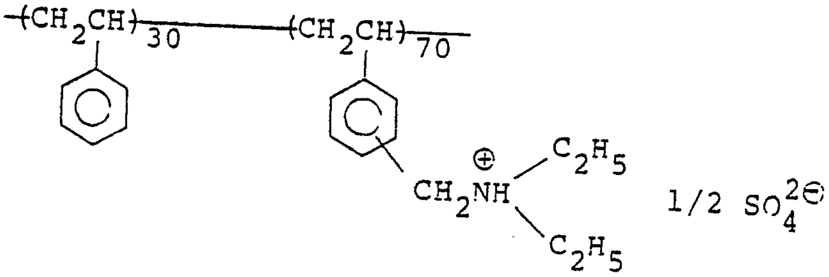


Table 1

Kind and Amount of polymer Mordant for Each sample		
Sample No.	Kind of Mordant	Amount of Mordant
I-1 (Comparison)	-	-
I-2 (Invention)	B-1	20
I-3 (Invention)	B-2	30
I-4 (Invention)	B-3	20
I-5 (Invention)	B-4	30

Each of the samples was exposed to white light through a continuous wedge for 1/100 second using a light source of 4800 °K in color temperature and processed by the following process.

Processing Step	Processing Time	Processing Temperature
Color Development	3 min. 15 sec.	38 °C
Bleach	6 min. 39 sec.	38 °C
Wash	2 min. 10 sec.	24 °C
Fix	4 min. 20 sec.	38 °C
Wash (1)	1 min. 05 sec.	24 °C
Wash (2)	1 min. 00 sec.	24 °C
Stabilization	1 min. 05 sec.	38 °C
Drying	4 min. 20 sec.	55 °C

Then, the compositions of the processing solutions used in the aforesaid process are shown below.

Color Developper

Diethylenetriaminepentaacetic Acid	1.0 g
1-Hydroxyethylidene-1, 1-diphosphonic Acid	3.0 g
Sodium Sulfite	4.0 g
Potassium Carbonate	30.0 g
Potassium Bromide	1.4 g
Potassium Iodide	1.5 mg
Hydroxylamine Sulfate	2.4 g
4-(N-Ethyl-N-β-hydroxyethylamino)- 2-methylaniline Sulfate	4.5 g
Water to make	1.0 liter
pH	10.05

Bleach Solution

Ethylenediaminetetraacetic Acid Ferric Sodium Trihydrate	100.0 g
Ethylenediaminetetraacetic Acid Di-sodium Salt	10.0 g
Ammonium Bromide	140.0 g
Ammonium Nitrate	30.0 g

Aqueous Ammonia (27%)	6.5ml
Water to make	1.0 liter
pH	6.0

Fix Solution

Ethylenediaminetetraacetic Acid Disodium Salt	0.5 g
Sodium sulfite	7.0 g
Sodium hydrogensulfite	5.0 g
Aqueous solution of Ammonium Thiosulfate (70%)	170.0 ml
Water to make	1.0 liter
pH	6.7

Stabiliziung Solution

Formalin (37%)	2.0 ml
Polyoxyethylene-p-monononyl Phenyl ether (Mean polymerization degree 10)	0.3 g
Ethylenediaminetetraacetic Acid Disodium Salt	0.05 g
Water to make	1.0 liter
pH	5.0 to 8.0

The results of the photographic properties obtained are shown in Table 2, where in the blue sensitivity (B sensitivity), green sensitivity (G sensitivity) and red sensitivity (R sensitivity) each was shown by the relative value of the reciprocal of the exposure amount giving fog + 0.2 in optical density of the color image of each light-sensitive emulsion layers with that of the comparison sample I-1 being 100.

Table 2

Effect of Each Mordan to B, G, R sensitivities			
Sample No.	B Sensty.	G Sensty.	R Sensty.
I-1 (Comparison)	100	100	100
I-2 (Invention)	101	132	115
I-3 (Invention)	102	172	126
I-4 (Invention)	101	175	129
I-5 (Invention)	101	178	130

Form the results shown above, it can be seen that in the samples of this invention, the diffusion of the light-collecting dye A-47 into other layers is prevented by the existence of the polymer mordant, whereby the occurrence of the desensitization is inhibited by a filter effect.

Example 2

In Example 1 using the light-collecting dye A-47 and the mordant B-1, each relative sensitivity of the G, G, and R sensitivities in the case of changing the addition amount of the mordant B-1 was determined. In this case, however, the mordant B-1 was used for the samples of this invention only. The results are shown in Table 3.

