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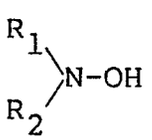
(54) Method for common development processing of two kinds of light-sensitive silver halide photographic material.

(57) There is disclosed a method for common development processing of two kinds of light-sensitive silver halide photographic material which comprises the step of development processing an internal latent type direct positive light-sensitive silver halide photographic material and a negative-type light-sensitive silver halide photographic material in the same development processing bath, and the step of applying whole surface exposure on the internal latent type direct positive light-sensitive silver halide photogrpahic material during development processing of the internal latent type direct positive light-sensitive silver halide photographic material, characterized in that the developing processing solution contains a compound represented by the formula (A) shown below:



(A)

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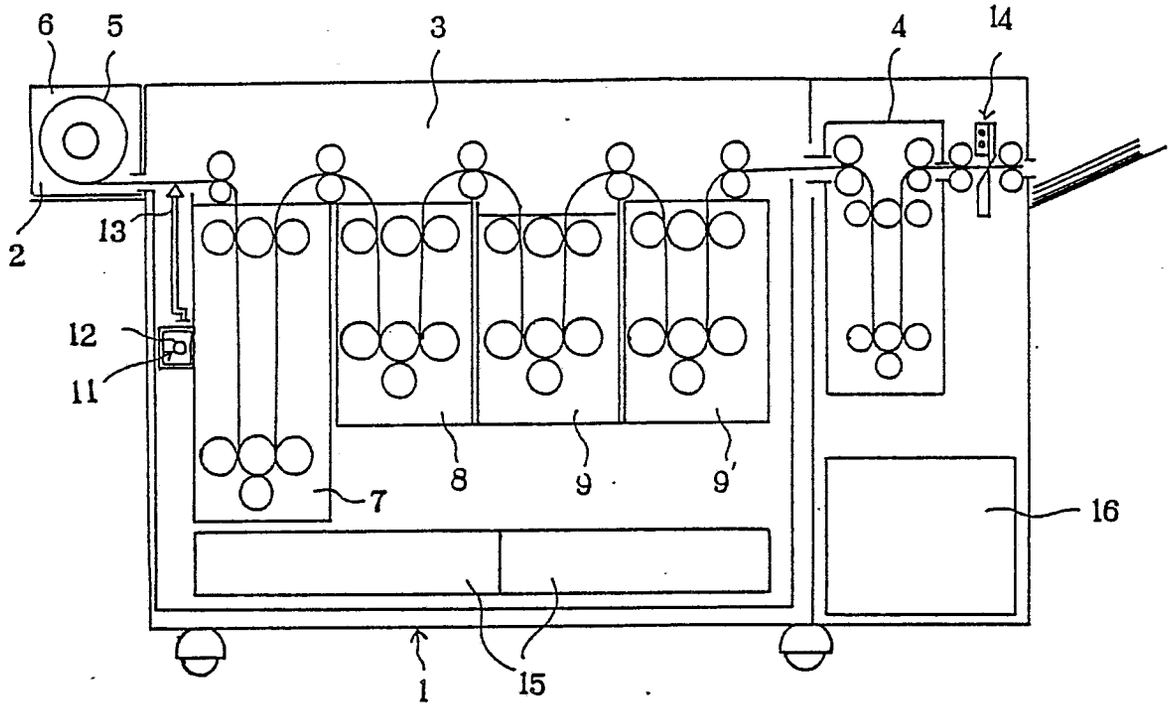
wherein R_1 and R_2 each represent hydrogen atom or an alkyl group having 1 to 5 carbon atoms which may have a substituent or may be combined with each other to form a heteroxyclic ring.

Fig. 1



Method for common development processing of two kinds of light-sensitive silver halide photographic material

BACKGROUND OF THE INVENTION

This invention relates to a method for development processing which processes an internal latent image positive silver halide photographic material (hereinafter called internal latent direct positive sensitive material) and a negative-type light sensitive silver halide photographic material (hereinafter called negative-type sensitive material) with a common developing solution.

The method used for preparation of a positive-image by use of an internal latent type direct positive sesnsitive material may be classified primarily into the two types, excluding special ones.

One type is to use a previously fogged silver halide emulsion and obtain a positive-image after development by destroying the fogged nuclei (latent image) at the exposed portion by utilizing solarization or Herschel effect, etc.

The other embodiment is to use an internal latent image type silver halide emulsion which is not fogged and obtain a positive-image by performing after image exposure surface development after application of fogging treatment or while applying fogging treatment.

The above internal latent image type silver halide emulsion refers to a silver halide photographic emulsion, having light-sensitive nuclei primarily internally of the silver halide grains, which can form latent images internally of the grains by exposure.

The method of the latter type has generally higher sensitivity as compared with the method of the former type, and is suitable for image formation requiring high sensitivity, and the present invention concerns the latter type.

In this technical field, various techniques have been hitherto known. For example, the principal techniques are disclosed in U.S. Patents No. 2,592,250, No. 2,466,957, No. 2,497,875, No. 2,588,982, No. 3,761,266, No. 3,761,276 and No. 3,796,577 and GB Patent No. 1,151,363, and by use of these methods, as the direct positive type, light-sensitive photographic materials with relatively high sensitivity can be prepared.

Although it is difficult to say that clear explanation has been given about details of the mechanism of forming direct positive images, the process of forming positive-image can be understood to some extent by the "sensitivity reduction action by internal latent images" as discussed in Mieth and James, "The Theory of the Photographic Process", Third Edition, page 161.

Shortly speaking, it seems likely that, due to the surface sensitivity reduction action caused by the so-called internal latent image produced internally of the silver halide grains by the internal image exposure, fogged nuclei are formed selectively only on the surfaces of the unexposed silver halide grains, and then photographic images are formed at the unexposed portion by conventional development.

As the means for forming selectively fogged nuclei as mentioned above, there have been known the method called "chemical fogging" in which fogging is effected by use of a fogging agent, and the method called "light fogging" in which fogging is effected by giving whole surface exposure.

Whereas, for processing an internal latent type direct positive sensitive material in a photographic developing station, it is a generall practice to perform processing by providing a processing line for exclusive use for the internal latent type direct positive sensitive material separately from the processing line for the negative-type sensitive material of the prior art.

The processing line for the negative-type sensitive material has, for example, the three kinds of instruments of an automatic developing machine for negative-film, an automatic developing machine for negative-paper and an automatic printing device arranged separately, while the processing line for the inner latent type direct positive sensitive material comprises two kinds of an automatic printing device for exclusive use and an automatic developing machine for exclusive use. Generally speaking, these respective instruments require working spaces of predetermined broadness there-around, and working spaces necessary for supplemental cock adjustment, vaporization correction, tank liquid exchange and supplement working must be ensured around these instruments.

Accordingly, when the above instruments are arranged separately, care must be taken so that the working spaces around the respective instruments may not overlap each other, whereby there is a fear that troubles may be brought ina narrow place in a small scale color photograph developing station. Thus, simplification of the processing method and miniaturization of the automatic developing machine are now becoming important tasks.

In view of the state of the art as described above, the present inventors have continued to study about processing of an internal latent type direct positive sensitive material and a negative-type sensitive material with a common developing solution, and first attempted to process an internal latent type direct positive sensitive material and a negative-type sensitive material with a developing solution of the same composition according to the chemical fogging method, but fogging occurred remarkable in the negative-type sensitive material. The developing solution for processing commonly an internal latent type direct positive sensitive material and a negative-type sensitive material is required to be maintained and managed more highly in activity than is required for other processing solutions, and furhter required to be set at a higher solution temperature than other processing solutions. Thus, it has been found not easy to inhibit generation fogging for the above negative-type sensitive material.

Accordingly, the present inventors have investigated about the light fogging method. More specifically, it has been attempted to turn the light source for giving the whole surface exposure ON during the development processing of an internal latert type direct positive sensitive material, while to turn the above light source OFF during development processing of a negative-type sensitive material. However, this light fogging method was found to involuve the following problem.

That is, by employment of the above light fogging method, although it has been rendered possible to process both an internal latent type direct positive sensitive material and a negative-type sensitive material with a common developing solution, even if developing solution may be supplemented corresponding to the respective light-sensitive materials, it has been found that coloration of the solution occurred, whereby the color formed dye density changed due to the filter effect of the secondary exposure.

Further, there ensured that problem that the exposure dose of light fogging for the internal latent type positive sensitive material was fluctuated and fluctuation in light fogging exposure dose was too great between the newly prepared solution and the fatigued solution after use for prolonged time, whereby no stable photographic performance could be obtained.

As the result of extensive studies by the present inventors, it has been found that the cause for giving rise to coloration of solution may be (1) firstly, oxidized colored product having absorption at specific wavelength, which may result in yellow coloration to cause lowering in color formed density of yellow dyes or stain, and (2) secondly, coloration of an anti-irradiation dye (hereinafter called AI dye) used for the purpose of improving sharpness of the light-sensitive material, whereby lowering in color formed density and generation of stain may be caused. These problems have particularly greater influencce when using an internal latent type direct positive sensitive material, but also generation of stain will occur even in a negative-type sensitive material.

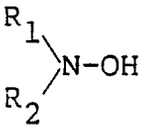
For this reason, it may be considered possible to solve the problem by reducing the amount of the AI dye added or using no such dye, but since it is one of the important elements for improvement of sharpness or control of sensitivity, it is impossible to employ such solution method.

And, this problem is an important problem to be solved, when an internal latent type direct positive sensitive material and a negative-type sensitive material are to be processed with a common developing solution.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for processing of a light-sensitive silver halide photographic material, which performs development processing of an internal latent type direct positive light-sensitive material with a common developer to give stable photographic performance.

In order to accomplish the above object, the present inventors have made various investigations, and consequently completed the present invention, and the method for development processing of a light-sensitive silver halide photographic materials has the step of development processing an internal latent type direct positive light-sensitive silver halide photographic material and a negative-type light-sensitive silver halide photographic material in the same development processing bath, and the step of applying whole surface exposure on said internal latent type direct positive light-sensitive silver halide photographic material during development processing of said internal latent type direct positive light-sensitive silver halide photographic material, characterized in that said developing processing solution contains a compound represented by the formula (A) shown below



(A)

wherein R_1 and R_2 each represent hydrogen atom or an alklyl group having 1 to 5 carbon atoms which may have a substituent, provided that R_1 and R_2 cannot be hydrogen atoms at the same time, or may be combined with each other to form a heterocyclic ring.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic illustration showing an example of the automatic developing machine whieh can be used for processing of the present invention, in which 7 is a development processing tank, 8 is a bleach-fixing processing tank, 9 and 9' are stabilizing tanks and 11 is an exposure device.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

By use of the compound represented by the formula (A), not only production of the component having absorption at a specific wavelength can be prevented, but also solution coloration with the Al dye dissolved out from the light-sensitive material can be prevented, to give the result that ccolor fluctuation and stain by the secondary reversal exposure can be rduced.

In the prior art, the Al dye has been said to form generally reduced leuco with sulfite ion, and recently Al dyes without reducing decoloration have been frequently used for improvement of sharpness. The present inventors have found in the same processing of an inernal latent type direct positive light-sensitive material and a negative-type light-sensitive material that the Al of the present invention effects decoloration very effectively in the presence of hydroxylamine in an amount of the present invention and dose not obstruct the light fogging effect of the internal latent type direct positive light-sensitive material, to accomplish the present invention.

The present invention performs development processing of an internal latent type direct positive light-sensitive material and a negative-type light-sensitive material with a common development processing solution, and also can use an automatic developing machine which enables control of the whole surface exposure may be given when the internal latent type direct positive light-sensitive material is conveyed in for the development processing layer, while no whole surface exposure may be given when the negative-type light-sensitive material is conveyed in for the development processing layer.

In the present invention, the negative light-sensitive material means color printing paper, color negative film, color reversal film and color reversal paper.

The processing step to be used in the present invention should be preferably a color developing step as the development processing.

Particularly, as the color development processing, it is preferably to practice a color development processing step, a bleaching processing step, a fixing processing step, a stabilizing processing step substituting for water washing, but in place of the processing step by use of a bleaching solution and the processing step by use of a fixing solution, a bleach-fixing processing step can be also practiced.

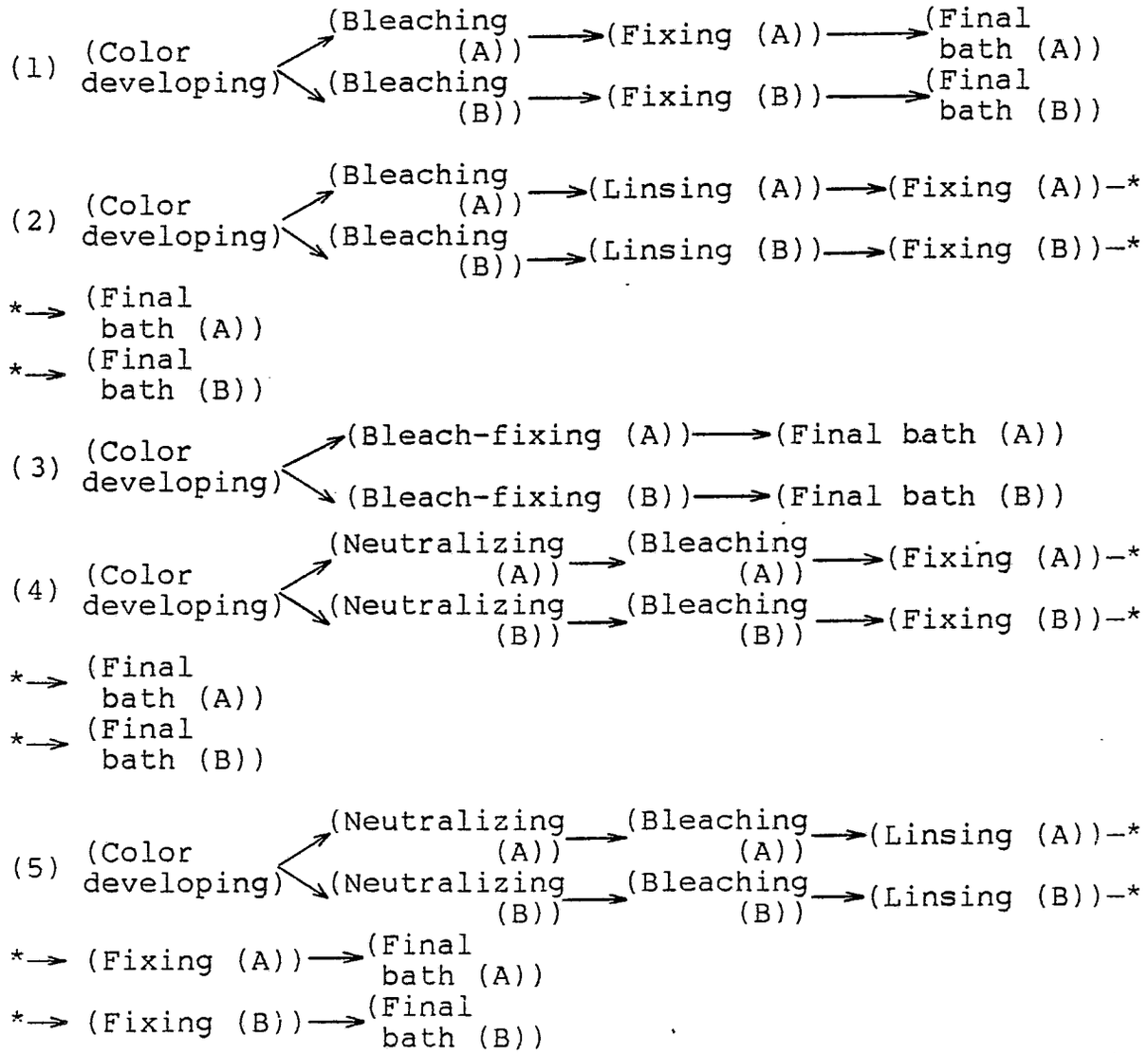
These processing step may be also combined with pre-film-hardening step, its neutralization step, stop fixing processing step, post-film-hardening step, etc. In these processings, in place of the color development processing step, the activator processing step may be also practiced, in which a color development agent or its precursor is incorporated in the light-sensitive material and the development processing is performed with an activator solution.

Representative examples of these processings are shown below. In these processings, as the final step (the final bath), either (1) the water washing processing step, (2) the stabilizing processing step substituting for water washing or (3) the water washing processing step and the stabilizing pro cessing step.

The processing method of the present invention employs a developing tank which is made substantiall common, and can also use the processing tanks made into a unit, which may be also linked together, if desired.

The processing tanks in the processing method of the present invention may have a constitution, employing the processing tanks according to the known processing steps.

Preferable representative examples in the processing steps of the invention



(6) (Color developing) → (Neutralizing (A)) → (Bleach-fixing (A)) → (Final bath (A))
(Color developing) → (Neutralizing (B)) → (Bleach-fixing (B)) → (Final bath (A))

(7) (Color developing) → (Bleaching) → (Fixing) → (Final bath)

(8) (Color developing) → (Bleach-Fixing) → (Final bath)

(9) (Color developing) → (Neutra-lizing) → (Bleach-ing) → (Fixing) → (Final bath)

(10) (Color developing) → (Newtra-lizing) → (Bleach-fixing) → (Final bath)

(11) (Pre-hard-ening) → (Neutra-lizing) → (Color developing) → (Neutra-lizing) → *
* → (washing) → (Bleaching) → (Fixing) → (Washing) → *
* → (Post-hard-ening) → (Final bath)

(12) (Black and white developing (B)) → (Neutraliz-ing (B)) → (Water washing (B)) → *
* → (Color developing) → (Bleaching) → (Fixing) → (Final bath)

In the above processing steps (1) to (12), the step enclosed with great parenthesis represents the common step, while the step enclosed with small parenthesis individual processing step, A representing use for the internal latent type direct positive light-sensitive and B use for the negative-type light-sensitive material.

In the present invention, "substantiall common processing tank" means generally one tank, but it is also inclusive of a counercurrent system (cascade system) partitioned into 2 to 3 tanks. As the ccountercurrent system, there may be included the cocurrent system of the countercurrent system when the flows are n parallel in the plan view in the direction in which the light-sensitive material to be treated is moved, and the parallel overflow system in which the flows are perpendicular to each other. Also, a processing tank com prising two tanks communicated by provision of a pipeline or a hole is also included. Details of these are in Japanese Provisional Patent Publication No. 139548/1987.

Next, the compound represented by the formula (A) is to be described.

R_1 and R_2 may be either the same or different and, when R_1 and/or R_2 represents an alkyl group, said alkyl group is inclusive of those having substituents. As said substituent, a sulfonic acid group, a hydroxy group, an alkoxy group (a methoxy group, an ethoxy group, propyloxy group and the like), a carboxyl group, an amino group, etc., may be included.

Preferred exemplary compounds represented by the formula (A) are enumerated below.

(1) NH_2-OH

(2) $CH_3-NH-OH$

(3) $C_2H_5-NH-OH$

(4) $iso-C_3H_7-NH-OH$

(5) $C_3H_7-NH-OH$

(6) $HO-CH_2-NH-OH$

(7) $CH_3-O-C_2H_4-NH-OH$

(8) $HO-C_2H_4-NH-OH$

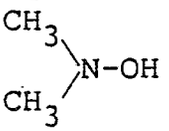
(9) $HOOC-C_2H_4-NH-OH$

(10) $HO_3S-C_2H_4-NH-OH$

(11) $H_2N-C_3H_6-NH-OH$

(12) $C_2H_5-O-C_2H_4-NH-OH$

(13) $HO-C_2H_4-O-C_2H_4-NH-OH$

(14)


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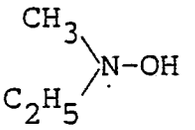

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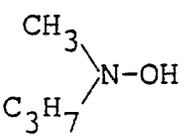

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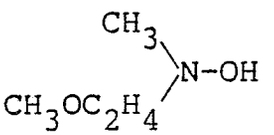

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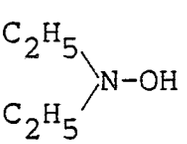

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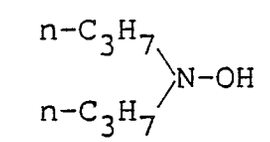

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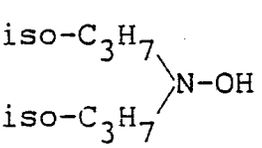

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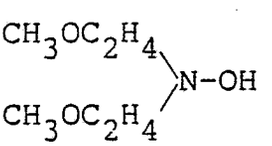
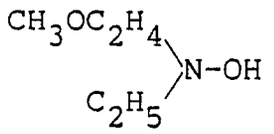
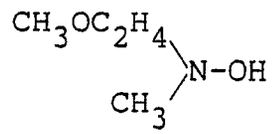
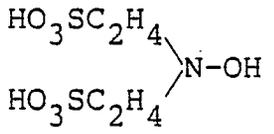
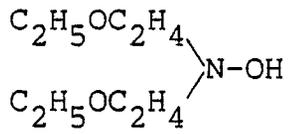
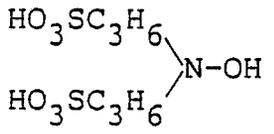


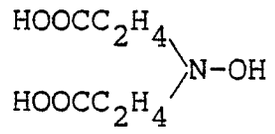
(22) 

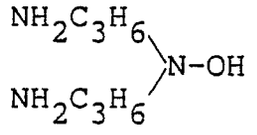
(23) 

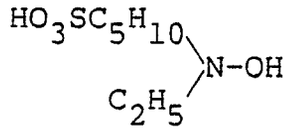
(24) 

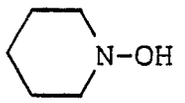
(25) 

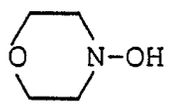
(26) 

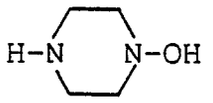
(27) 

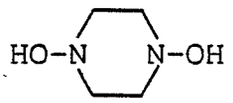
(28) 

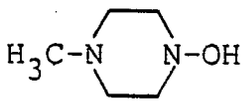
(29) 

(30) 

(31) 

(32) 

(33) 

(34) 

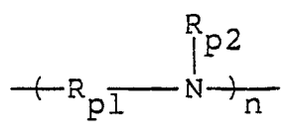
These compounds may be generally used in the form of salts such as hydrochlorides, sulfates, p-toluenesulfonates, oxalates, phosphates, acetates, etc.