Table 3

Amount of Mordant B-1 and Effect Thereof to B, G, and R Sensitivities				
Sample No.	Amount of B-1	B Sensty.	G Sensty.	R Sensty.
I-1 (Comparison)	-	100	100	100
II-1 (Invention)	10	100	105	103
II-2 (Invention)	20	100	115	106
II-3 (Invention)	35	101	134	110
II-4 (Invention)	72	101	155	116

From the results shown above, it can be seen that with the increase of the addition amount of the mordant B-1, the mordanting power is more intensified to inhibit the diffusion of the dye A-47 into other layers, whereby the desensitization of the emulsion layers, in particular, the green-sensitive emulsion layer is inhibited by a filter effect.

Also, in the samples of this invention thus processed, the light-collecting dye was substantially removed and the deterioration of color images by residual color was not observed.

Example 3

A multilayer color photographic light-sensitive material having the following layers on a cellulose triacetate film support having subbing layer was prepared as the base sample. Then, a comparison sample containing light-collecting dye A-47 in the 1st and 2nd green-sensitive emulsion layers of the base sample was prepared. Also, the samples of this invention further containing the mordants B-1, B-2, and B-3, respectively, in the green-sensitive emulsion layers were prepared.

The compositions of the layers of the base sample were as follows.

Layer 1 (Antihalation Layer)

A gelatin layer (dry thickness of 2 µm) containing

Black Colloid Silver	0.25 g/m^2
Ultraviolet Absorbent U-1	0.04 g/m^2
Ultraviolet Absorbent U-2	0.1 g/m^2
Ultraviolet Absorbent U-3	0.1 g/m^2
High-Boiling Organic Solvent O-1	0.1 ml/m^2

Layer 2 (Interlayer)

A gelatin layer (dry thickness of 1 µm) containing

Compound H-1	0.05g/m^2
High-Boiling Organic Solvent O-2	0.05 ml/m^2

Layer 3 (1st Red Sensitive Emulsion Layer)

A gelatin layer (dry thickness of 1 µm) containing

Silver iodobromide emulsion spectrally sensitized by sensitizing dyes S-1 and S-2 (iodine content 4 mole%, mean grain size 0.3 m)	0.5 g/m2 as Ag
Coupler C-1	0.2 g/m2

Coupler C-2 0.05 g/m2
High-Boiling Organic Solvent O-2 0.12 ml/m2

Layer 4 (2nd Red Sensitive Emulsion Layer)

A gelatin layer (dry thickness of 2.5 µm) containing
Silver iodobromide emulsion spectrally sensitized by sensitizing dyes S-1 and S-2 (iodine content 2.5 mole%, mean grain size 0.55 m) 0.8 g/m2 as Ag
Coupler C-1 0.55 g/m2
Coupler C-2 0.14 g/m2
High-Boiling Organic Solvent O-2 0.33 ml/m2

Layer 5 (Interlayer)

A gelatin layer (dry thickness of 1 µm) containing
Compound H-1 0.1 g/m^2
High-Boiling Organic Solvent O-2 0.1 ml/m^2

Layer 6 (1st Green-Sensitive Emulsion Layer)

A gelatin layer (dry thickness of 2.5 µm) containing
Silver iodobromide emulsion spectrally sensitized by sensitizing dyes S-3 and S-4 (iodine content 3 mole%, mean grain size 0.3 µm) 0.7 g/m2 as Ag
Coupler C-3 0.35 g/m2
High-Boiling Organic Solvent O-2 0.26 ml/m2

Layer 7 (2nd Green-Sensitive Emulsion Layer)

A gelatin layer (dry thickness of 2.5 µm) containing
Silver iodobromide emulsion spectrally sensitized by sensitizing dyes S-3 and S-4 (iodine content 2.5 mole%, mean grain size 0.8 µm) 0.7 g/m2 as Ag
Coupler C-4 0.25 g/m2 High-Boiling Organic Solvent O-2 0.05 ml/m2

Layer 8 (Interlayer)

A gelatin layer (dry thickness of 1 µm) containing
Compound H-1 0.05 g/m^2
High-Boiling Organic Solvent O-2 0.1 ml/m^2

Layer 9 (Yellow Filter Layer)

A gelatin layer (dry thickness of 1 µm) containing
yellow Colloid Silver 0.1 g/m^2
Compound H-1 0.02 g/m^2
Compound H-2 0.03 g/m^{2}High-
Boiling Organic Solvent O-2 0.04 ml/m^2

Layer 10 (1st Blue-Sensitive Emulsion Layer)

A gelatin layer (dry thickness of 1.5 µm) containing
Silver iodobromide emulsion spectrally sensitized by sensitizing dyes S-5 (iodine content 2.5 mole%, mean

grain size 0.7 µm) 0.6 g/m2 as Ag
Coupler C-5 0.5 g/m2
High-Boiling Organic Solvent O-2 0.1 ml/m2

Layer 11 (End Blue-Sensitive Emulsion Layer)

A gelatin layer (dry thickness of 3 µm) containing
Silver iodobromide emulsion spectrally sensitized by sensitizing dyes S-5 (iodine content 2.5 mole%, mean grain size 1.2 µm) 1.1 g/m2 as Ag
Coupler C-5 1.2 g/m2
High-Boiling Organic Solvent O-2 0.23 ml/m2

Layer 12 (1st Protective Layer)

A gelatin layer (dry thickness of 2 µm) containing
Ultraviolet Absorbent U-1 0.02 g/m^2
Ultraviolet Absorbent U-2 0.03 g/m^2
Ultraviolet Absorbent U-3 0.03
g/m^{2}Ultraviolet Absorbent U-4 0.29 g/m^2
High-Boiling Organic Solvent O-1 0.28 ml/m^2

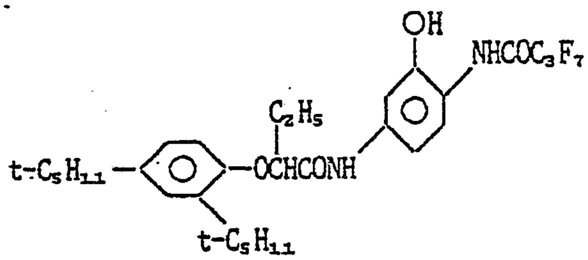
Layer 13 (2nd Protective Layer)

A gelatin layer (dry thickness of 0.8 µm) containing
Surface-fogged fine grain silver iodobromide emulsion (iodine content 1 mole%, mean grain size 0.06 µm) 0.1 g/m2 as Ag
Polymethyl Methacrylate Particles (mean grain size 1.5 µm) 0.2 g/m2

Each of the aforesaid layers contained a gelatin hardener H-3 and a surface active agent in addition to the aforesaid components.

The compounds used for making the sample are shown below.

C-1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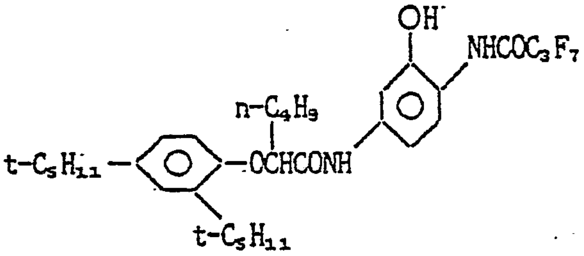
NHCOC3F7
C2H5
t-C5H11
OCHCONH
t-C5H11

C-2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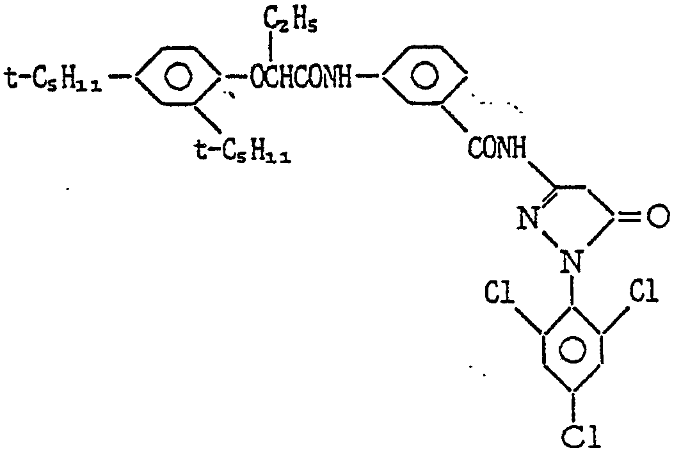
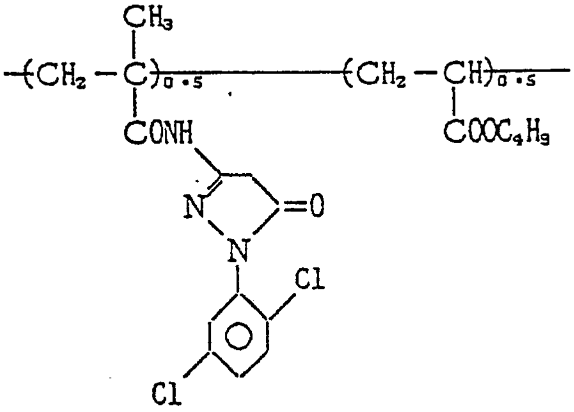
NHCOC3F7
n-C4H9
t-C5H11
OCHCONH
t-C5H11