These compounds can be easily synthesized according to the methods as described in U.S. Patents No. 3,287,125, No. 3,293,035, No. 3,287,124 etc.

The color developing solution may contain the compound represented by the above formula (A) at a concentration generally of, for examples, preferably 0.05 g/liter to 50 g/liter, more preferably 0.3 g/liter to 30 g/liter, particularly preferably 0.5 g/liter to 20 g/liter/

The above ccompounds may be used either individually or as a combination of two or more compounds.

The color developing solution contains a poly(alkyleneimine) or an alkanolamine. The poly-(alkyleneimine) comprises a substituted or unsubstituted recurring alkylene chain units bonded mutually through nitrogen atom. These are also commercially available. Representative poly(alkyleneimine) may include the compound represented by the following formula (P - I):



(P - I)

wherein R_{p1} represents an alkylene group having 1 to 6 carbon atoms; R_{p2} represents an alkyl group; and n is an integer of 500 to 20,000.

The alkylene group have 1 to 6 carbon atoms represented by the above R_{p1} may be either straight or branched, preferably an alkylene group having 2 to 4 carbon atoms such as an ethylene group, a propylene group, a butene group, an isobutene group, a dimethylethylene group, an ethylethylene group, and the like. The alkyl group represented by R_{p2} may be preferable an alkyl group having 1 to 4 carbon atoms such as a methyl group, an ethyl group, a propyl group and the like, and is also inclusive of those having substituents

(e.g., a hydroxyl group, etc.). n represents the number of reccurring units in the polymer chain, representing an integer of 500 to 20,000, preferably 500 to 2,000. A poly(ethyleneimine) in which R_{p1} is an ethylene group is the most preferable for the object of the present invention.

Specific examples of the poly(alkyleneimine) to be used in the color developing solution are shown below, but they are not limitative of the present invention.

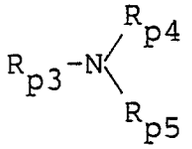
[Exemplary compounds]

PAI - 1 Poly(ethyleneimine)
PAI - 2 Poly(propyleneimine)
PAI - 3 Poly(buteneimine)
PAI - 4 Poly(isobuteneimine)
PAI - 5 Poly(N-methylethyleneimine)
PAI - 6 Poly(N-β-hydroxethylethyleneimine)
PAI - 7 Poly(2,2-dimethylethyleneimine)
PAI - 8 Poly(2-ethylethyleneimine)
PAI - 9 Poly(2-methylethyleneimine)

The poly(alkyleneimine) can be used inthe color developing solution in any desired amount which can accomplish the object of the present invention, but is generally preferred to be 0.1 to 500 g, more preferably 0.5 to 300 g, per one liter of the color developing solution.

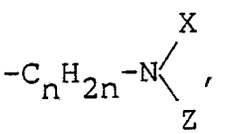
Japanese Provisional Patent Publication No. 94349/1981 discloses that the poly(alkyleneimine) of the present invention can be used together with hydroxylamine in the color developing solution to improve storage stability of the color developing solution and also lower the sulfite salt concentration. However, the above Patent Publication is entirely silent on the fact that the poly(alkyleneimine) can effectively solve the problem of coloration of the solution which occurs during processing of an internal latent image type positive light-sensitive material and the negative type light-sensitive material with a common developer. Thus, it has been entirely unexpected that the poly(alkyleneimine) can effectively solve coloration of such solution.

The color developing solution of the present invention can also accomplish the above objects by incorporating an alkanolamine in place of or in combination with poly(alkyleneimine). Said alkanolamine may be preferably a compound represented by the following formula (P - II):



(P - II)

wherein R_{p3} represents a hydroxyalkyl group having 2 to 6 carbon atoms, R_{p4} and R_{p5} each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, a benzyl group or a formula:



n in the above formula being an integer of 1 to 6, X and Z each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms or a hydroxyalkyl group having 2 to 6 carbon atoms.

Of the compounds represented by the above formula (P - II), particularly those in which R_{p3} represents a hydroxyalkyl group having 2 to 4 carbon atoms, and R_{p4} and R_{p5} each represents an alkyl group having 1 to 4 carbon atoms or a hydroxyalkyl group having 2 to 4 carbon atoms are preferred.

Preferred specific examples of the compounds represented by the above formula (P - II) are as follows: ethanolamine, diethanolamine, triethanolamine, diisopropanolamine, 2-methylaminoethanol, 2-ethylaminoethanol, 2-dimethylaminoethaol, 2-diethylaminoethanol, 1-diethylamino-2-propanol, 3-diethylamino-1-propanol, 3-dimethylamino-1-propanol, isopropylaminoethanol, 3-amino-1-propanol, 2-amino-2-, methyl-1,3-propanediol, ethylenediaminetetraisopropanol, benzylethanolamine, 2-amino-2-

(hydroxymethyl)-1,3-propanediol.

Among them, ethanolamine and diethanolamine are preferred, and particularly ethanolamine is the most preferred.

The above compound may be added either singly or as a combi nation of two or more kinds in the color developing solution.

The amount may be preferably 0.1 g to 200 g, more preferably 0.3 g to 50 g, per one liter of the developing solution.

In the present invention, the development processing solution should preferably contain the compound represented by the above formula (A) as the prepresentative.

In the present invention, it is particularly preferred to use a sulfite or sulfite ion releasing compound together with the compound represented by the formula (A). That is, the effect of preventing the solution coloration as described above will become further conspicuous in the presence of a sulfite or a sulfite ion releasing compound.

Specific examples of sulfite or sulfite ion releasing compounds may include potassium sulfite, sodium sulfite, ammonium sulfite, sodium metabisulfite, potassium metabisulfite, sulfurous acid adduct of formaldehyde, sulfurous acid adduct of acetaldehyde, sulfurous acid adduct of glutaraldehyde, etc.

The concentration of the above compound may be in the range from 1.0×10^{-4} to 1.0×10^{-1} mole/liter of the color developing solution, but when a sulfite or sulfite ion releasing compound exists in a large amount, lowering in color formed density of the dye in the light-sensitive material is liable to occur, and therefore, it should preferably be 5.0×10^{-4} to 5.0×10^{-2} mole per liter.

The color developing solution to be used in the present invention means a surface developing solution containing substantially no silver halide solvent, and the color developing agent contained in the color developing solution is an aromatic primary amine type color developing agent, including aminophenol type and p-phenylenediamine type derivatives. These color developing agents can be used as the salts of organic acids and inorganic acids, for example, hydrochlorides, sulfates, p-toluenesulfonates, sulfites, oxalates, benzenesulfonates, etc.

These compounds are generally at concentration of about 0.1 g to about 200 g, more preferably about 1 g to 50 g, per one liter of the color developing solution.

The processing temperature of these color developing solution may preferably be 10°C to 65 °C, more preferably 25 °C to 45 °C.

These above amino phenol type developing agent may include, for example, o-aminophenol, p-aminophenol, 5-amino-2-oxy-toluene, 2-amino-3-oxy-toluene, 2-oxy-3-amino-1,4-dimethyl-benzene, etc.

Particularly useful aromatic primary amine type color developing agents are N,N'-dialkyl-p-phenylenediamine type compounds, of which alkyl group and phenyl group may be either substituted or not. Among them, particularly useful compound examples may include N,N'-dimethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine hydrochloric, N,N'-diethyl-p-phenylenediamine hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)toluene, N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, N-ethyl-N-β-hydroxyethyl-aminoaniline, 4-amino-3-methyl-N,N'-diethylaniline, 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluenesulfonate and the like.

Also, the above color developing agent may be used either singly or as a combination of two or more kinds. Further, the above color developing agent may be internally included within the color photographic material. For example, there may be employed the method in which the color developing agent is included as a metal salt as in U.S. Patent No. 3,719,492 ; the method in which the color developing agent is included as a Schiff salt as disclosed in Research Disclosure No. 15159 (1976); the method in which it is included as a dye precursor as disclosed in Japanese Provisional Patent Publications No. 65429/1983 and No. 24137/1983; or the method in which it is included as the color developing agent precursor as disclosed in U.S. Patent No. 3,342,597. In this case, the light-sensitive halide color photographic material can be also processed with an alkaline solution (activator solution) in place of the color developing solution, and subjected to a bleach-fixing processing immediately after the alkaline solution processing.

The color developing solution to be used in the present invention can contain alkali agents conventionally used in developing solutions, such a sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, sodium sulfate, sodium metaborates or borax, and further additives can be contained therein, such as benzyl alcohol, alkali metal halides, for example, potassium bromide or potassium chloride, etc. Also, as the development controller, for example, citradinic acid, etc. may be contained. Further, various defoaming agents, surfactants, or organic solvents such as methanol, dimethylformamide or dimethyl sulfoxide may be suitably contained.

Also, the color developing solution to be used in the present invention can optionally contain antioxidants succh as tetronic acid, tetronimide, 2-anilinoethanol, dihydroxyacetone, aromatic secondary

alcohols, hydroxamic acid, pentose or hexose, pyrogallol-1,3-dimethyl ether, etc.

In the color developing solution to be used in the present invention, various chelating agents can be used in combination as the sequestering agent. For example, as said chelating agent, there may be included aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethlenetriaminopentaacetic acid, etc.; organic phosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid, etc.; aminopolyphosphonic acids such as aminotri(methylenephosphonic acid) or ethylenediaminetetraphosphoric acid, etc.; oxycarboxylic acids such as citric acid or gluconic acid; phosphonocarboxylic acids such as 2-phosphonobutane-1,2,3-tricarboxylic acid, etc.; polyphosphoric acids such as tripolyphosphoric acid or hexamethanoic acid.; polyhydroxy compounds; and the like.

The whole surface exposure to be used in the present invention is effected in the initial stage of development, which is preferably in the sense of shortening the development time, and in that case, it is advantageous to initiate exposure after the developing solution has been sufficiently penetrated into the emulsion layer.

In the present invention, as the means for controlling lighting of the whole surface exposure, it is possible to utilize the exposure devices as disclosed in Japanese Utility Model Publication No. 22351/1985, Japanese Provision Utility Model Publications No. 145049/1981, No. 87051/1984 and No. 87052/1984, and Japanese Provisional Patent Publication No. 114237/1986.

In the present invention, for controlling lighting of the whole surface exposure, for example, the operator of an automatic developing machine can judge previously which one of the above light-sensitive materials is to be processed and, when the light-sensitive material is to be processed is the internal latent image type, truns on manually the switch of the exposure device before the light-sensitive material to be processed enters the development processing solution, or alternatively, when the light-sensitive material to be processed is a negative-type, can turn off manually the switch before the light-sensitive material enters the developing solution. Also, in place of the manual change-over of the switch of the reversal exposure device by the operator, with the use of notch or bar code in the light-sensitive material as the detection mark, the light-sensitive material can be automatically judged whether it is the internal latent image type or the negative-type to control automatically lighting of the whole surface exposure. Further, discrimination judgement may be automatic, and said judgement result may be informed to the operator by sound or mark display and lighting change-over for the whole surface exposure may be performed manually by the operator.

As the light source for light fogging to be used in the present invention, at least one light source within the sensitive wavelength for the light-sensitive photographic material may be employed, but it desired to use at least one light source having a broad spectral distribution over the range from 400 to 700 nm in the visible light region as the light source for the light-sensitive color photographic material, for example, a fluorescent lamp with high color rendering. Also, tow or more kinds of light sources with different emission distribution or color temperatures may be used in combination, or various filters such as color temperature conversion filter, etc. may be used.

The illuminance of the whole surface exposure, namely light fogging to be used in the present invention may be preferably an illuminance which does not cause illuminance irregularity during light fogging, which may differ depending on the light-sensitive material, but generally 0.01 to 2000 lux, preferably 0.05 to 30 lux, further preferably 0.1 to 5 lux. The light fogging illuminance may be adjusted by varying the luminosity of the light source, or can be done by utilizing light reduction with various filters, the distance between the light-sensitive material and the light source of the angle between the light-sensitive material and the light source, etc. Also, for shortening the light fogging exposure time, there may be employed the method in which fogging is effected with weak light at the initiation of exposure of light fogging, and then fogging is effected with stronger light than that. Also, it is possible to practive advantageously the method in which the whole surface exposure is effected while increasing the illuminance as described in Japanese Patent Publication No. 117286/1983.

As the exposure device to be used for the whole surface exposure, there may be advantageously used the devices as described in Japanese Utility Model Publication No. 22351/1985, Japanese Provisional Utility Model Publications No. 145049/1981, No. 87051/1984 and No. 87052/1984, and Japanese Provisional Patent Publication No. 114237/1986.

The bleaching processing step as mentioned in the present invention refers to the step of bleaching the silver image developed after the color development processing step with an oxidizing agent (bleaching agent).

As the bleaching agent, a metal complex of an organic acid may be preferably used, for example, metal ions such as of iron, cobalt, copper, etc. coordinated with organic acid such as polycarboxylic acid, aminopolycarboxylic acid, or oxalic acid, citric acid, etc. Among the above organic acids, the most preferred

organic acid may include polycarboxylic acid or aminopolycarboxylic acid. These polycarboxylic acids may be alkali metal salts, ammonium salts or water-insoluble amine salts. Specific examples of these may include the following compounds, namely ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, pentasodium diethylenetriaminepentaacetate and the like. These bleaching agents are used in amounts of 5 to 450 g/liter, more preferably 20 to 250 g/liter.

In the bleaching solution, other than the bleaching agent as mentioned above, a halide such as ammonium bormide may be preferably added. As the above halide, other than ammonium bromide, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, potassium bromide, sodium iodide, potassium iodide, ammonium iodide and the like can be also used.

In the present invention, the fixing processing step refers to the step of fixing by desilverization with a fixing solution containing a silver halide fixing agent. As the silver halide fixing agent to be used in said fixing solution, there may be included compounds forming water-soluble complexes through the reaction with silver halide used in conventional fixing processing, of which representative examples are thiosulfates such as potassium thiosulfate, sodium thiosulfate; thiocyanates such as ammonium thiocyanate; thiourea; thioether; etc. These fixing agents are used in amounts of 5 g/liter or more in the range which can be dissolved, generally from 70 g/liter to 250 g/liter.

In the present invention, it is preferred to perform the bleaching processing step and the fixing processing step in one processing step with a bleach-fixing solution, and the metal complex of an organic acid as the bleaching agent to be used in said bleach-fixing solution comprises metal ions such as iron, cobalt, copper, etc. coordinated with organic acids such as aminopolycarboxylic acid or oxalic acid, citric acid, etc. As the organic acid to be used for formation of such metal complex of organic acid, the same acids as mentioned for the bleaching solution can be used.

As the silver halide fixing agent to be contained in the bleach-fixing solution, compounds forming water-soluble complexes through the reaction with silver halide as used in conventional fixing processing may be used.

After processing with a processing solution having a fixing ability, conventional water washing processing may be performed, but it is particularly preferred in the present invention to apply stabilizing processing substantially without including water washing step.

The stabilizing processing substantially without including water washing step refers to performing stabilizing processing substituting for water washing according to a single tank or a multiple tank countercurrent system, etc. immidiately after processing with a processing solution having a fixing ability, but processing steps other than water washing in general such as rinsing, auxiliary water washing and known water washing promoting bath, etc. may be also included.

In the stabilizing processing step in the present invention, the method of bringing a stabilizing solution into contact with a light-sensitive silver halide material may be preferably to dip the light-sensitive silver halide photographic material in a bath similarly as in the case of processing solutions in general, but it may be coated on the emulsion surface of the light-sensitive silver halide photographic material and both surfaces of the conveying leader, the conveying belt, with sponge, synthetic fiber cloth, etc., or sprayed by means of a spray, etc. In the following, description is made primarily about the case of using a stabilizing bath according to the dipping method.

The above stabilizing solution should preferably contain a chelating agent with a chelate stabilizing constant of 6 or more relative to iron ion.

As the chelating agent having a chelate stabilizing constant of 6 or more relative to iron ion may include organic carboxylic chelating agents, organic phosphoric chelating agents, inorganic phosphoric chelating agents, polyhydroxy compounds may be employed. The above iron ion means ferric ion (Fe^{3+}).

Specific compound examples of chelating agents having a chelate stabilizing constant of 6 or more relative to ferric ion may include deithelenetriaminepentaacetic acid, nitrilotriacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, etc.

The amount of the above chelating agent employed may be in the range from 0.01 to 50 g, preferably from 0.05 to 20 g.

Further, preferable compounds to be added in the stabilizing solution may include antifugal agents, water-soluble metal salts, ammonium compounds, etc. Examples of the above antifugal agent may include hydroxybenzoic acid type compounds, phenolic compounds, isothiazole type compounds, pyridine type compounds, guanidine type compounds, carbamate type compounds, morpholine type compounds, quaternary phosphonium type compounds, ammonium type compounds, urea type compounds, isoxazole type compounds, propanolamine type compounds, sulfamide type compounds, amino acid type compounds and benztirazole type compounds.

Further, as the metal salts, there may be included metal salts of Ba, Ca, Ce, Co, In, La, Mn, Ni, Pb, Sn,

Zn, Ti, Mg, Al and Sr, which can be supplied as halides, hydroxides, inorganic salts such as sulfates, carbonates, phosphates, acetates, etc. or water-soluble chelating agents. The metal salt may be employed in an amount ranging from 1×10^{-4} to 1×10^{-1} mole, preferably from 4×10^{-4} to 2×10^{-2} mole, further preferably from 8×10^{-4} to 1×10^{-2} mole, per liter of the stabilizing solution.

In the stablizing solution, in addition to the above compounds, various additives for amelioration and expansion of the processing effect may be added as desired, including fluorescent brighteners; organic sulfur compounds; onium salts; film hardeners; droplet irregularity preventives such as quaternary salts, polyethyleneoxide derivatives, siloxane derivatives, etc.; pH controllers such as boric acid, citric acid phosphotic acid, acetic acid, or sodium hydroxide, sodium acetate, potassium citrate, etc.; organic solvents such as methanol, ethanol, dimethyl sulfoxide, etc.; dispersing agents such as ethylene glycol, polyethylene glycol, etc.; and other tone controllers; etc.

As the method for adding the above compound or other additives, the above compound or other additives may be added as a concentrated solution into the stabilizing tank or into the stabilizing solution to be supplied into the stabilizing tank to provide a feeding solution into the stabilizing solution, or alternatively they can be added into the previous bath before the stabilizing processing step to be contained in the light-sensitive silver halide photographic material and exist in the stabilizing bath. Any additional method may be available.

The method for feeding the stabilizing solution in the stabilizing processing step in the case of the multi-tank counter-current system should preferably be one in which the solution is fed to the later bath and overflowed from the earlier bath.

The pH value of the processing solution in the stabilizing bath should be preferably in the range of pH 4 to 8.

Control of pH can be done with the use of the pH controller as mentioned above.

The processing temperature during the stabilizing processing may be, for example, 20 °C to 50 °C, preferably in the range from 25 °C to 40 °C.

The processing time should be preferably as short as possible from the standpoint of rapid processing, but generally 20 seconds to 5 minutes, most preferably 30 seconds to 2 minutes, and in the multi-tank countercurrent system, processing time should be shorter for earlier step and longer for later step.

In the present invention, no water washing processing is required before and after the stabilizing processing, but there may be optionally provided a processing tank for rinsing with a small amount of water within a short time, surface cleaning with sponge, and stabilizing the image or controlling the surface characteristics of the light-sensitive silver halide photographic material.

As the material for stabilizing the image or controlling the surface characteristics of the light-sensitive silver halide photographic material as mentioned above, there may be employed activators such as formalin and derivatives thereof, siloxane derivatives, polyethylene oxide compounds, quaternary salts, etc.

In the present invention, other than processing steps as described above, additional processing steps may be provided above, additional processing step may be provided as desired. From the above stabilizing solution as a matter of course, and also from the processing solutions containing soluble silver complexs such as the fixing solution, the bleach-fixing solution, etc., silver may be recovered according to a known method.

Also, by practitcing the stabilizing processing as described above, substantially no water washing step is required, and therefore no pipeline equipment for water washing processing is required, whereby ther is the advantage that the apparatus itself can be set handily at any desired place.

Other than these processings, processing may be performed by use of the developing method for increasing the dye amount produced such as the method, in which the developing solution produced by color developing is subjected to halogenation bleaching and then again applied with color developing, or various augmentation methods (amplification processing), etc. as disclosed in Japanese Provisional Patent Publication No. 154839/1983.

Each processing step is performed generally by dipping the light-sensitive material into the processing solution, but it may be also possible to use other methods such as the spray system in which the processing solution is fed in atomized state, the web system in which processing is effected by contact with a carrier impregnated with the processing solution or the method in which viscous development processing is effected.

The internal latent image type silver halide emulsion is an emulsion which forms latent images primarily internally of silver halide grains, thus having most of light-sensitive nuclei internally of the grains, and may include any silver halide, such as silver bromide, silver chloride, silver chlorobromide, silver iodobromide, silver chloroiodobromide, etc. Particularly, with respect to grains with great developing rate, silver chloride, silver chlorobromide, silver chloroiodobromide, silver iodochloride are preferred.

The internal latent image type silver halide grains to be used in the present invention should preferably be not chemically sensitized, if any, to slight extent.

Specifically, there may be included, for example, the conversion type silver halide emulsion disclosed in U.S. Patent No. 2,592,250; the core/shell type silver halide emulsion doped with internally chemically sensitized neclei or polyvalent metal ions disclosed in U.S. Patent No. 3,761,266 and No. 3,761,276; the lamination type silver halide emulsion disclosed in Japanese Provisional Patent Publications No. 8524/1975, No. 38525/1975 and 2408/1978; and otherwise those emulsions as disclosed in Japanese Patent No. 1,377,173.

Hereinafter, the silver halide emulsion of the present invention refers comprehensively to the internal latent type direct positive silver halide emulsion and the negative-type silver halide meulsion, unless otherwise specifically noted.

The silver halide grains to be used in the silver halide emulsion of the present invention may be one obtained according to any of the acidic method, the neutral method and the ammoniacal method. Said grains may be grown at one time, or grown after preparation of seed grains. The method for preparing the seed grains and the method for growing the seed grains may be either the same or different.

The silver halide emulsion of the present invention may be prepared either by simultaneous mixing of the halide ions and silver ions or by mixing of the other with a solution in which one exists. Also, it may be formed by adding successively the halide ions and the silver ions while controlling pH and pAg in the mixing kettle in view of the critical growth rate of silver halide crystals. By this method, silver halide grains with regular crystal forms and grain sizes approximate to uniform can be obtained. After the growth, the halide composition of the grains may be varied by use of the conversion method.

The silver halide emulsion of the present invention can be controlled in grain size of silver halide grains, shape of grains, grain size distribution and growth rate of grains by using optionally a silver halide solvent during its preparation.

The silver halide grains to be used in the silver halide emulsion of the present invention can be added with metal ions by use of at least one selected from cadmium slats, zinc salts, lead salts, thallium salts, iridium salts (compleses containing the same) and iron salts (complexes containing the same) in the process of forming grains and/or the process of growing the same, thereby incorporating these metal elements internally of the grains and/or on the surfaces of the grains, or can be placed in an appropriate reducing atmosphere to impart reducing sensitizing neclei to the inner portions and/or the surfaces of the grains.

The silver halide emulsion of the present invention may have unnecessary soluble salts removed or contained as such after completion of growth of silver halide grains. When said salts are to be removed, it can be practiced on the basis of the method as disclosed in Research Disclosure No. 17643.

The silver halide grains to be used in the present invention may have a uniform silver halide composition distribution within the grain or core/shell grains with different silver halide compositions between the inner portions and the surface layers of the grains.

The silver halide grains to be used in the silver halide emulsion of the present invention may have regular crstal forms such as cubic, octahedral, tetradecahedral forms, or irregular shapes such as spheres or plates. In these grains, any desired ratio of the {100} plane to the {111} plane can be used. Also, these crystal forms may have a composite form, and grains with various crystal forms may be mixed therein.

The silver halide grains of the present invention may have an average grain size (grain size: as defined below) preferably of 5 μm or less, particularly preferably 3 μm or less.

The silver halide emulsion to be used in the present invention may have any desired grain size distribution. An emulsion with a broad size distribution (called polydispersed emulsion) or an emulsion with a narrow grain size distribution (called monodispersed emulsion. The monodispersed emulsion as herein mentioned refers to one with the value of the standard deviation of the grain size distribution divided by the average grain size of 0.20 or less, preferably 0.15 or less. Here, the grain size refers to the diameter in the case of spherical silver shape.) either alone or as a mixture of several kinds. Also, the polydispersed emulsion and the monodispersed emulsion can be used as a mixture.

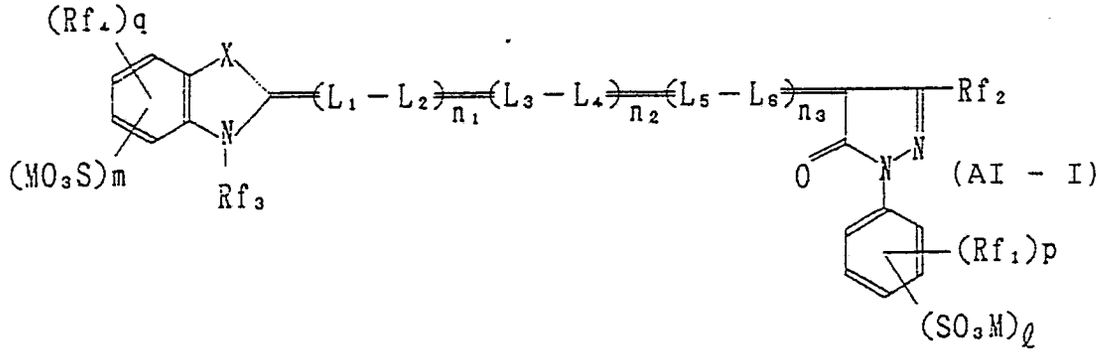
The silver halide emulsion of the present invention may be also prepared by mixing two or more kinds of silver halide emulsions separately formed.

The silver halide emulsion can be chemically sensitized in conventional manner. More specifically, the sulfur sensitizing method, the selenium sensitizing method, the reducing sensitizing method, the noble metal sensitizing method by use of gold and other noble metal compounds, etc. may be used either singly or in combination.

The silver halide emulsion of the present invention can be optically sensitized to desired wavelength region by use of a dye known as the sensitizing dye in the field of photography. The sensitizing dye may

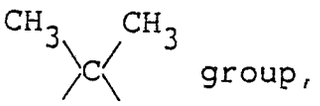
be used alone, but a combination of two or more kinds may be employed. Together with a sensi tizing dye, a potentiating sensitizer which is a compound having itself no spectral sensitizing dye or absorbing substantially no visible light, but potentiating the sensitizing action of the sensitizing dye, may be also contained in the emulsion.

In the light-sensitive silver halide photographic material of the present invention, for improving sharpness, it is preferable to use an AI dye, particularly an AI dye represented by the formula (AI - I), (AI - I'), (AI - II), (AI - III) or (AI - IV) for the purpose of decoloration.

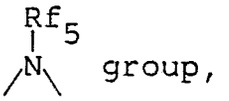


(AI - I)

wherein X represents a chalcogen atom,

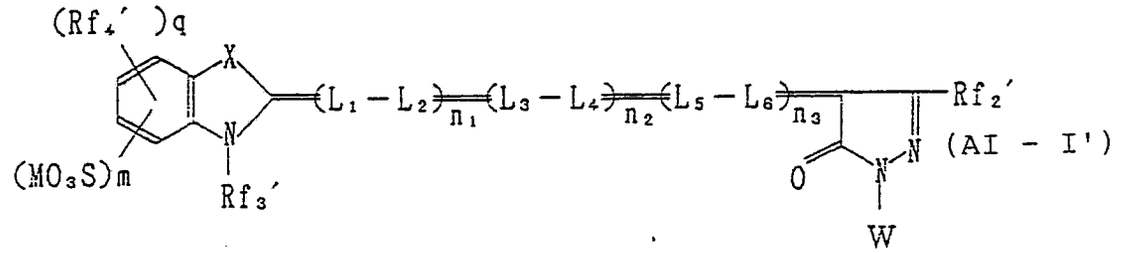


group,



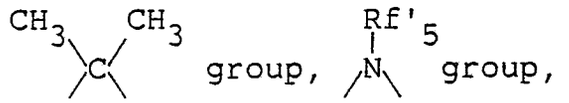
group,

L_1, L_2, L_3, L_4, L_5 and L_5 each represent a methine group; Rf_5 represents an alkyl group or an aryl group; Rf_1 represents a substitutable group; Rf_2 represents an aryl group, a heretocyclic group, an amino group, an acylamino group, an imide group, a ureido group, a carboxyl group, an alkoxycarbonyl group, a carbamoyl group, an alkoxy group, an aryloxy group, a hydroxy group, an alkyl group or a cyano group; Rf_3 represents an alkyl group; Rf_4 represents a substitutable group; M represents a hydrogen atom or a cation; l represents 0.1 or 2; m represents 0, 1 or 2; n_1, n_2 and n_3 each represent 0 or 1; p represents an integer of 0 to 5; and q represents an integer of 0 to 4; provided that $l + m \neq 0$.



(AI - I')

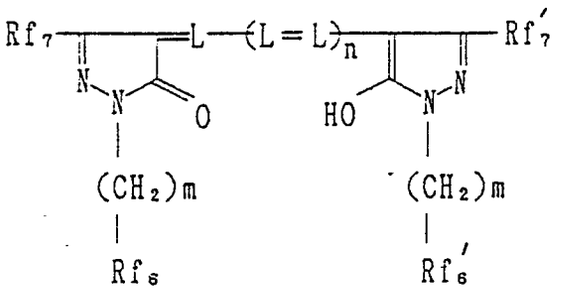
wherein W represents a hydrogen atom, an alkyl group or a heterocyclic group; Rf_2' represents an alkyl group, an aryl group, a heretocyclic group, an amino group, an acylamino group, an imide group, a ureido group, a carboxy group, an alkoxycarbonyl group, a carbamoyl group, an aryloxy group, an alkoxy group, a hydroxy group or a cyano group; Rf_3' represents an alkyl group; Rf_4' represents a substitutable group; X represents a chalcogen atom,



group,

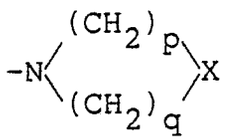
group,

L_1, L_2, L_3, L_4, L_5 and L_5 each represent a methine group; Rf_5' represents an alkyl group or an aryl group; M represents a hydrogen atom or a cation; m represents 0, 1 or 2; n_1, n_2 and n_3 each represent 0 or 1; and q represents an integer of 0 to 4.

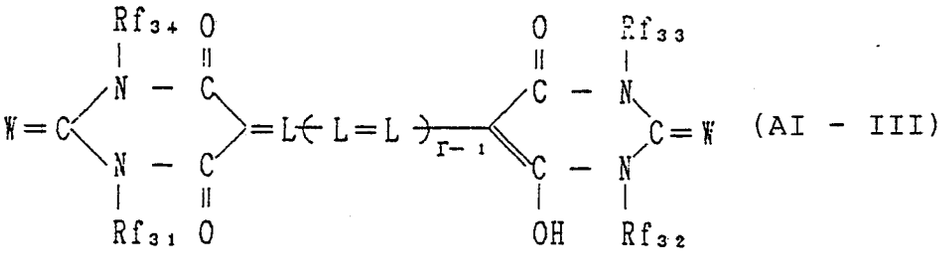


(AI - II)

wherein Rf_6 and Rf_6' each represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; Rf_7 and Rf_7' each represent a hydroxy group, an alkoxy group, a substituted alkoxy group, a cyano group, a trifluoromethyl group, $-COORf_8$, $-CONHRf_8$, $-NHCORf_8$, an amino group, a substituted amino group, substituted with a alkyl group having 1 to 4 carbon atoms or a cyclic amino group represented by:

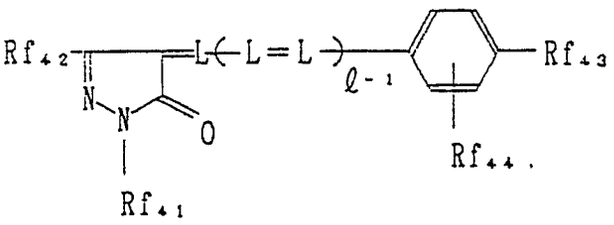


(where p and q each represent 1 or 2, and X represents an oxygen atom, a sulfur atom or $-CH_2$-group); Rf_8 represents a hydrogen atom, an alkyl group or an aryl group; L represents a methine group; n represents 0, 1, 2; and m represents 0 or 1.



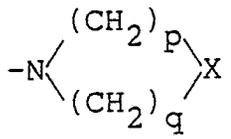
(AI - III)

wherein r represents an integer of 1 to 3; W represents an oxygen atom or a sulfur atom; L represents a methine group; Rf_{31} to Rf_{34} each represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a heterocyclic group, of which at least one is a substituent other than the hydrogen atom.

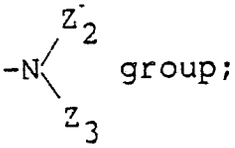


(AI - IV)

wherein l represents an integer of 1 or 2; L represents a methine group; Rf_{41} represents an alkyl group, an aryl group or a heterocyclic group; Rf_{42} represents a hydroxy group, an alkyl group, an alkoxy group, a substituted alkoxy group, a cyano group, a trifluoromethyl group, $-COORf_8$, $-CONHRf_8$, $-NHCORf_8$, an amino group, a substi tuted amino group substituted with an alkyl group having 1 to 4 carbon atoms, or a cyclic amino group represented by:



(where p and q each represent 1 or 2, and X represents an oxygen atom, a sulfur atom or -CH_2-group); Rf_8 represents a hydrogen atom, an alkyl group or an aryl group; Rf_{43} represents -OZ_1 group or a group:



Z_1, Z_2 and Z_3 each represent a hydrogen atom or an alkyl group, Z_2 and Z_3 may be either the same or different, or can be bonded together to form a ring; Rf_{44} represents a hydrogen atom, an alkyl group, a chlorine atom or an alkoxy group.

First, the formula (AI - I) is to be described in more detail.

Rf_1 represents a group which can be substituted on a phenyl group, and example of substituents may include an alkyl group (e.g., a methyl group, an ethyl group, a butyl group, etc.), which may be further substituted with, for example, a halogen atom, a cyano group, a sulfo group (which can be further substituted); an alkoxy group (e.g., a methoxy group, an ethoxy group, a butoxy group, etc.); a hydroxy group; a cyano group; a halogen atom (e.g., a chlorine atom, a bromine atom, a fluorine atom, etc.), a carbamoyl group; a sulfamoyl group; an acyloxy group (e.g., an acetyloxy group, etc.); an alkoxycarbonyl group (e.g., a methoxycarbonyl group, an ethoxycarbonyl group, etc.); a carboxy group; a sulfo group; and aryl group (e.g., a benzyl group); an aryloxy group (e.g., a phenoxy group, etc); and the like.

The aryl group represented by Rf_2 may include, for example, respective group of a phenyl group, a tolyl group, a p-meth oxyphenyl group, p-pentadecyloxyphenyl group, a p-sulfophenyl group, a p-carbamoyl group, a phenyl group, a p-cyanophenyl group, a p-butylsulfonylphenyl group and the like.

The heterocyclic group represented by Rf_2 may include, for example, a thienyl group, a furyl group, a benzofuranyl group and the like.

The amino group represented by Rf_2 is inclusive of substituted amino groups, as exemplified by an n-butylamino group, a phenylamino group and others.

The acylamino group represented by Rf_2 may include, for example, a benzoylamino group, an acetylamino group, a 2-(2,4-di-t-pentylphenoxy)butyrylamino group and the like.

The imide group represented by Rf_2 may include, for example, a phthalimide group, a succinimide group and the like.

The ureido group represented by Rf_2 may include, for example, an N'-methylureido group, an N'-(2-chlorophenyl)ureido group and the like.

The alkoxycabonyl group represented by Rf_2 may include, for example, an ethoxycarbonyl group, a hydroxyethoxyethoxycarbonyl group and the like.

The carbamoyl group represented by Rf_2 is inclusive of substituted carbamoyl groups, as exemplified by an N-phenylcarbamoyl group, an N-p-methylsulfonylphenylcarbamoyl group, an N-p-carboxylphenylcarbamoyl group and the like.

The aryloxy group represented by Rf_2 may include, for example, a phenoxy group, a p-tolyloxy group and the like.

The alkoxy group represented by Rf_2 may include, for example, a methoxy group, an ethoxy group and the like.

The alkyl group represented by Rf_2 may include unsubstituted alkyl groups such as a methyl group, an ethyl group, an n-butyl group, a t-butyl group, a dodecyl group and the like; and substituted alkyl groups. As the substituent of the substituted alkyl group, there may be included a halogen atom (e.g., a fluorine atom, a chlorine atom, a bromine atom, etc.), a cyano atom, a sulfo group, a hydroxy group, a carboxy group, an alkoxycarbonyl group (e.g., a methoxycarbonyl group, an ethoxycarbonyl group, etc.).

Rf_3 represents an alkyl group (preferably an alkyl group having 1 to 12 carbon atoms). Said alkyl group is also inclusive of substituted alkyl groups other than unsubstituted alkyl groups (e.g., a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an n-hexyl group, etc.), and as the substituent, it may have a halogen atom (e.g., a chlorine atom, a bromine atom, etc.), a cyano group, a carboxy group, a sulfo group, sulfoalkoxy group having 1 to 6 carbon atoms (e.g., a sulfopropoxy group), an

alkoxycarbonyl group having 1 to 6 carbon atoms (e.g., an ethoxycarbonyl group, a butoxycarbonyl group, etc.).

Rf_4 represents a substitutable group, and examples of substituent may include a halogen atom, an alkyl group, an alkoxy group, an aryloxy group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, etc. The halogen atom represented by Rf_4 may be, for example, a fluorine atom, a chlorine atom and a bromine atom; the alkyl group may be, for example, a methyl group, an ethyl group, a t-butyl group, a methoxymethyl group, carboxymethyl group, etc.; the alkoxy group may be, for example, a methoxy group, an ethoxy group, etc.; the aryloxy group may be, for example, a phenoxy group; the alkoxycarbonyl group may be, for example, an ethoxycarbonyl group, a butoxycarbonyl group, etc.; the carbamoyl group may be, for example, an N,N-dimethylcarbamoyl group, an N,N-tetramethylenecarbamoyl group, a morpholinocarbamoyl group, etc.; the sulfamoyl group may be, for example, an N,N-dimethylsulfamoyl group, a piperazinosulfonyl group, etc. As the calcogen atom represented by X, there may be included, for example, an oxygen atom, a sulfur atom, a selenium atom and a tellurium atom.

The alkyl group represented by Rf_5 may be the same as the alkyl group mentioned for Rf_3. Examples of the aryl group represented by Rf_5 may include a phenyl group, a tolyl group, a p-sulfophenyl group, a p-carboxyphenyl group, a p-sulfamoylphenyl group and the like.