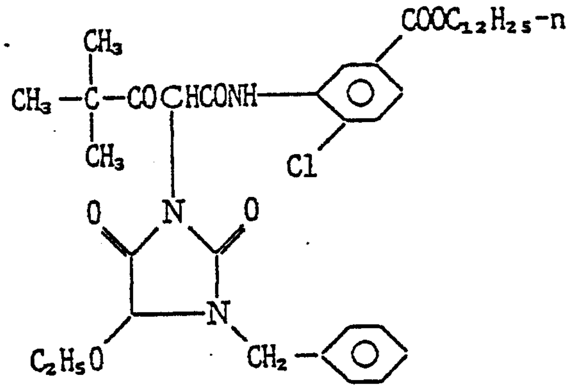
C-3


C2H5
t-C5H11
OCHCONH
t-C5H11
CONH
N
N
=O
Cl
Cl
Cl

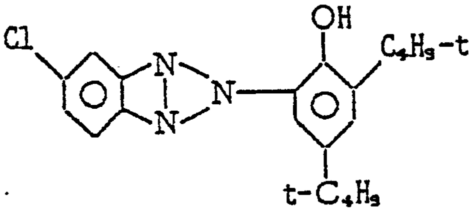
C-4


CH3
CH2
C
0.5
CH2
CH
0.5
CONH
COOC4H9
N
N
=O
Cl
Cl

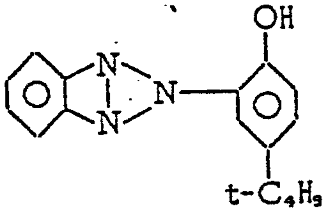
C-5


COOC12H25-n
CH3
CH3-C-COCHCONH
CH3
Cl
O
N
O
N
C2H5O
CH2

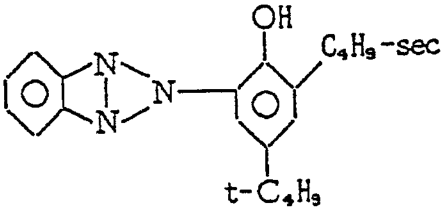
U-1


Cl
OH
C4H9-t
N
N
N
t-C4H9

U-2


OH
N
N
N
t-C4H9

U-3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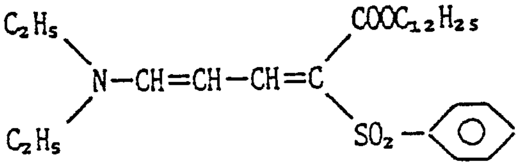
C4H9-sec
N
N
N
t-C4H9

U-4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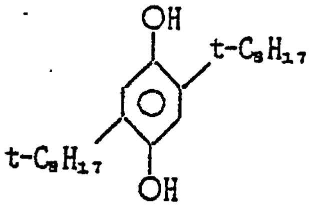
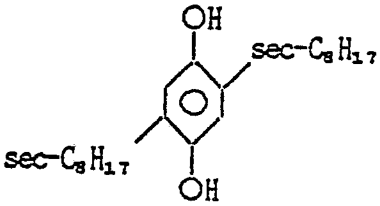
N-CH=CH-CH=C
C2H5
COOC12H25
SO2

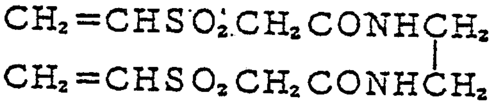
H-1



H-2

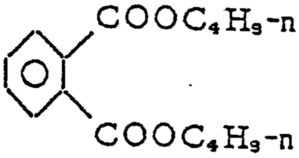


H-3

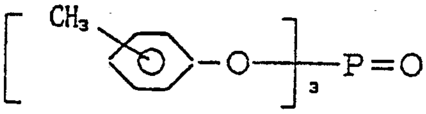


$$\begin{array}{l} CH_2=CHSO_2CH_2CONHCH_2 \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2=CHSO_2CH_2CONHCH_2 \end{array}$$