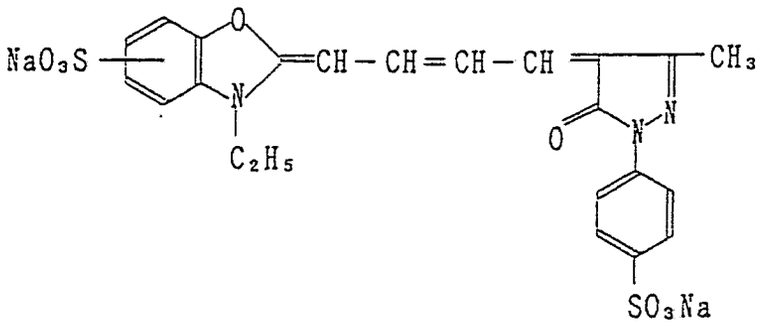
The methine group represented by L_1, L_2, L_3, L_4, L_5 and L_5 may be substituted and examples of the substituent may include a lower alkyl group having 1 to 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, an isobutyl group, etc.), an aryl group (e.g., a phenyl group, a p-tolyl group, a p-chlorophenyl group, etc.), an alkoxy group having 1 to 4 carbon atom (e.g., a methoxy group, an ethoxy group, etc.), an aryloxy group (e.g., a phenoxy group, etc.), an aralkyl group (e.g., a benzyl group, a phenethyl group, etc.), a heterocyclic group (e.g., a thienyl group, a furyl group, etc.), a substituted amino group (e.g., a dimethylamino group, a teramethyleneamino group, an anilino group, etc.), an alkylthio group (e.g., a methylthio group) and the like. Also, L_2 and L_4, or L_4 and L_5 can be linked together to form a 5-or 6-membered carbon ring.

The cation represented by M may include alkali metals (e.g., lithium, sodium, potassium, etc.), alkaline earth metals (e.g., magnesium, calcium, barium, etc.), ammonium or organic base cations (e.g., triethylammonium, pyridinium, piperidinium, morpholium, etc.) and the like.

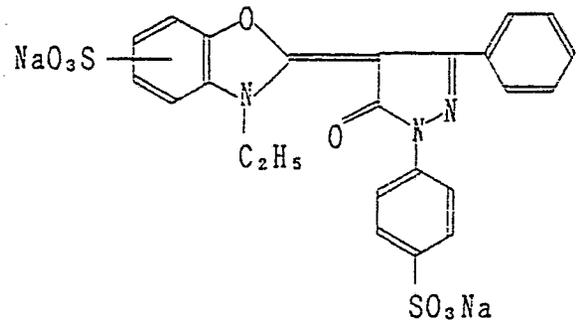
Specific examples of the AI dye represented by the above formula (AI - I) are shown below, but the dye according to the present invention is not limited by these at all.

(Exemplary compounds)

(I - 1)



(I - 2)



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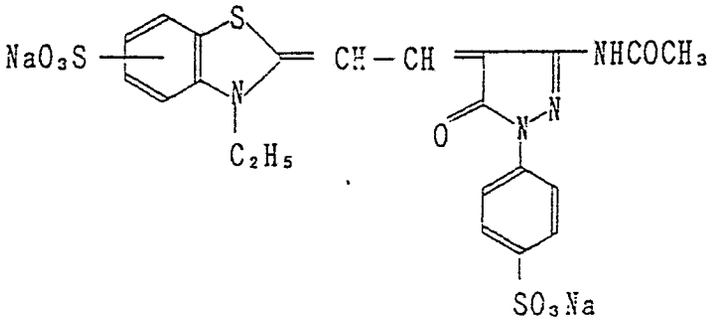

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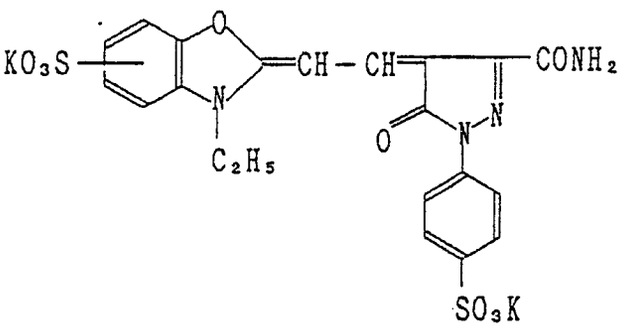

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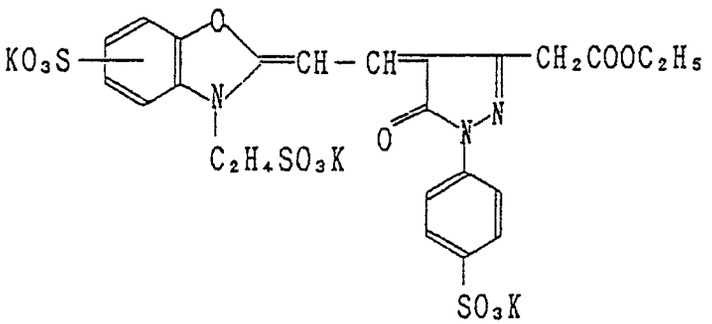

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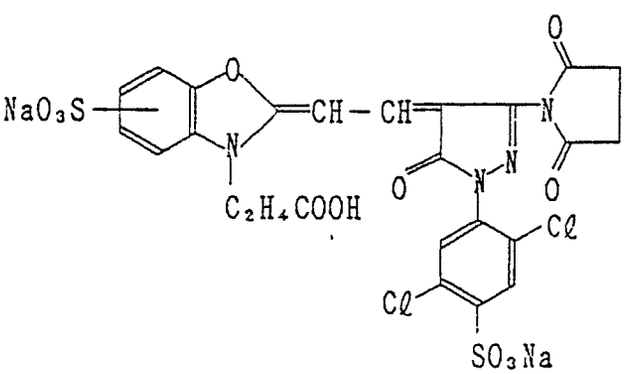

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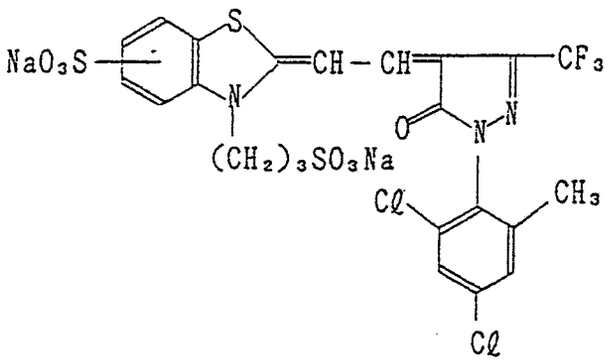

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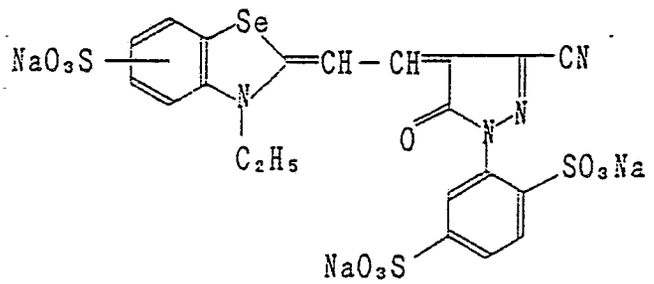

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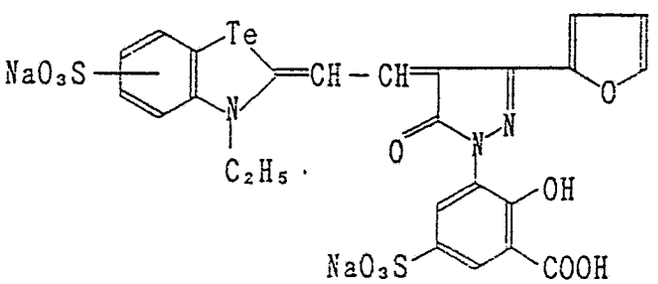

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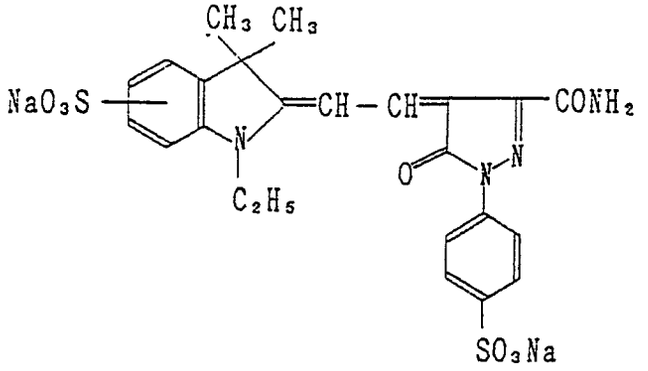

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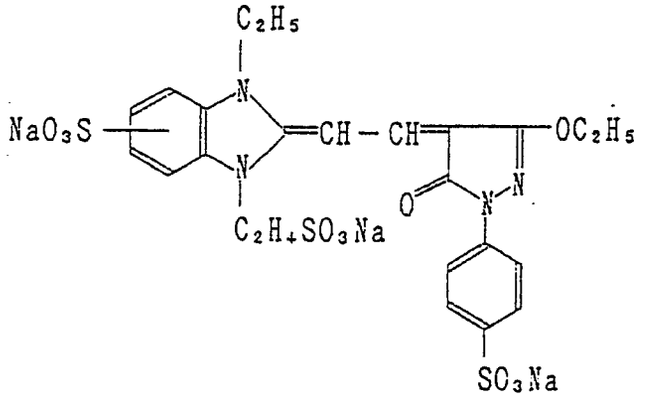

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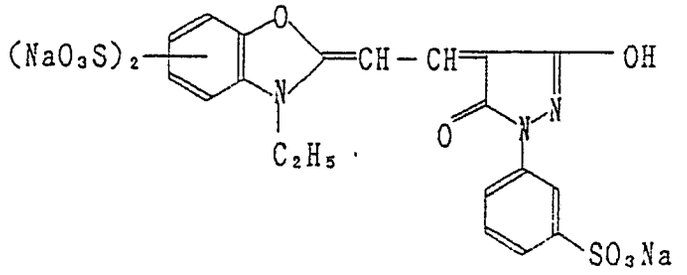

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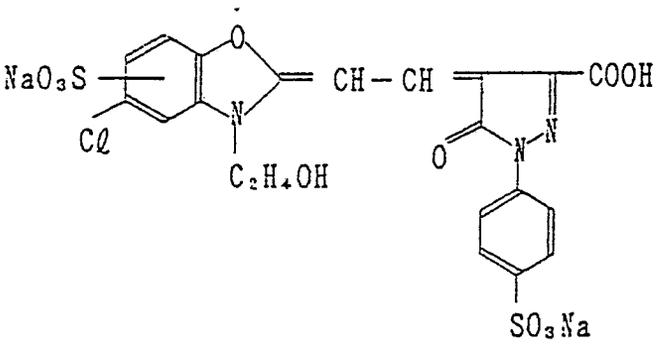

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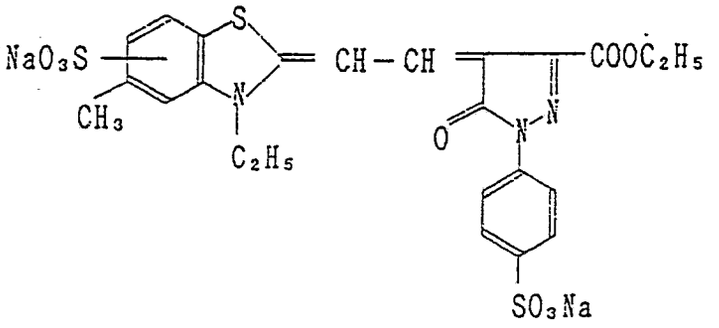

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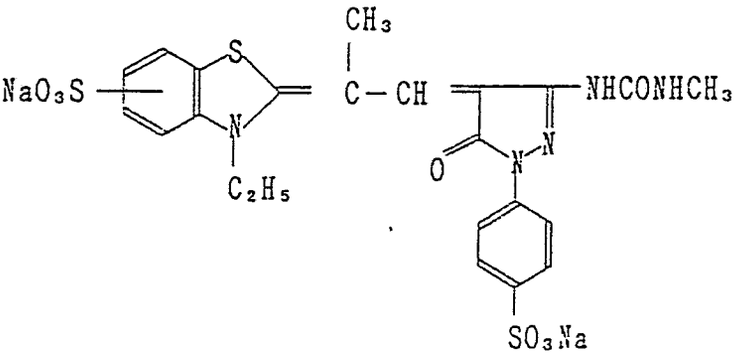

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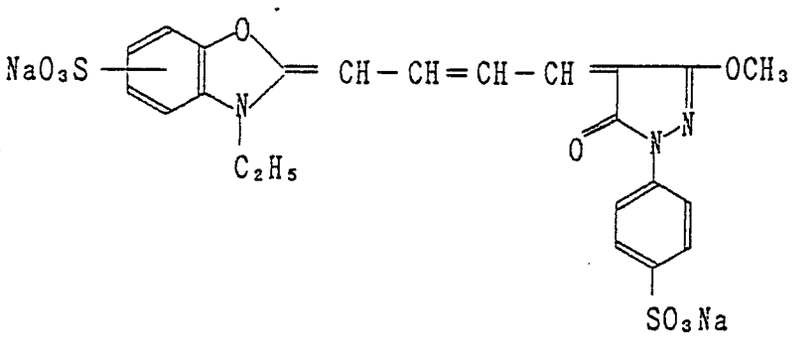

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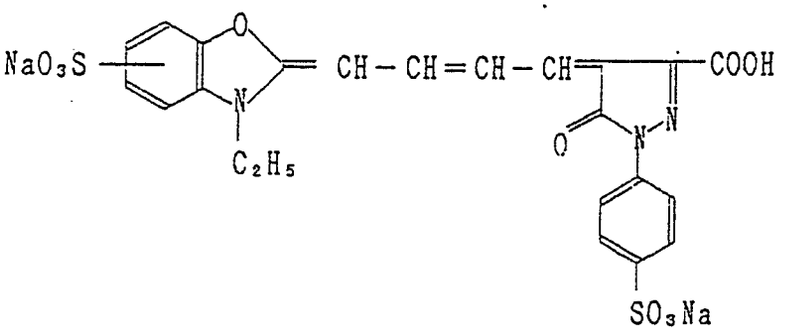

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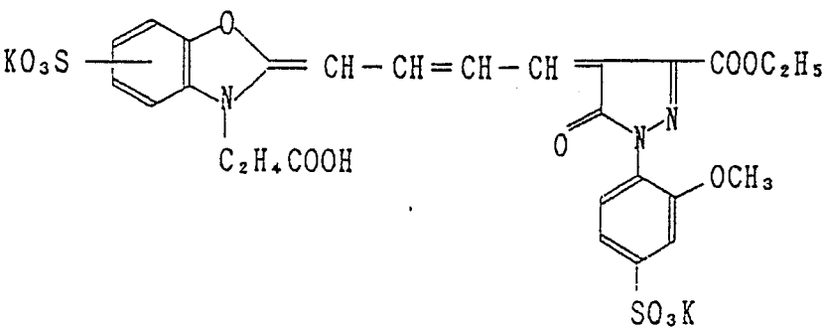

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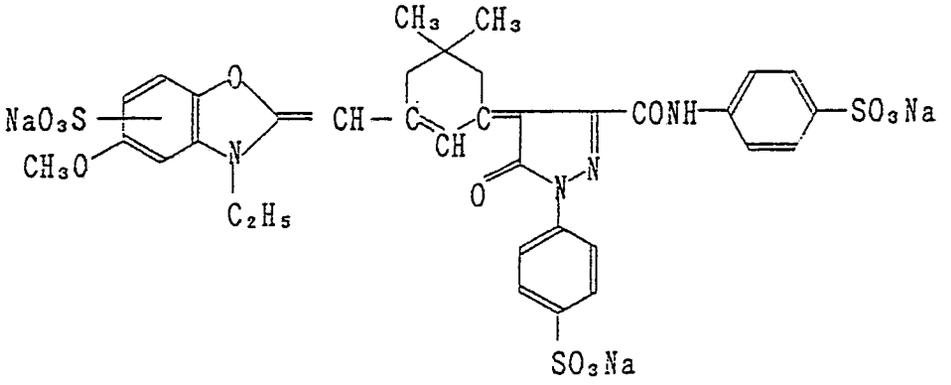

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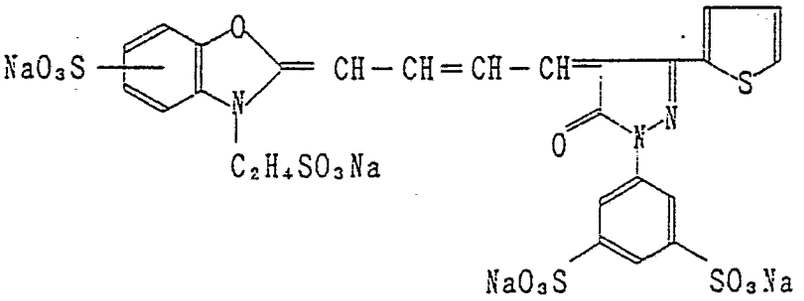

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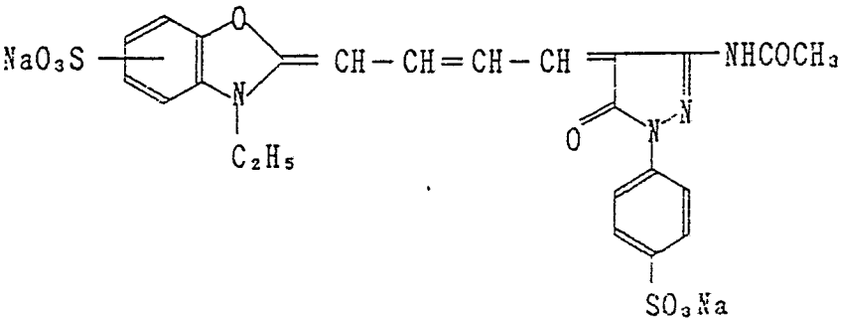

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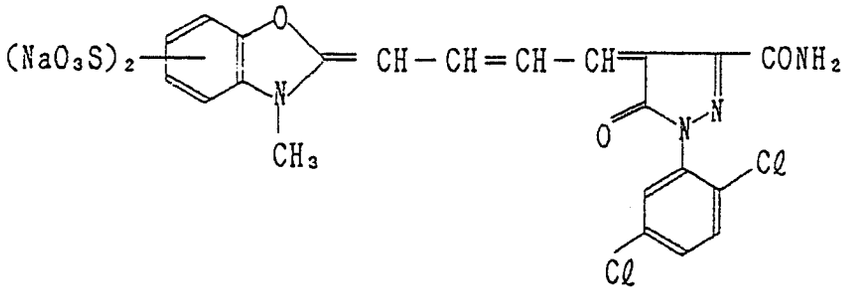

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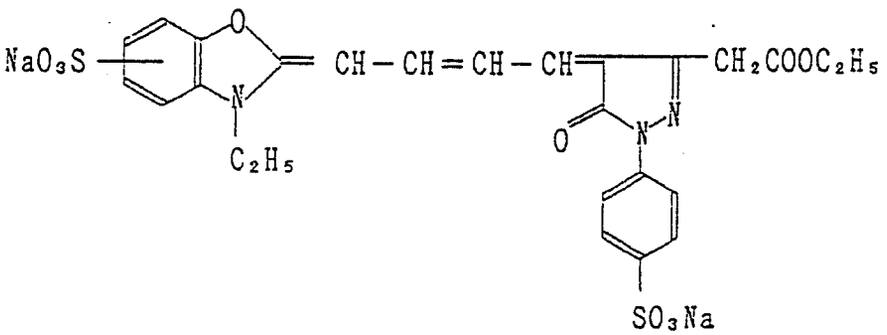

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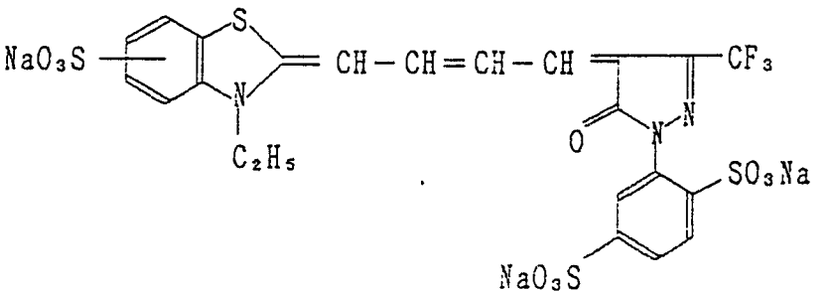

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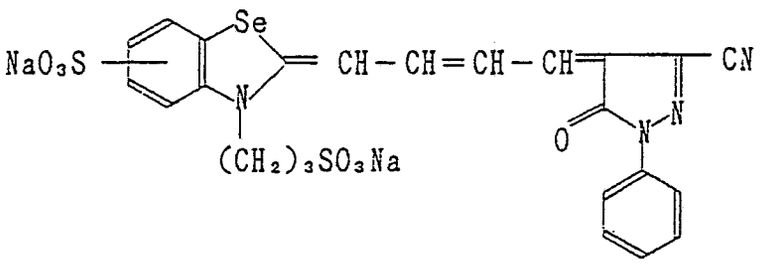

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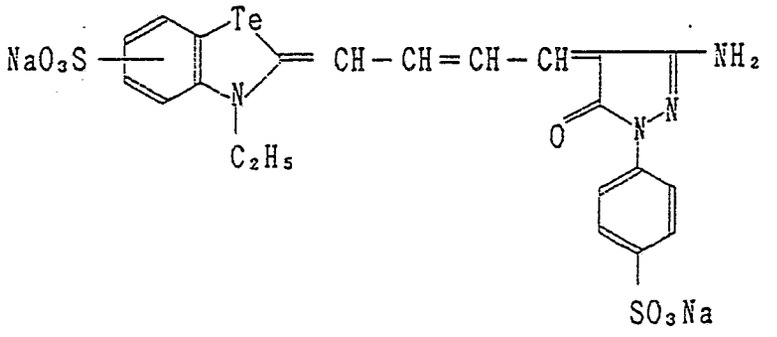

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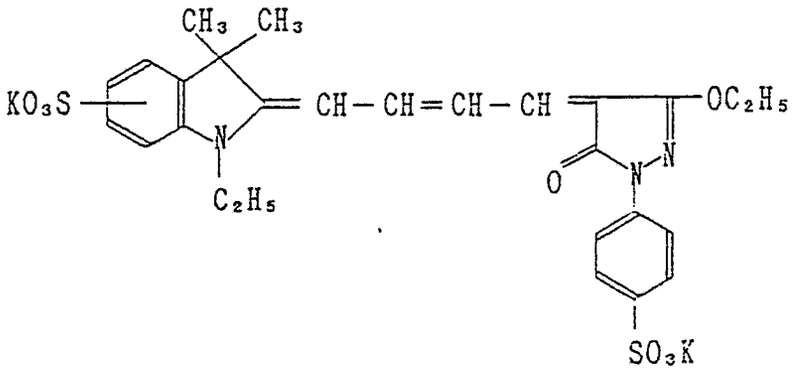

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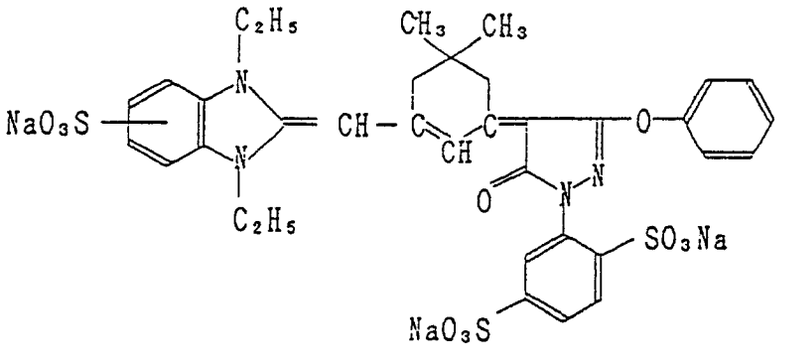

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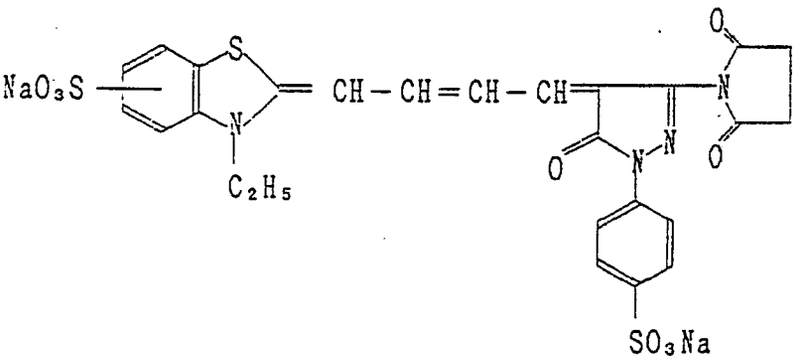

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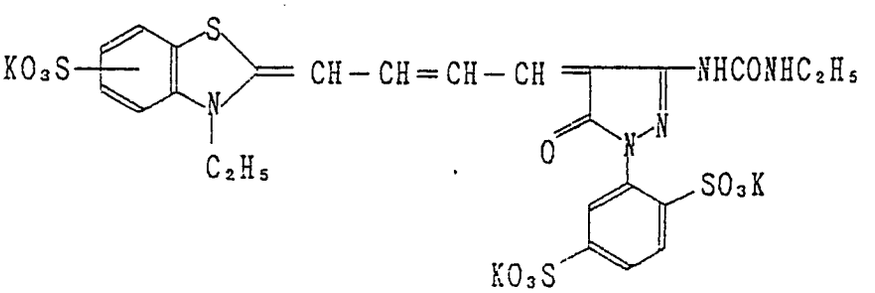

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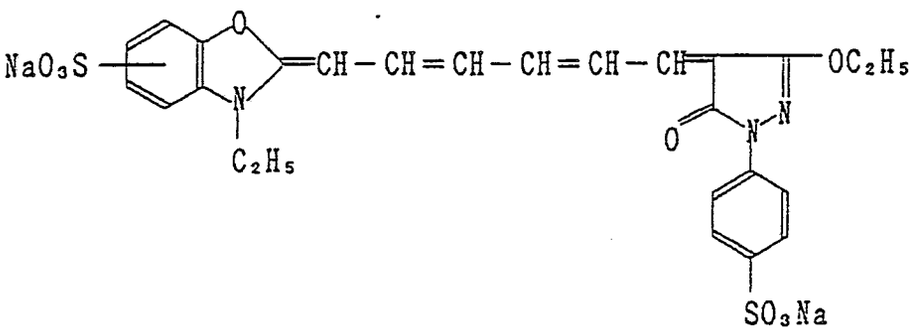

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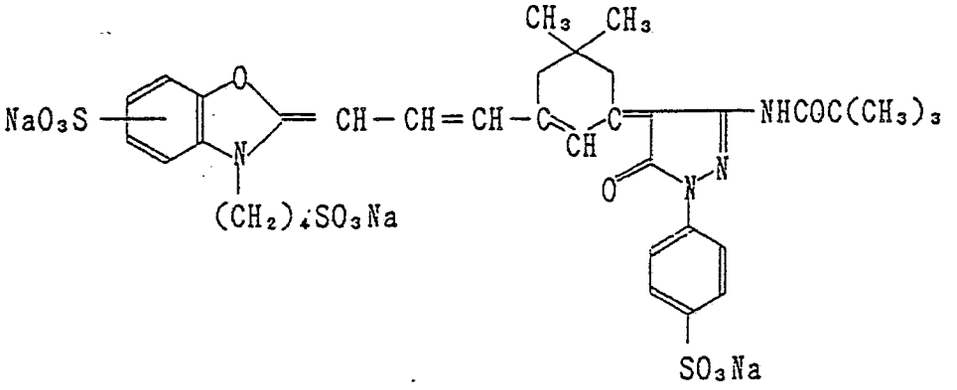

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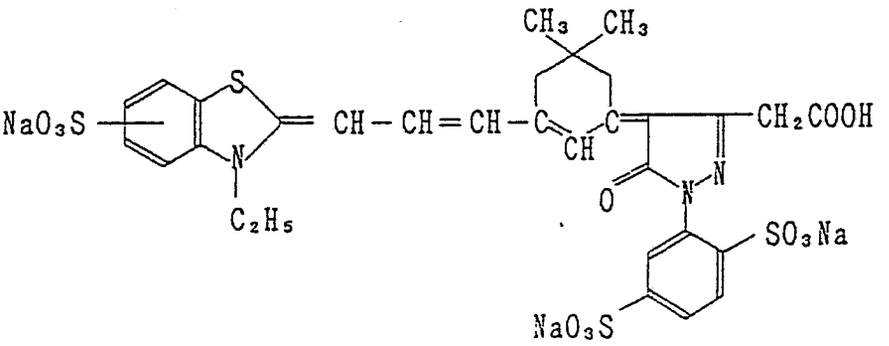

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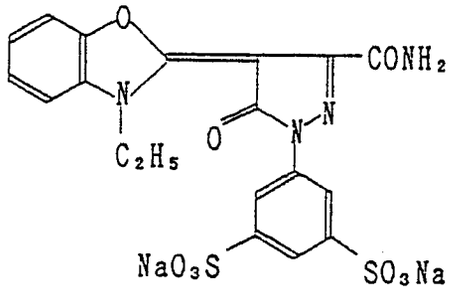

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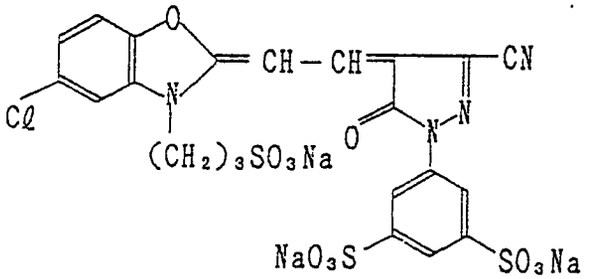

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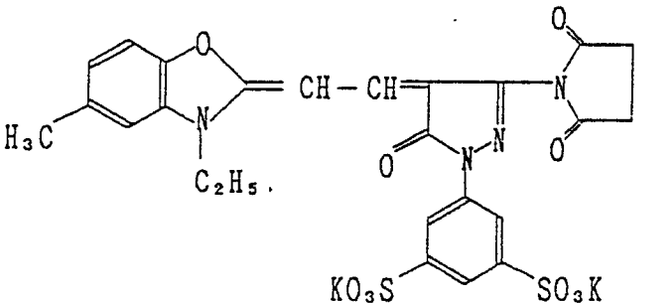

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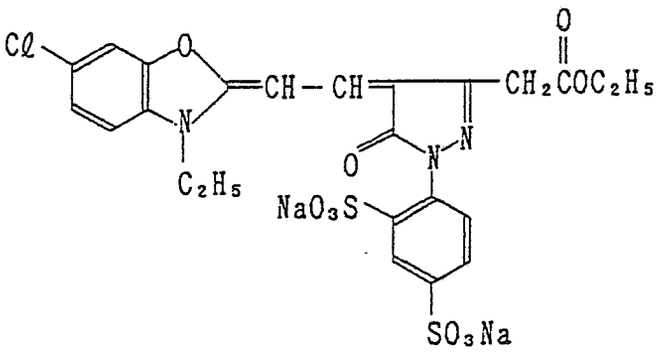
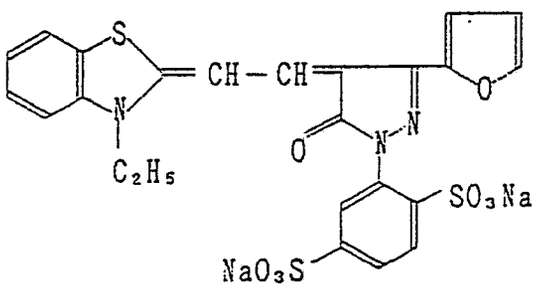


(I－38)



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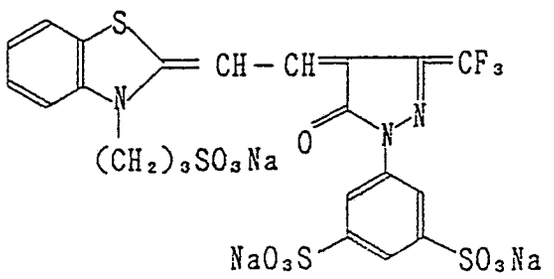

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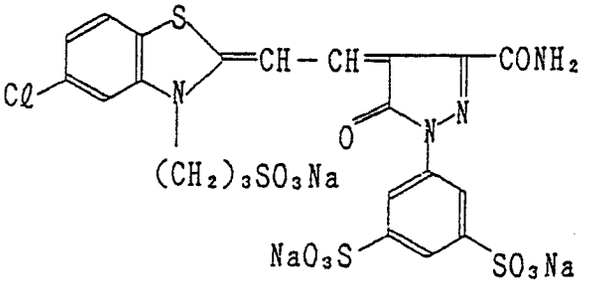

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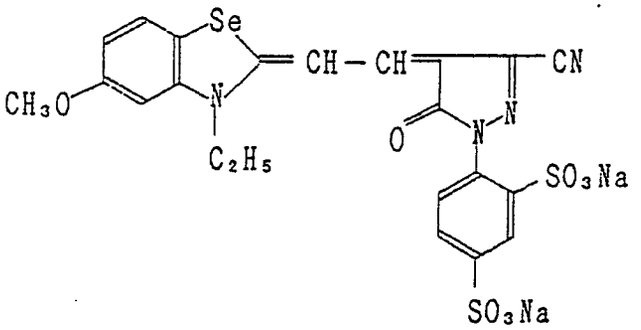

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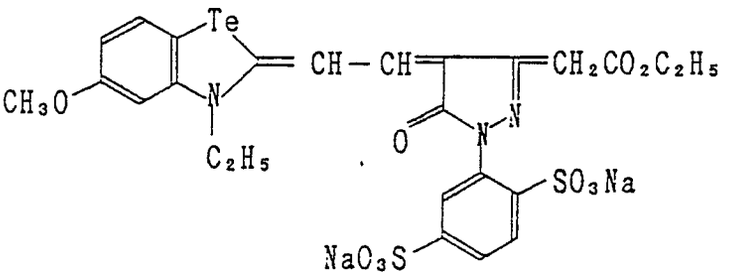

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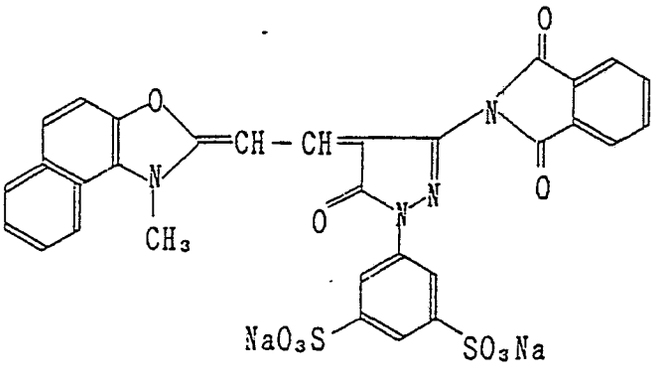

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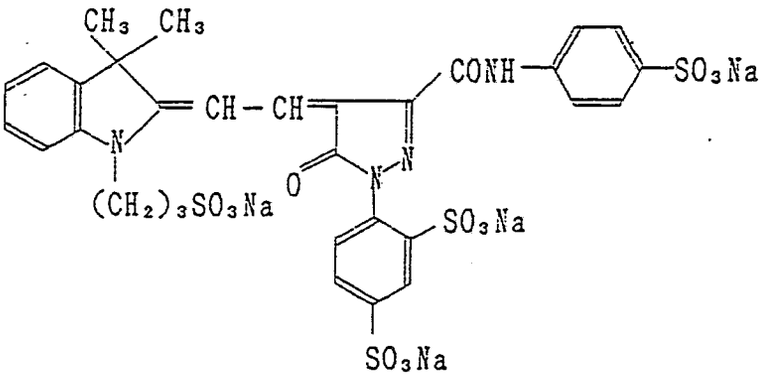

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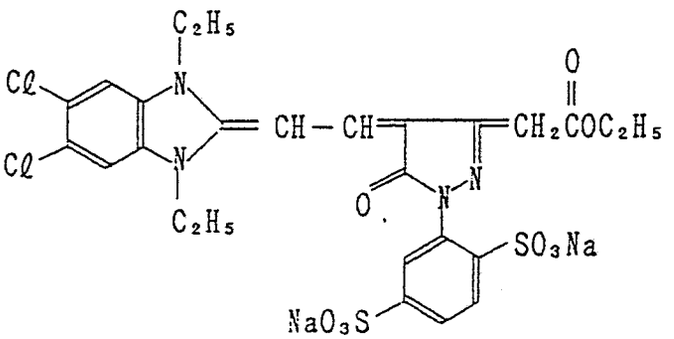

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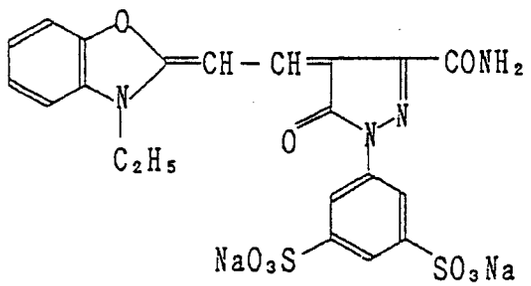

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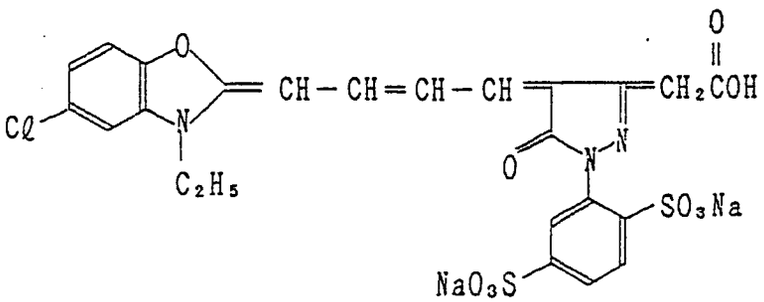

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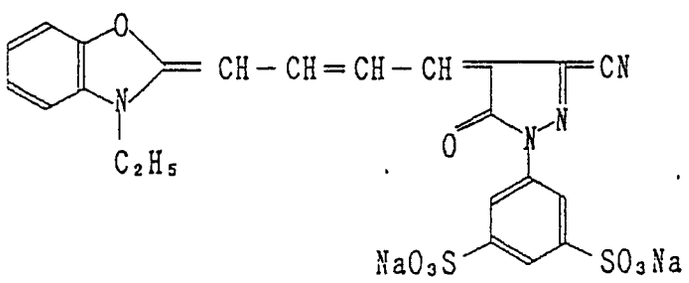
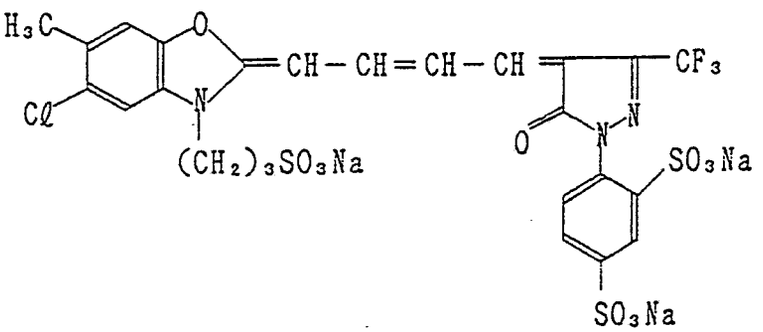


(I-49)



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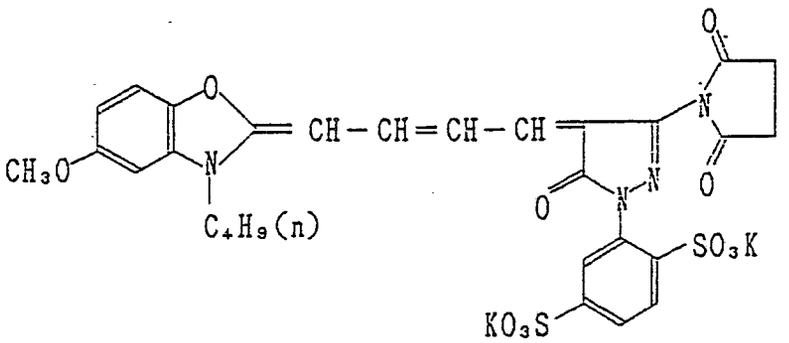

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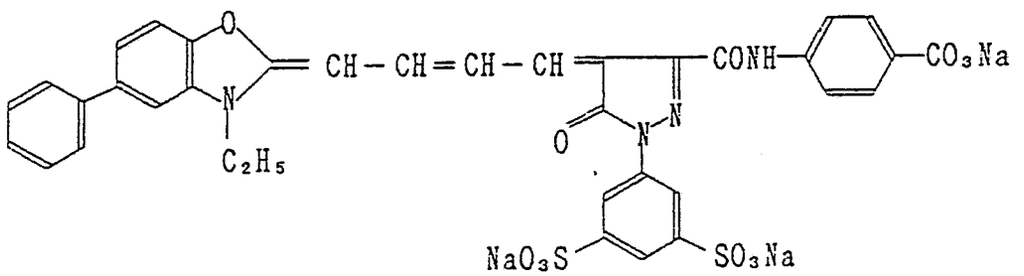