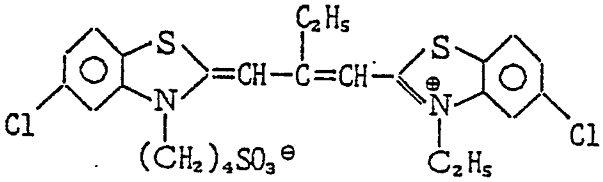
O-1



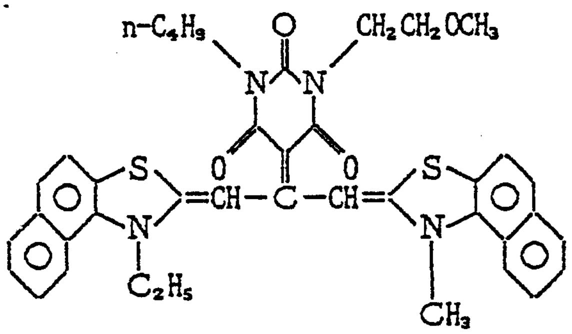
O-2



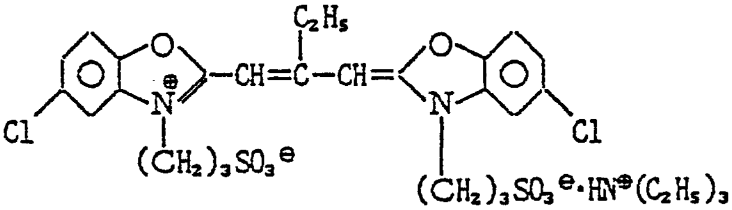
S-1



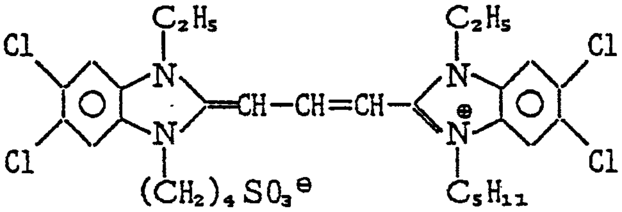
S-2



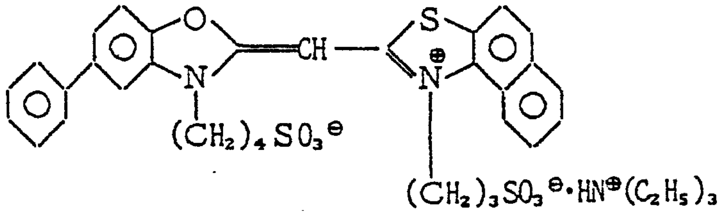
S-3



S-4



S-5



As in Example 1, comparison sample III-1 was prepared by adding light-collecting dye A-47 to the 1st and 2nd green-sensitive emulsion layers of the base sample in a total amount of 28 moles per dm^2 of gelatin and samples III-2, III-3, III-4 and III-5 of this invention were prepared by adding mordants B-1, B-2, B-3 and B-4, respectively to the green-sensitive emulsion layers of the comparison sample III-1. The amount of each mordant was shown by the ratio of the gram equivalent number as the cation to the mole number of the dye A-47 and shown in Table 4. The addition amount of the mordant was sufficient for giving a mordant power of each mordant.

Table 4

Kind and Amount of Mordant in Each sample		
Sample No.	Kind of Mordant	Amount of Mordant
III-1 (Comparison)	-	-
III-2 (Invention)	B-1	20
III-3 (Invention)	B-2	30
III-4 (Invention)	B-3	20
III-5 (Invention)	B-4	30

Each of these samples was exposed to white light through a continuous wedge for 1/100 second using a light source of 4800 °K in color temperature and processed by the following process.

Processing Step	Time	Temperature
1st Development	6 min.	38 °C
Wash	2 min.	38 °C
Reversal	2 min.	38 °C
Color Development	6 min.	38 °C
Control	2 min.	38 °C
Bleach	6 min.	38 °C
Fix	4 min.	38 °C
Wash	4 min.	25 °C
Stabilization	1 min.	25 °C

The compositions of the processing solutions used in the aforesaid process were as follows.

<u>1st Developer</u>

Nitrilo-N,N,N-trimethylenephosphonic Acid Penta-sodium Salt	2.0 g
Sodium Sulfite	30 g
Hydroquinone. Potassium Monosulfonate	20 g
Potassium Carbonate	33 g
1-Phenyl-4-methyl-4-hdyroxymethyl- 3-pyrazolidone	2.0 g
Potassium Bromide	2.5 g
Potassium Thiocyanate	1.2 g
Potassium Iodide	2.0 mg
Water to make	1.0 liter
pH	9.60

The pH was adjusted by hdyrochloric acid or potassium hydroxide.

<u>Reversal Solution</u>

Nitrilo-N,N,N-trimethylenephosphonic Acid. Penta-sodium Salt	3.0 g
Stannous Chloride. Di-hydrate	1.0 g
p-Aminophenol	0.1 g

Sodium Hydroxide	8 g
Glacial Acetic Acid	15 ml
Water to make	1.0 liter
pH	6.00

The pH was adjusted by hdyrochloric acid or potassium hydroxide.

Color developer

Nitrilo-N,N,N-trimethylenephosphonic Acid. Penta-sodium Salt	2.0 g
Sodium Sulfite	7.0 g
Tro-sodium Phosphate. 12 H_2O	36 g
Potassium Bromide	1.0 g
Potassium Iodide	90 mg
Sodium Hydroxide	3.0 g
Citrazinic Acid	1.5 g
N-Ethyl-N-(β-methanesulfonamidoethyl) -3-methyl-4-aminoaniline Sulfate	11 g
3,6-Dithiaoctane-1, 8-diol	1.0 g
Water to make	1.0 liter
pH	11.80

The pH was adjusted by hdyrochloric acid or potassium hydroxide.