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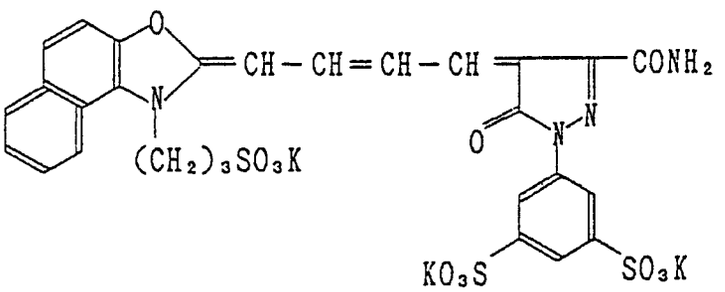

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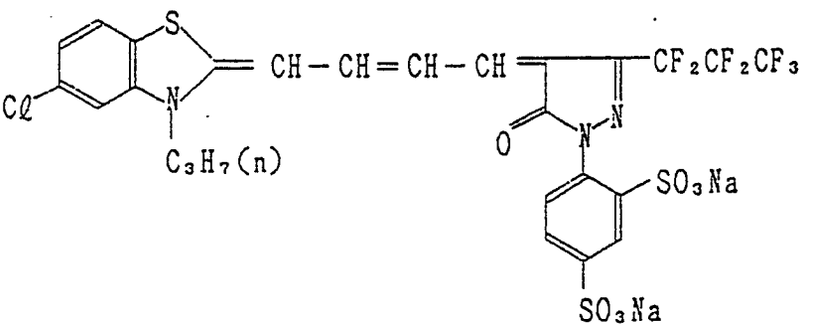

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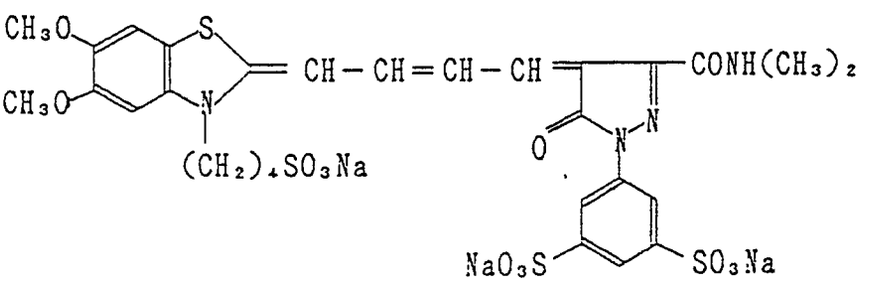

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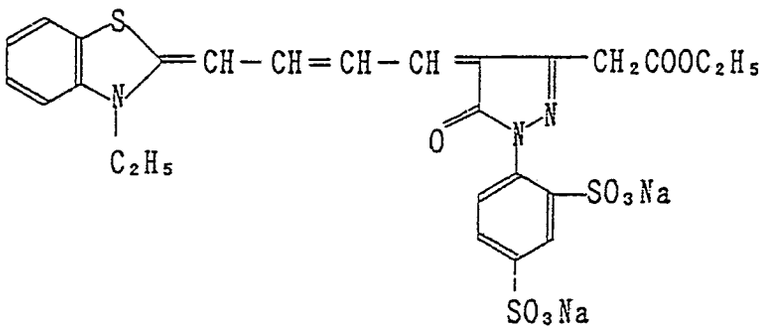

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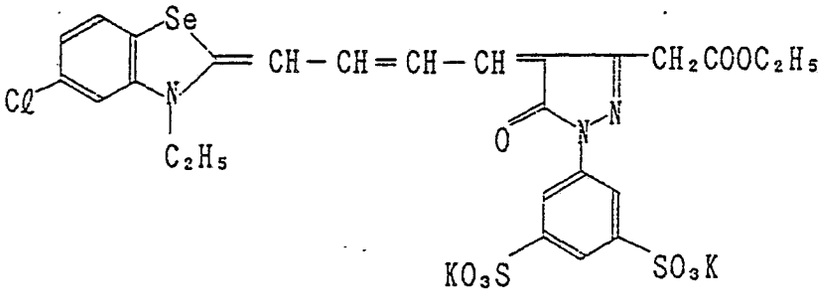

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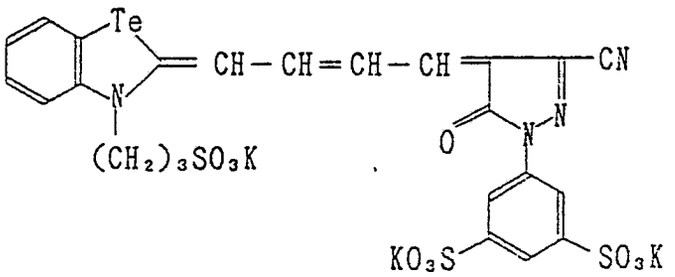

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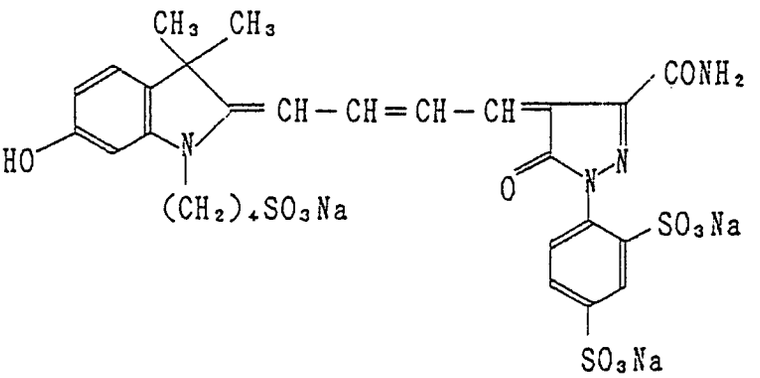
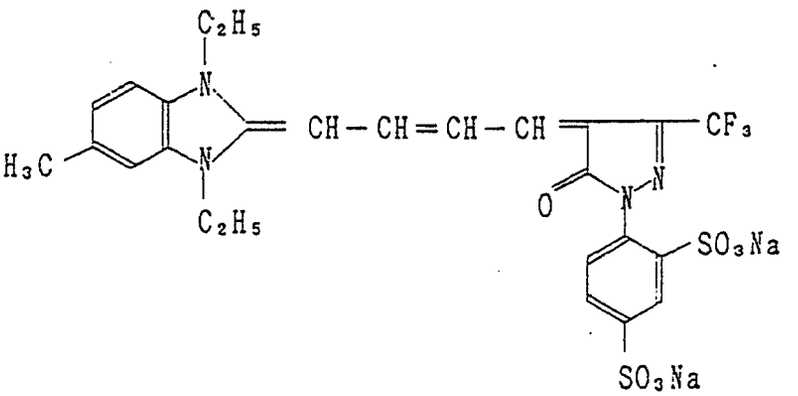
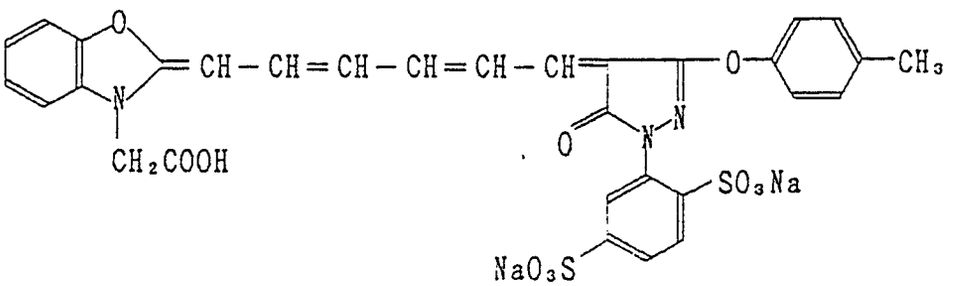


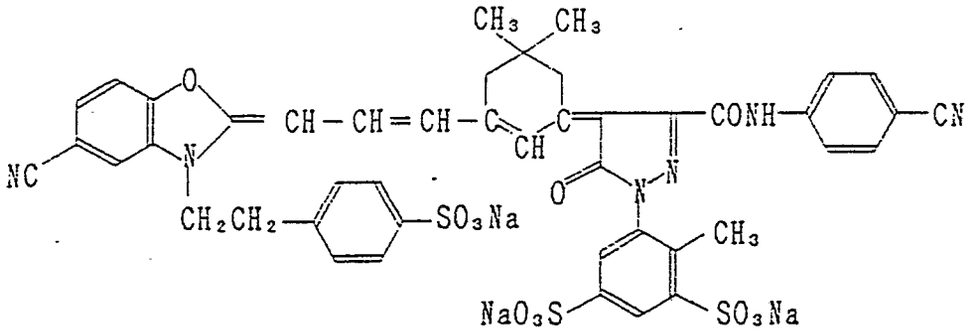
(I－59)



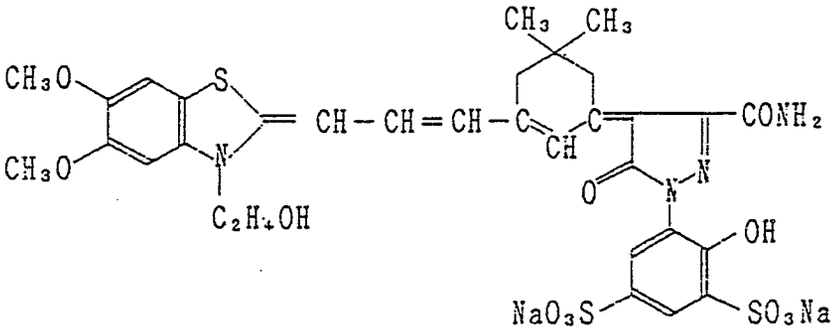
(I－60)



(I - 61)



(I - 62)



The AI dye represented by the above formula (AI - I) can be easily synthesized according to the synthetic methods as described in U.S. Patents No. 2,493,747 and No. 3,148,187.

Next, the formula (AI - I') is to be described.

The alkyl group represented by W is inclusive of those having substituents and may include, for example, straight or branched groups such as a methyl group, an ethyl group, an isobutyl group, etc.; cyclic groups such as cyclopentyl group, a cyclohexyl group, etc.; substituted alkyl groups such as an allyl group, a benzyl group, a 2-hydroxyethyl group, a hydr oxyethoxyethyl group, a 2-methylsulfonylethyl group, a 2-carbamoylethyl group, a 2-sulfamoylethyl group, a 2-(N,N-dimethylamino)ethyl group, a 2-cyanoethyl group, a 2-(22,23-tetrafluoro)propyloxyethyl group, a 3-ethoxycarbonylpropyl group, a 3-succinimidopropyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a carboxymethyl group, a carboxyethyl group, a p-sulfobenzyl group, a p-carboxyphenethyl group, etc. The heterocyclic group represented by w is inclusive of aromatic and saturated types, including substituted or unsubsituted groups such as a 1,1-dioxothiolanyl group, a 2-sulfo-5-pyridyl group, a 6-sulfo-2-benzothiazolyl group, a 2-pyridyl group, a 2-pyrimidyl group, etc., but W may be preferably a group substituted with an acidic group.

The alkyl group represented by Rf_2' is inclusive of those having substituent, and examples thereof may be straight or branched groups such as a methyl group, an ethyl group, a t-butyl group, a dodecyl group, a 2-ethylhexyl group and the like; substituted alkyl group such as an allyl group, a benzyl group, a carbamoylethyl group, an ethoxycarbonylmethyl group, a cyanomethyl group, a 2-sulfamoylethyl group, a 2-phenoxyethyl group, a carboxymethyl group, a p-sulfobenzyl group and the like.

As the aryl group, a heterocyclic group, an amino group, an acylamino group, an imide group, an ureido group, a carboxy group, an alkoxycarbonyl group, a carbamoyl group, an aryloxy group, an alkoxy group, a hydroxy group and a cyano group, those mentioned as examples for Rf_2' in the above formula (AI - I) can be enumerated as specific examples, respectively.

The alkyl group represented by Rf_3' is inclusive of those having substituents, and examples thereof may include a methyl group, an ethyl group, a 2-(2,2,3,3-tetrafluoropropyloxy)ethyl group, an allyl group, a

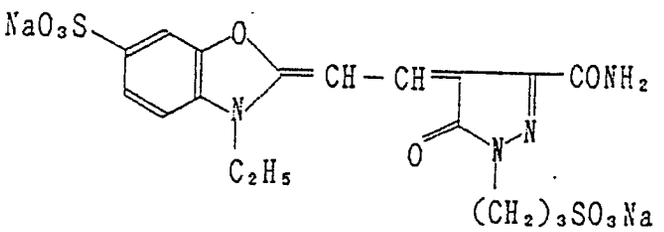
benzyl group, an ethoxycarbonylethyl group, a 2-hydroxyethyl group, a carbamoyl methyl group, a 2-cyanoethyl group, a carboxymethyl group, a p-carboxyphenethyl group, a p-sulfobenzyl group, a 3-sulfopropyl group, a 2-sulfoethyl group, a 4-sulfobutyl group, etc., preferably alkyl groups substituted with acidic group such as carboxymethyl groups, a p-carboxyphenethyl group, a p-sulfobenzyl group, a 3-sulfopropyl group, a 2-sulfoethyl group, a 4-sulfobutyl group, etc.

For Rf_4', Rf_5', L_1 to L_6 and m, the respective descriptions for Rf_4, Rf_5, L_1 to L_6 and m are applicable.

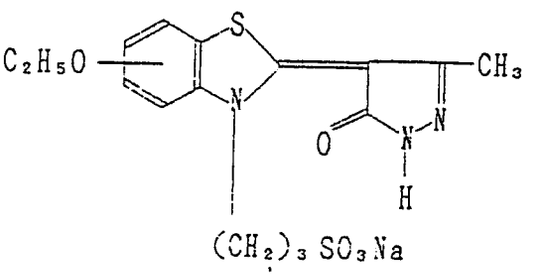
In the following specific examples of the AI dye represented by the formula (AI - I') are set forth.

(Exemplary compounds)

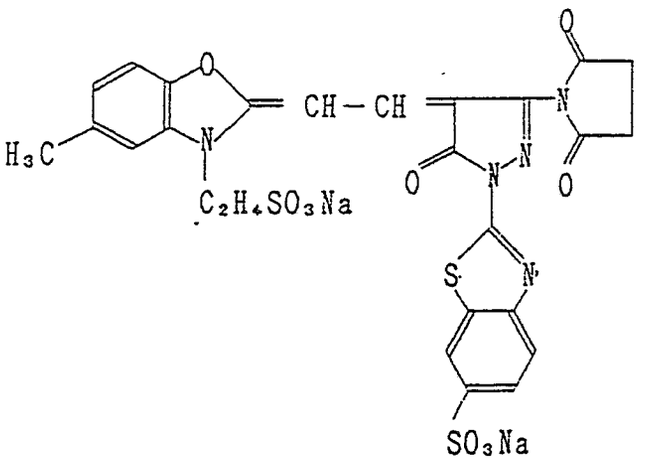
(I′ − 1)



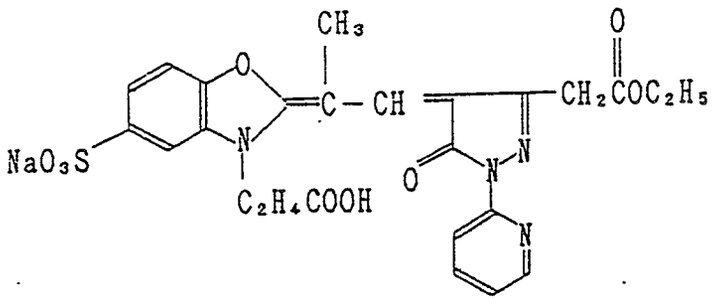
(I′ − 2)



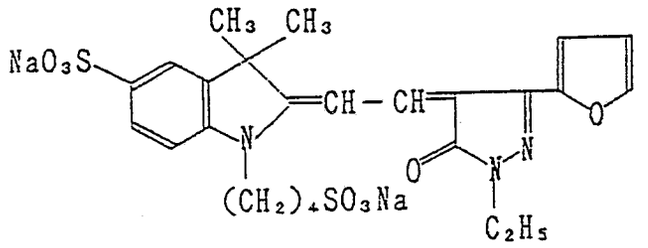
(I′ − 3)



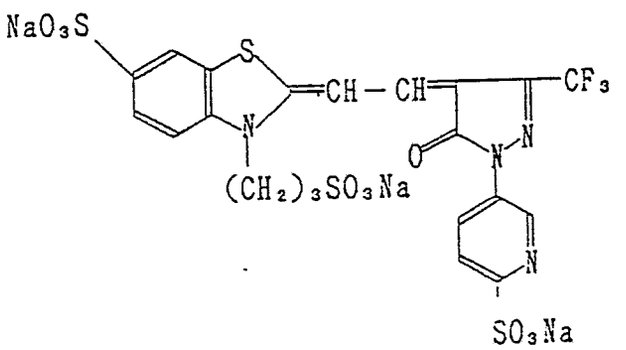
(I′ − 4)



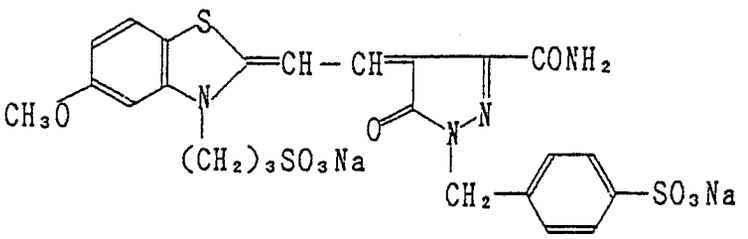
(I′ − 5)



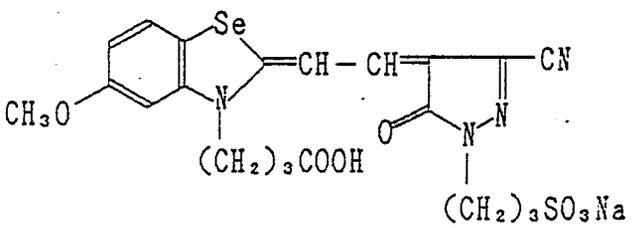
(I′ − 6)



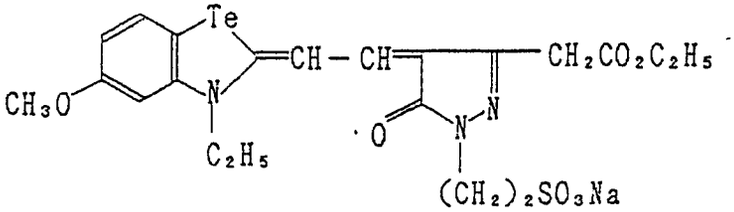
(I′ − 7)



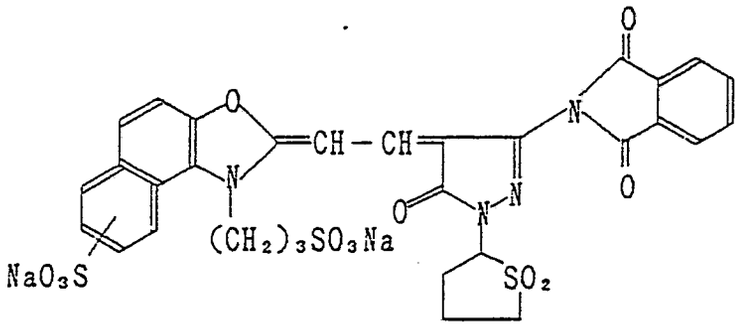
(I′ − 8)



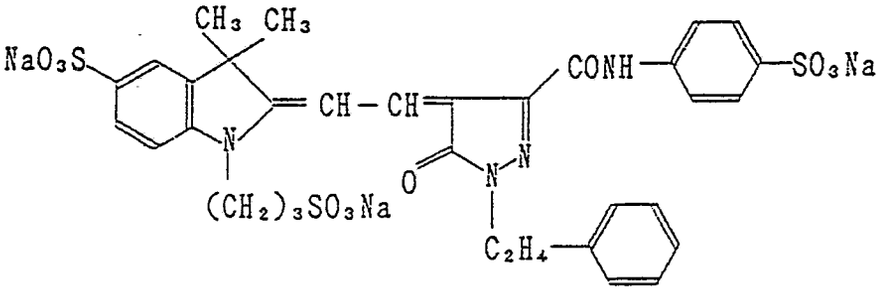
(I′ − 9)



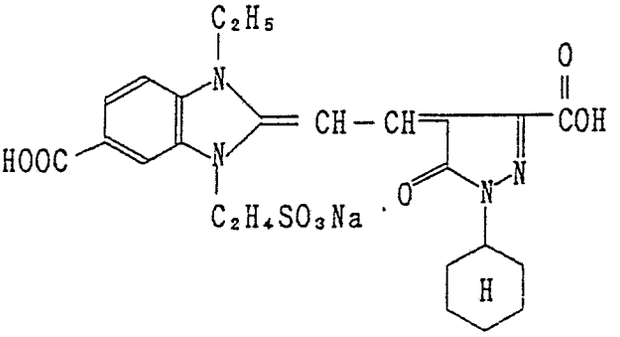
(I′ −10)



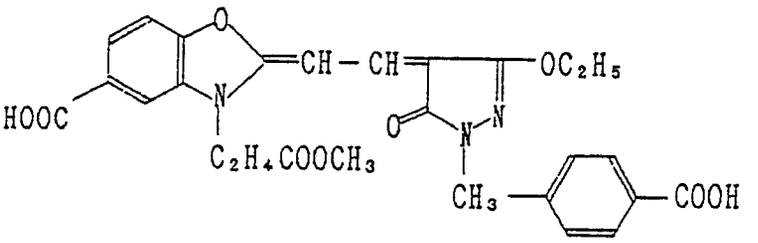
(I′ −11)



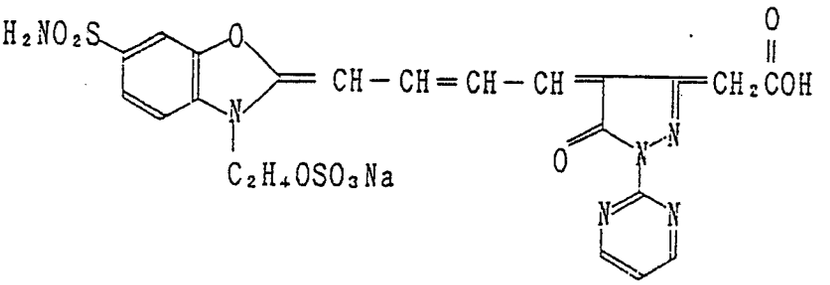
(I′ −12)



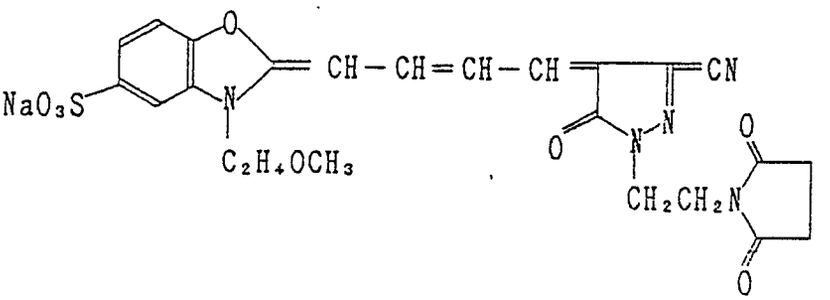
(I′ −13)



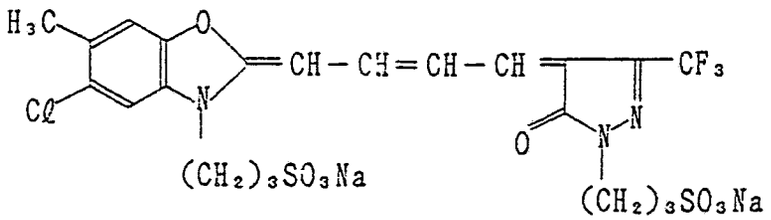
(I′ −14)



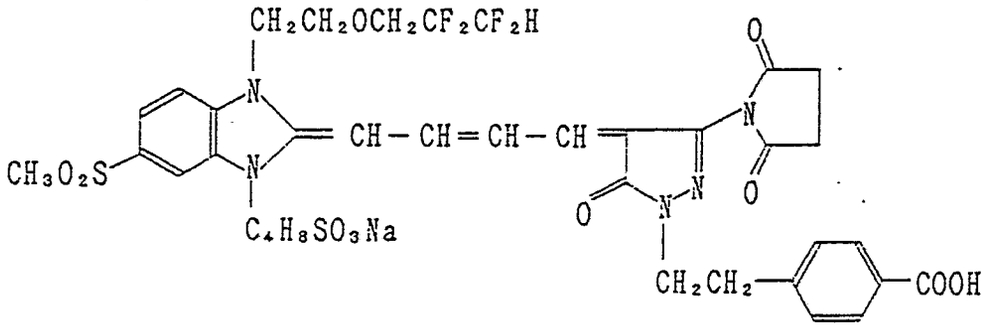
(I′ −15)



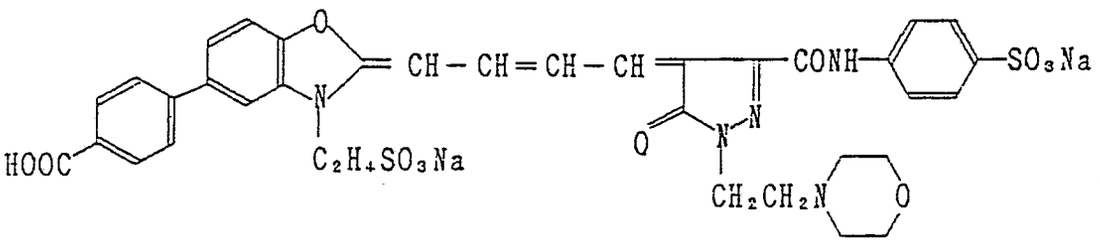
(I′ −16)



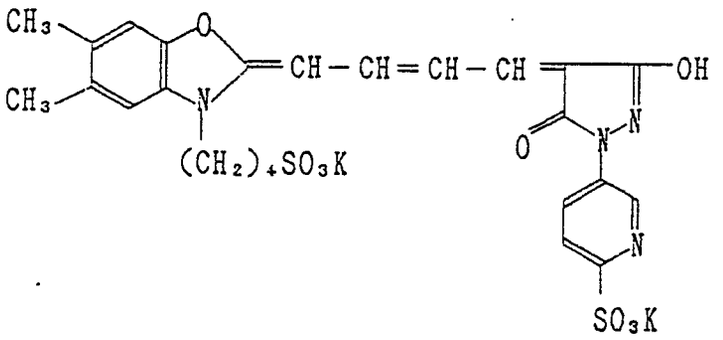
(I′ −17)



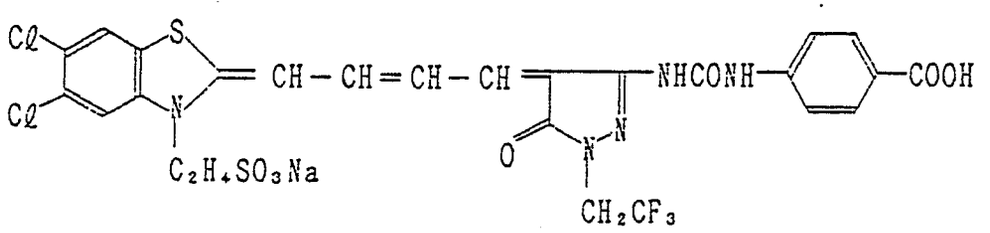
(I′ −18)



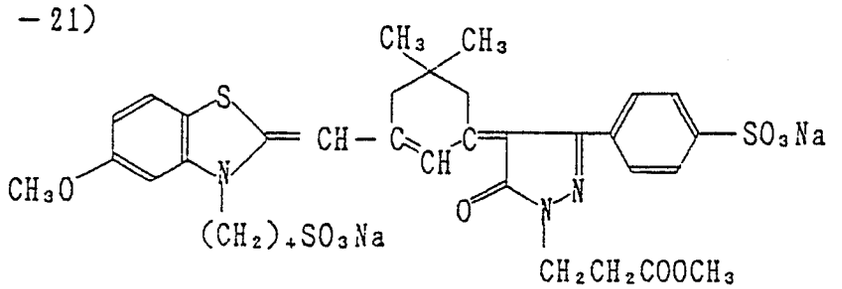
(I′ −19)



(I′ −20)



(I′ −21)



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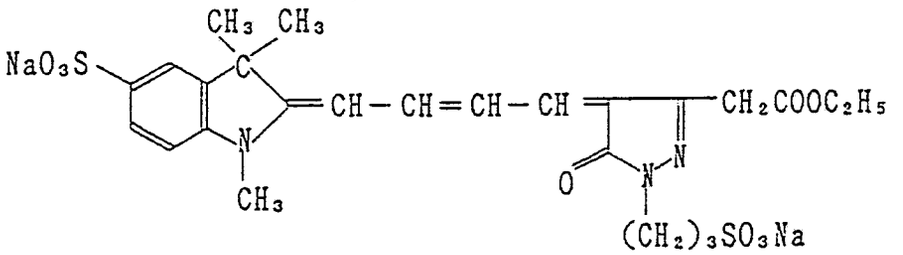
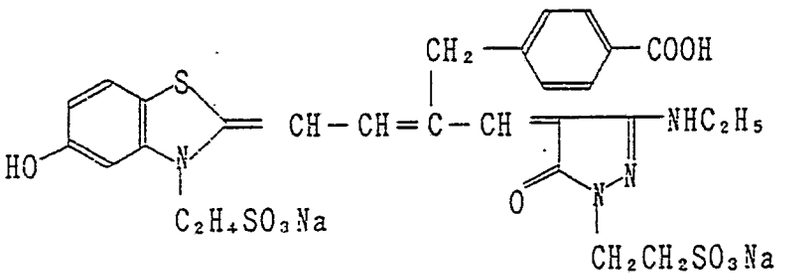
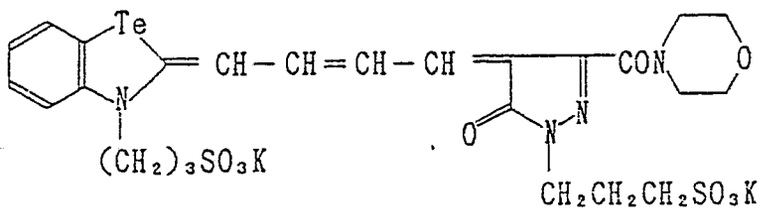


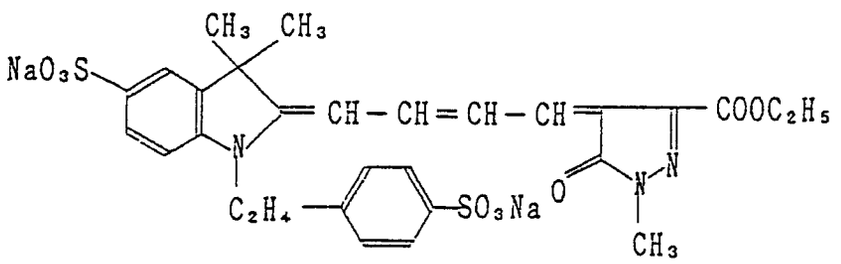
(I′ −23)



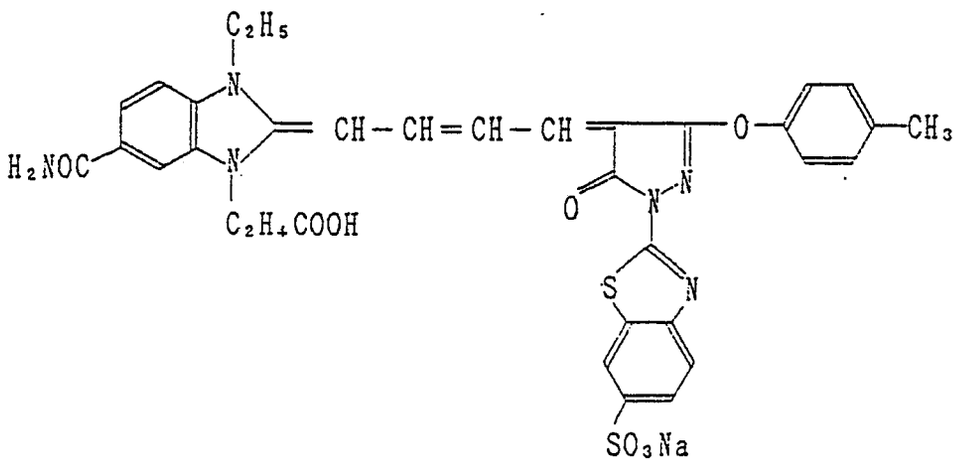
(I′ −24)



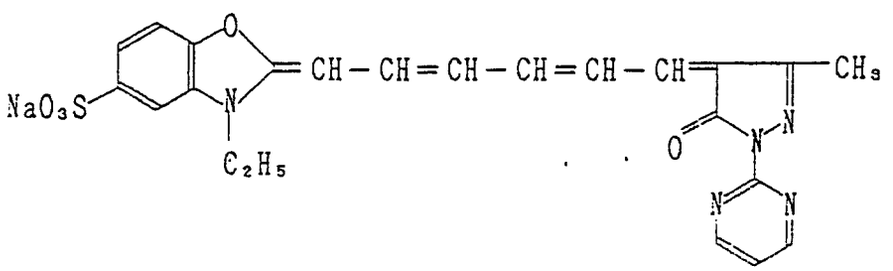
(I′ −25)



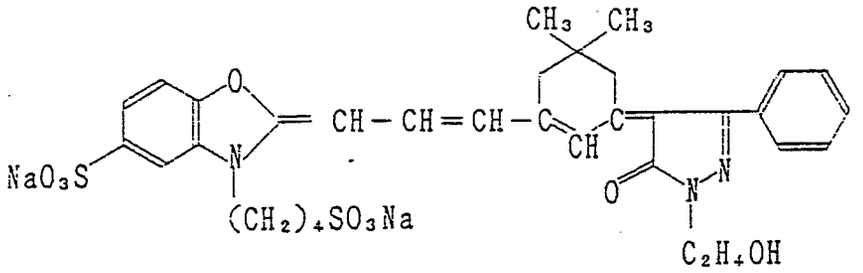
(I′ −26)



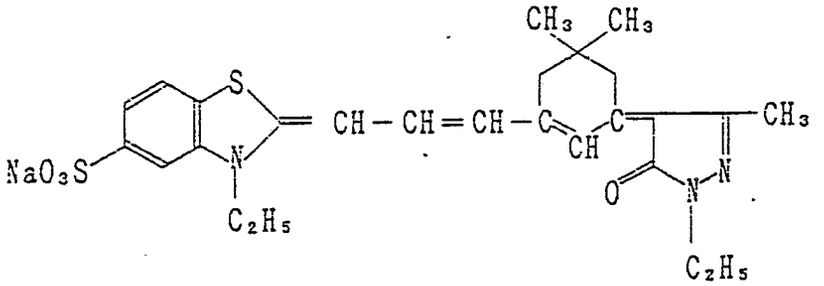
(I′−27)



(I′ -28)



(I′ -29)



In the formula (AI - II), Rf_6 and Rf_6' each represent a hydrogen atom or an alkyl group, an aryl group or a heterocyclic group which may be each substituted, and the aryl group may be a 4-sulfophenyl group, a 4-(α-sulfobutyl)phenyl group, a 3-sulfophenyl group, a 2,5-disulfophenyl group, a 3,5-disulfophenyl group, a 6,8-disulfo-2-naphthyl group, a 4,8-disulfo-2-naphthyl group, a 3,5-dicarboxyphenyl group, a 4-dicarboxyphenyl group, etc., and the aryl group can have a sulfo group, a sulfoalkyl group, a carboxy group, an alkyl group having 1 to 5 carbon atoms (e.g., a methyl group, an ethyl group, etc.), a halogen atom, (e.g., a chlorine atom, a bromine atom, etc.), an alkoxy group having 1 to 4 carbon atoms (e.g., a methoxy group, an ethoxy group, etc.), or a phenoxy group, and others.

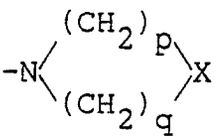
The sulfo group may be bonded through a divalent organic group to an aryl group to form, for example, a 4-(4-sulfophenoxy)phenyl group, a 4-(2-sulfoethyl)phenoxy group, a 3-(sulfomethylamino)phenyl group, a 4-(2-sulfoethoxy)phenyl group and the like.

The alkyl group represented by Rf_6 and Rf_6' may be either straight, branched or cyclic, having preferably 1 to 4 carbon atoms, such as an ethyl group, a β-sulfoethyl group and the like.

Examples of the heterocyclic group may include a 2-(6-sulfo)benzothiazolyl group, a 2-(6-sulfo)-benzoxazolyl group and the like, which may have substituents such as a halogen atom (e.g., a fluorine atom, a chlorine atom, a bromine atom, etc.), an alkyl group (e.g., a methyl group, an ethyl group, etc.), an aryl group (e.g., a phenyl group, etc.), a carboxyl group, a sulfo group, a hydroxy group, an alkoxy group (e.g., a phenoxy group, etc.).

Rf_7 and Rf_7' each represent a hydroxy group; an alkoxy group having 1 to 4 carbon atoms (e.g., a methoxy group, an ethoxy group, an isopropoxy group, an n-butyl group, etc.); an substituted alkoxy group such as alkoxy groups having 1 to 4 carbon atoms substituted with a halogen atom or an alkoxy group with up to 2 carbon atoms (e.g., a β-chloroethoxy group, a β-methoxyethoxy group, etc.); a cyano group; a trifluoromethyl group; -COORfa; -CONHRfa; -NHCORfa (where Rfa represents a hydrogen atom; an alkyl group, preferably an alkoxy group having 1 to 4 carbon atoms; or an aryl group such as a phenyl group, a naphthyl group, and said alkyl group and aryl group may have a sulfo group or a carboxy group as the substituent); an amino group; a substituted amino group substituted with an alkyl group having 1 to 4

carbon atoms (e.g., an ethylamino group, a dimethylamino group, a diethylamino group, a di-n-butylamino group, etc.); or a cyclic amino group represented by:



(where p and q each represent an integer of 1 or 2, and X represents an oxygen atom, a sulfur atom or $-CH_2-$group) (e.g., a morpholino group, a piperidino group, a piperazino group, etc.).

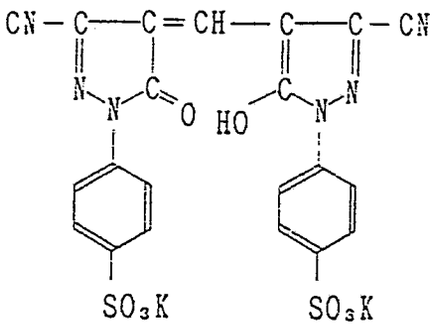
The methine group represented by L may be substituted with an alkyl group having 1 to 4 carbon atoms (e.g., a methyl group, an ethyl group, an isopropyl group, a tert-butyl group, etc.) or an aryl group (e.g., a phenyl group, a tolyl group, etc.).

Also, at least one of a sulfo group, a sulfoalkyl group and a carboxy group of the compounds may form salts with alkali metals (e.g., sodium, potassium, etc.), alkaline earth metals (e.g., calcium, magnesium, etc.), ammonium or organic bases (e.g., a diethylamino group, a triethylamino group, a morpholino group, a pyridinyl group, a piperidinyl group, etc.). n represents 0, 1 or 2. m represents 0 or 1.

Specific examples of the compound represented by the above formula (AI - II) are shown below, but the present invention is not limited by these at all.