Control Solution

Ethylenediaminetetraacetic Acid Disodium Salt Di-hydrate	8.0 g
Sodium Sulfite	12 g
1-Thioglycerol	0.4 ml
Water to make	1.0 liter
pH	6.20

The pH was adjusted by hdyrochloric acid or potassium hydroxide.

Bleach Solution

Ethylenediaminetetraacetic Acid. Disodium Salt. Di-hydrate	2.0 g
Ethylenediaminetetraacetic Acid. Fe(III) Ammonium. Di-hydrate	120 g
Potassium Bromide	100 g
Ammonium Nitrate	10 g
Water to make	1.0 liter
pH	5.70

The pH was adjusted by hdyrochloric acid or potassium hydroxide.

Fix Solution

Ammonium thiosulfate	80 g
Sodium Sulfite	5.0 g
Sodium Hydrogensulfite	5.0 g
Water to make	1.0 liter
pH	6.50

The pH was adjusted by hdyrochloric acid or potassium hydroxide.

Stabilization Solution

Fromalin (37%)	5.0 ml
Polyoxyethylene-p-monononyl Phenyl Ether (mean polymerization degree 10)	0.5 ml

Water to make 1.0 liter
pH not adjusted

The result of the photographic properties obtained are shown in Table 5, wherein the blue sensitivity (B sensitivity), the green sensitivity (G sensitivity), and the red sensitivity (R sensitivity) each was shown by the grelative value of the reciprocal of the exposure amount iving a density of 1.0 in the color images of each layer with that of comparison sample•III-1 being 100.

Table 5

Effect of Each Mordant to B. G. And R sensitivities			
Sample No.	B Sensity.	G Sensity.	R Sensity.
III-1 (Comparison)	100	100	100
III-2 (Invention)	103	113	110
III-3 (Invention)	102	162	123
III-4 (Invention)	102	173	125
III-5 (Invention)	103	175	126

From the results shown above, it can be seen that in color reversal photographic materials, the diffusion of the light-collecting dye into other layers can be prevented by the mordant.

Also, in the samples of this invention after processing, substantial no residual color by the light-collecting dye was observed.

Example 4

Comparison sample IV-1 was prepared by adding light-collecting dye A-56 to the 1st, 2nd, and 3rd red-sensitive emulsion layer of the comparison sample I-1 in Example 1 in total amounts of 28 m moles per dm^3 of gelatin and also light-collecting dye A-3 to the 1st and 2nd blue-sensitive emulsion layers of the same comparison sample in total amounts of 28 m moles per dm^3 of gelatin. Thus, the comparison sample IV-1 contained light-collecting dyes A-56, A-47 and A3 in the red-sensitive emulsion layers, green-sensitive emulsion layers, and blue-sensitive emulsion layers, respectively.

On the other hand, sample IV-2 of this invention was prepared by adding polymer mordant B-1 to all the light-sensitive emulsion layers of the comparison sample IV-1 in 20 gram equivalent per mole of each light-collecting dye in each emulsion layer. Also, sample IV-3 of this invention was also prepared by using light-collecting dye B-2 in place of B-1 used for the sample IV-2 of this invention in an amount of 30 g equivalent per mole of each light-collecting dye. Furthermore, sample IV-4 or IV-5 of this invention was similarly prepared respectively by adding 20 gram equivalent per mole of polymer mordant B-3 or 30 gram equivalent per mole of polumer mordant B-4 in place of B-1 in each light-collecting dye.

Each of these samples was exposed to white light through a continuous wedge for 1/100 second using a light source of 4800 °K and processed as in Example 1. The results obtained are shown in Table 6, wherein the sensitivity was same as in Example 1, however, in this example the sensitivity of the comparison sample IV-1 being defined as 100.

Table 6

Relative Sensitivity of Each Sample			
Sample No.	B Sensity.	G Sensity.	R Sensity.
IV-1 (Comparison)	100	100	100
IV-2 (Invention)	123	133	138
IV-3 (Invention)	142	174	162
IV-4 (Invention)	138	175	168
IV-5 (Invention)	148	182	170

From the results shown in the above table, it can be seen that in the samples of this invention, the diffusion of the light-collecting dye into other layers is inihibited by the existence of the polymer mordant, whereby the occurrence of desensitization by a filter effect and a substantially reduction in the concentration of the dye is inhibited.

Also, residual color after processing was scarcely observed.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modification can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide photographic material having at least one silver halide emulsion layer spectrally sensitized by spectral sensitizing dye(s), wherein the silver halide emulsion layer contains in the hydrophilic dispersion medium a hydrophilic polymer having a cationic structure or a dispersion of the hydrophilic polymer and a luminous dye having a relatively weak adsorptive property to silver halide and simultaneously satisfying following conditions 1), 2), and 3), with the proviso that the light-collecting dye and the spectral sensitizing dye may be the same compound:

1) the equilibrium adsorption amount of the dye in an aqueous 5% gelatin solution containing silver bromide the outer surface of which is substantially composed of a {III} plane is not more than 10^{-6} mole/m^2 per surface area of the silver bromide at a temperature of 40 °C, pH of 6.5 ±0.05, and a dye concentration in solution phase of 10^{-4} mole/liter;

2) the luminous quantum yield of the dye is at least 0.1 at room temperature and at a concentration in dry gelatin of 10^{-4} mole/dm^3; and

3) the dye has a luminous band at least partially overlapping the optical absorption band of the adsorptive spectral sensitizing dye on the silver halide.

2. The silver halide photographic material as claimed in claim 1, wherein the adsorptive spectral sensitizing dye is a merocyanine dye, a cyanine dye having at least one of a thiazole nucleus, a selenazole nucleus, a quinoline nucleus, and an indolenine nucleus in the molecule, or a cyanine dye having at least two of oxazole nuclei or at lest two of imidazole nuclei, these basic heterocyclic ring nucleus, aliphatic hydrocarbon ring, and/or aromatic hydrocarbon ring contained in the cyanine dye may be fused with each other.

3. The silver halide photographic material as claimed in claim 1, wherein the solubility for water of the luminous dye dispersed in the hydrophilic dispersion medium is at least 10^{-2} mole/liter at 25 °C and pH 7.0.

4. The silver halide photographic material as claimed in claim 1, wherein the equilibrium adsorption amount of the luminous dye dispersed in the hydrophilic dispersion medium onto the {III} plane of the silver bromide is not more than 10^{-7} mole/m^2.

5. The silver halide photographic material as claimed in claim 1, wherein the luminous quantum yield of the luminous dye is at least 0.3.

6. The silver halide photographic material as claimed in claim 1, wherein the luminous quantum yield of the luminous dye is at least 0.5.

7. The silver halide photographic material as claimed in claim 1, wherein the absorption maximum wavelength of the luminous dye in the photographic material is from 420 n.m. to 740 n.m.

8. The silver halide photographic material as claimed in claim 6, wherein the concentration of the luminous dye in the hydrophilic dispersion medium is at least 2 x 10^{-3} mole/dm^3.

9. The silver halide photographic material as claimed in claim 8, wherein the concentration of the luminous dye in the hydrophilic dispersion medium is less than 10 mole/dm^3.

10. The silver halide photographic material as claimed in claim 1, wherein the luminous dye is a water-soluble cyanine dye having at least 4 sulfonic groups and/or carboxylic acid groups in the molecule.

11. The silver halide photographic material as claimed in claim 10, wherein the luminous quantum yield of the luminous dye is at least 0.5.

12. The silver halide photographic material as claimed in claim 1, wherein the wavelength giving the luminous maximum of the luminous dye is not over the wavelength of the maximum absorption of the dye having absorption at the longest wavelength region in the dyes adsorbed on the silver halide.

13. The silver halide photographic material as claimed in claim 1, the wavelength giving the luminous maximum is disposed within 60 n.m. from the maximum absorption wavelength to a shorter wavelength side.

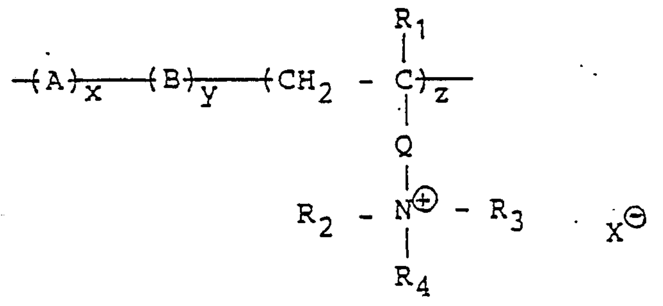
14. The silver halide photographic material as claimed in claim 1, wherein the stoke shift of luminescence (wavelength difference between the absorption peak and the luminous peak) given by the luminous dye in dry gelatin at room temperature and at a concentration of 10^{-4} mole/dm^3 is within 40 n.m.

15. The silver halide photographic material as claimed in claim 13, wherein the stokes shift of luminescence given by the luminous dye is within 20 n.m.

16. The silver halide photographic material as claimed in claim 1, wherein the reduction photographic material as claimed in claim 1, wherein the reduction potential of the luminous dye in a mixed solution of water and ethanol (1:1 by volume ratio) is baser than -1.0 volt to a saturated calomel reference electrode.

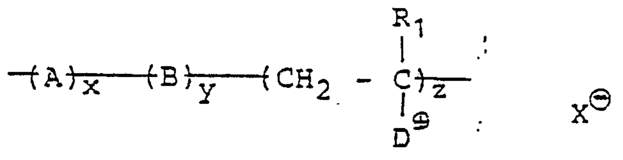
17. The silver halide photographic material as claimed in claim 1, wherein when the luminous dye is dissociated in an aqueous media, the total static charges are negative.

18. The silver halide photographic material as claimed in claim 1, wherein the cationic polymer is represented by formula (I), (II), or (III):



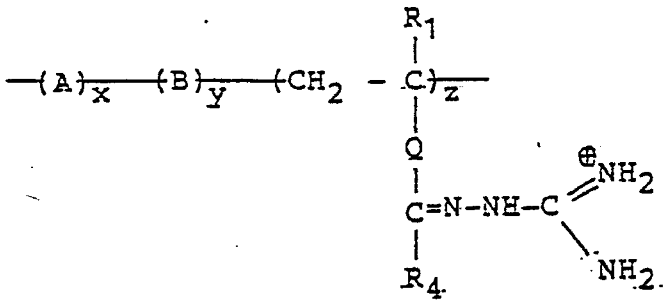
$$-(A)_x-(B)_y-\Big(CH_2-\overset{\displaystyle R_1}{\underset{\displaystyle Q}{\overset{|}{\underset{|}{C}}}}\Big)_z- \qquad Q:\ R_2-\overset{\displaystyle |}{\underset{\underset{\displaystyle R_4}{|}}{N^{\oplus}}}-R_3 \quad X^{\ominus} \tag{I}$$

(I)



$$-(A)_x-(B)_y-\Big(CH_2-\overset{\displaystyle R_1}{\underset{\displaystyle D^{\oplus}}{\overset{|}{\underset{|}{C}}}}\Big)_z- \qquad X^{\ominus} \tag{II}$$

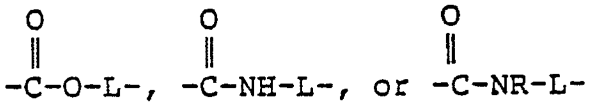
(II)



$$-(A)_x-(B)_y-(CH_2-\overset{R_1}{\underset{\underset{\underset{R_4}{C}=N-NH-C(=\overset{\oplus}{N}H_2)(NH_2)}{|}}{Q}}{C}})_z- \quad X^{\ominus}$$

(III)

wherein A represents a monomer unit having at least two copolymerizable ethylenically unsaturated groups and copolymerized with a copolymerizable monomer having at least one of the aforesaid ethylenically unsaturated groups at the side chain thereof; B represents a monomer unit copolymerized with a copolymerizable ethylenically unsaturated monomer; R_1 represents a hydrogen atom, a lower alkyl group, or an aralkyl group; and R_2, R_3, and R_4, which may be the same or different, each represents a hydrogen atom, an alkyl group, or an aralkyl group, wherein in formula (I), optional two or three groups of R_2, R_3, and R_4 may form a 5-membered or 6-membered ring or such a heterocyclic ring together with nitrogen atom; Q represents an alkylene group, a phenylene group, an aralkylene group,



$$-\overset{O}{\overset{\|}{C}}-O-L-,\ -\overset{O}{\overset{\|}{C}}-NH-L-,\ \text{or}\ -\overset{O}{\overset{\|}{C}}-NR-L-$$

(wherein L represents an alkyl group, an arylene group, or an aralkylene group and R represents an alkyl group), wherein in formula (III), Q may be a single bond; $X^{\ominus}$ represents an anion; $D^{\oplus}$ represents a 5-membered or 6-membered heterocyclic ring having 1 or 2 nitrogen atoms, wherein the nitrogen atom is positively charged; $D^{\oplus}$ may have substituent; x, y, and z represent mole percentage, and x is from 0 to 60 mole%, y is from 0 to 60 mole%, and z is from 30 to 100 mole%.

19. The silver halide photographic material as claimed in claim 1, wherein the cationic polymer is water-soluble and forms a uniform solution of the polymer in water.

20. The silver -halide photographic material as claimed in claim 1, wherein the addition amount of the cationic polymer is from 0.5 gram equivalent to 100 gram equivalent as cation per mole of the luminous dye.

21. The silver halide photographic material as claimed in claim 1, wherein the addition amount of the cationic polymer is from 1 gram equivalent to 50 gram equivalent as cation per mole of the luminous dye.