(Exemplary compounds)

(Ⅱ－1)



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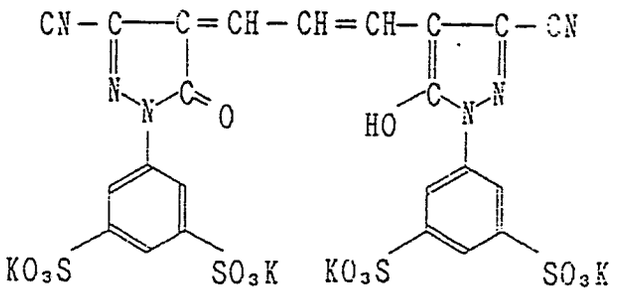

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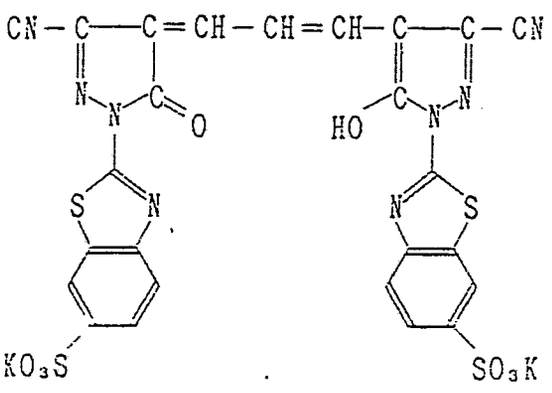

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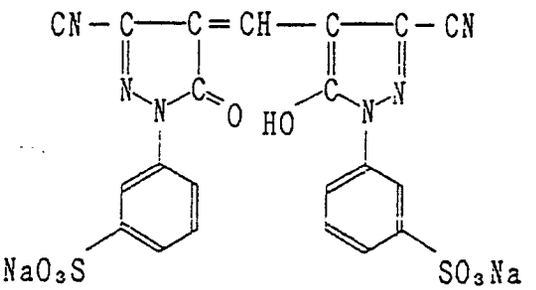

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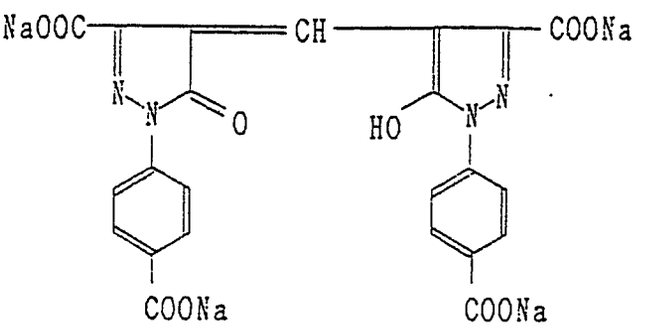

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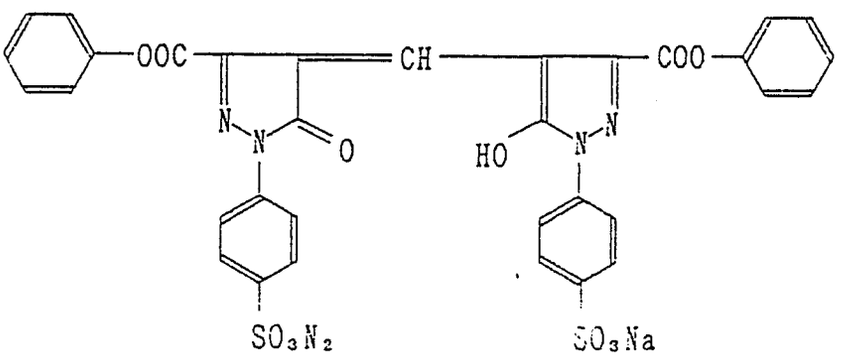

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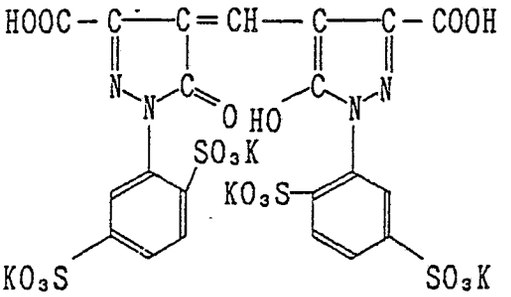

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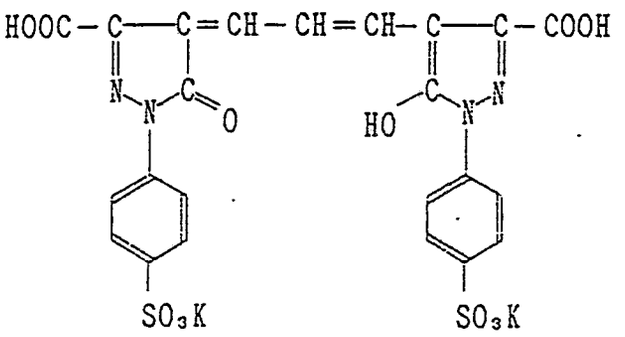
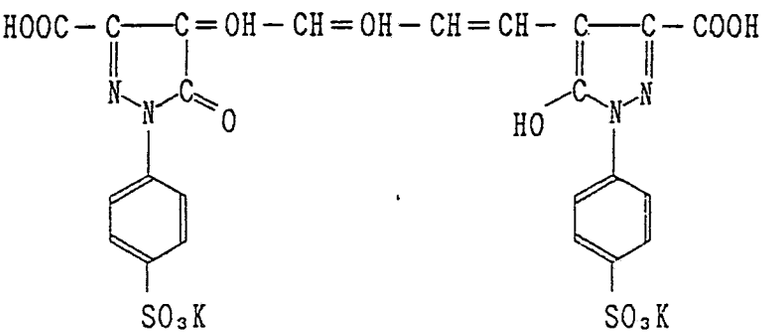
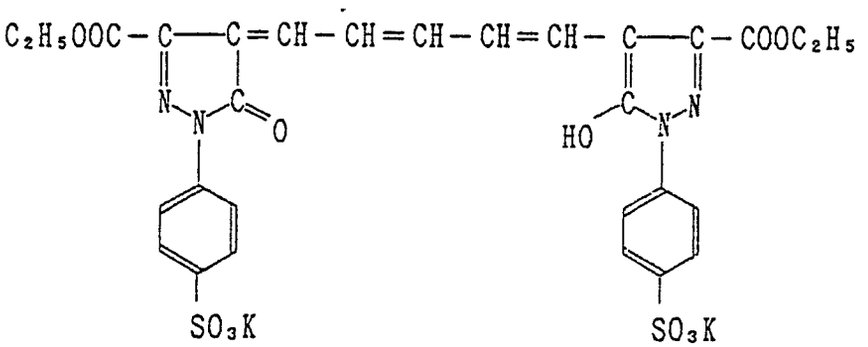


(Ⅱ－9)



(Ⅱ－10)



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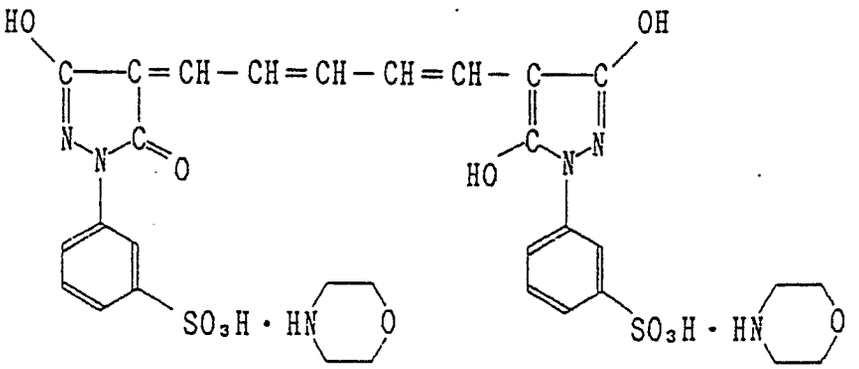
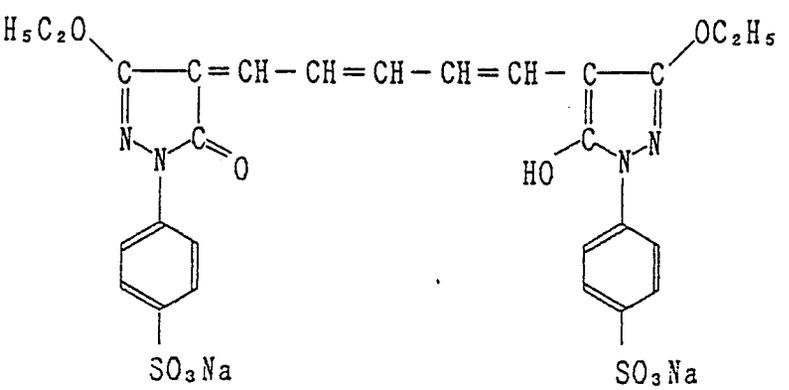
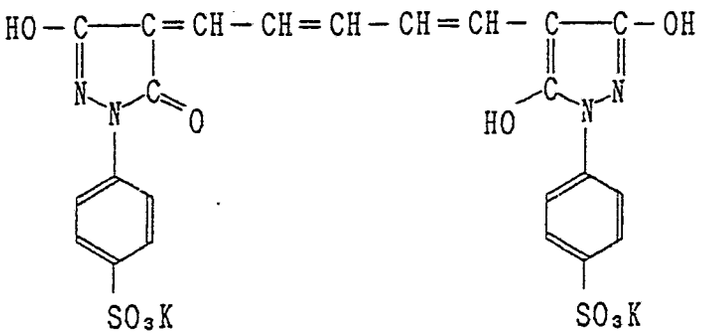


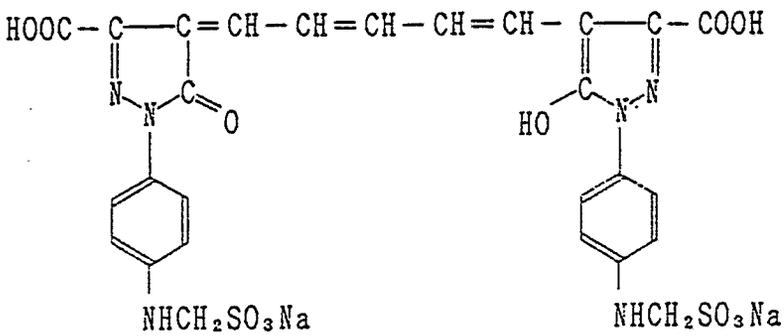
(Ⅱ－12)



(Ⅱ－13)



(Ⅱ－14)



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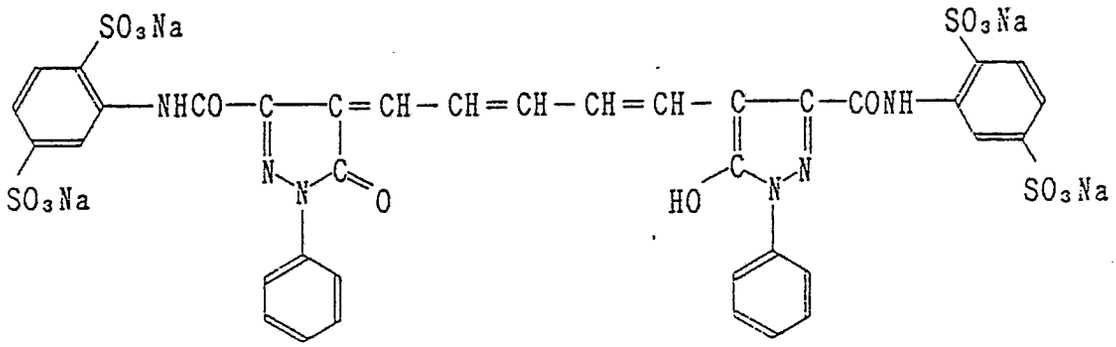

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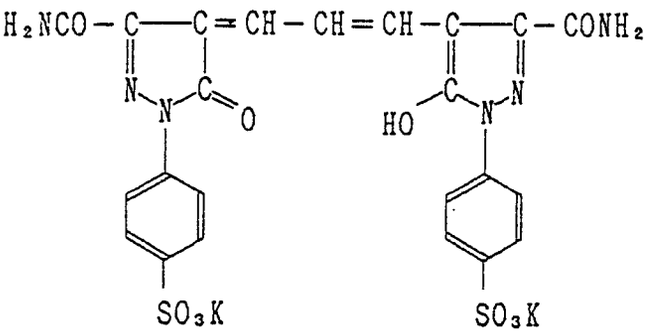

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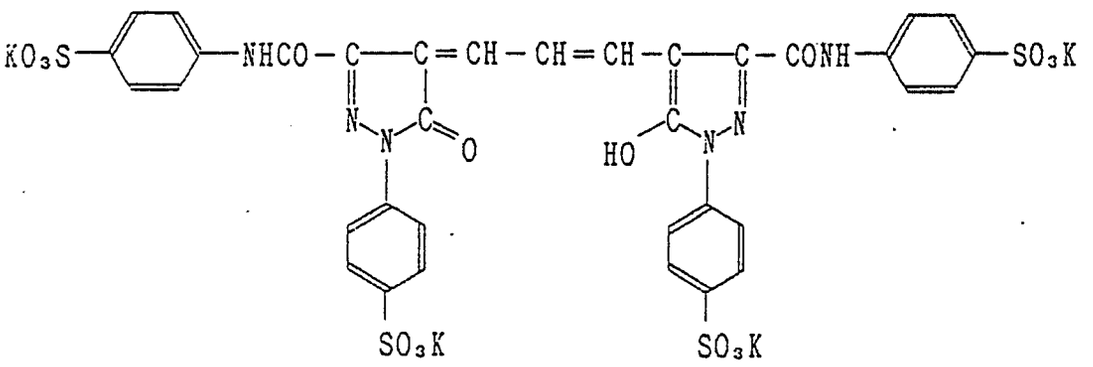

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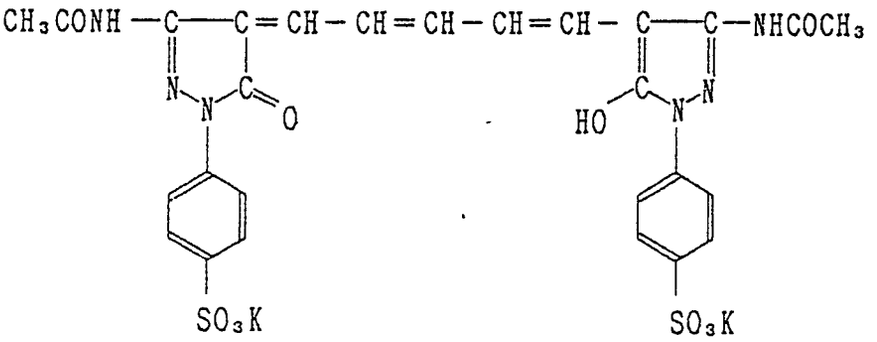

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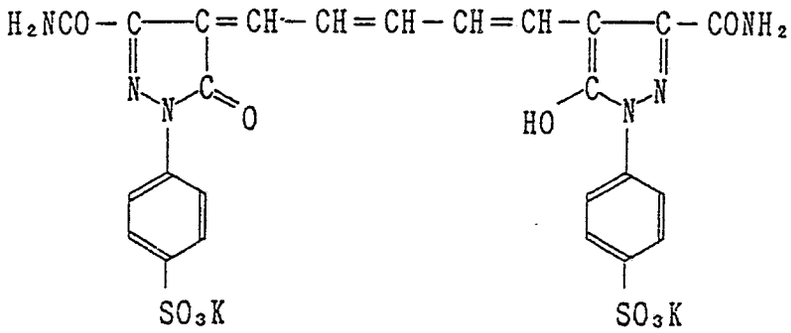

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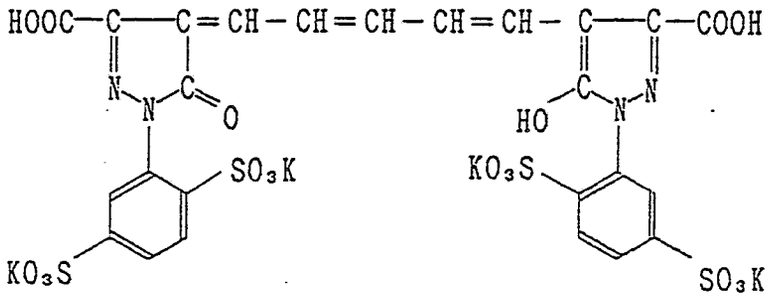

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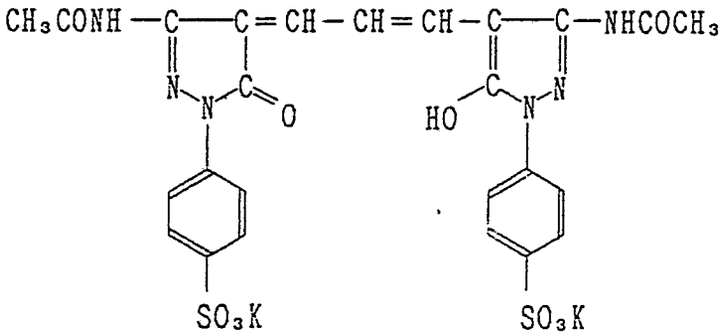
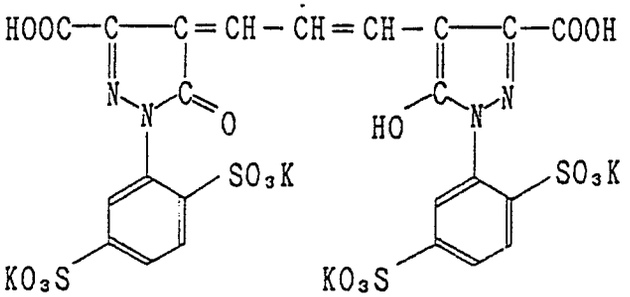
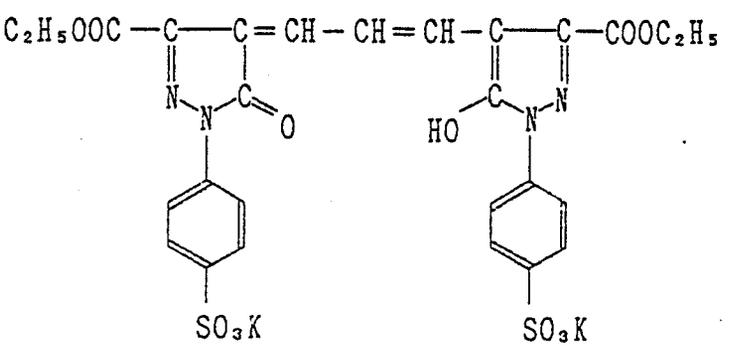


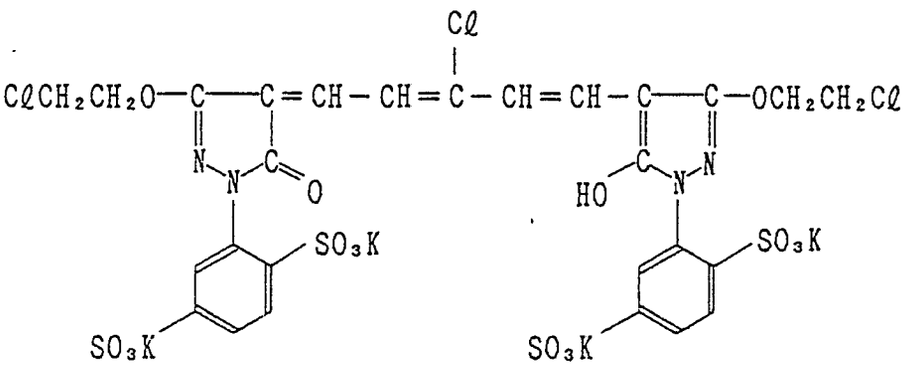
(II－22)



(II－23)



(II－24)



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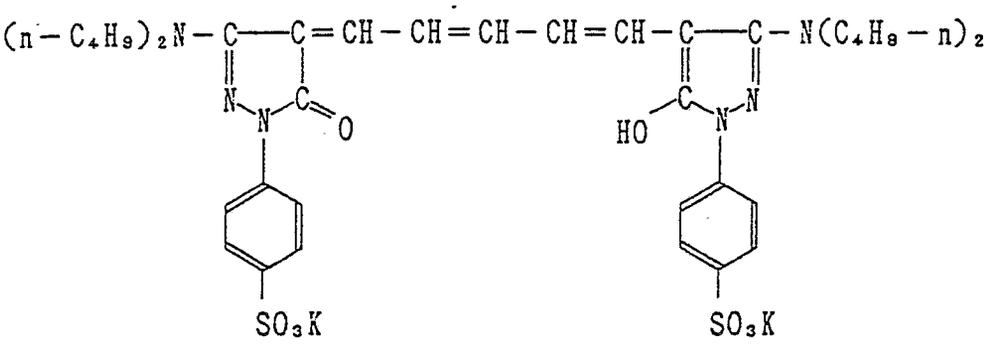

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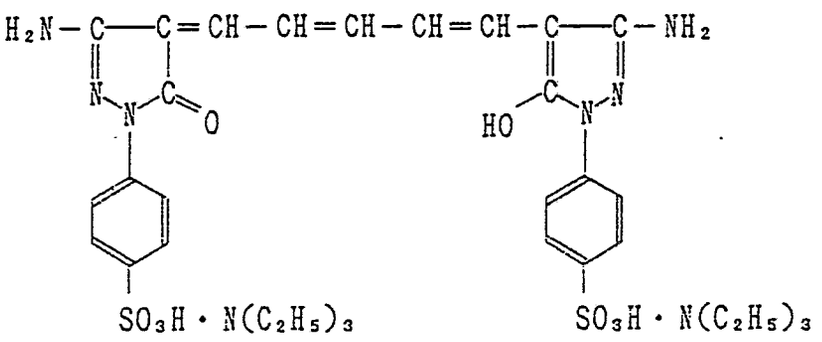

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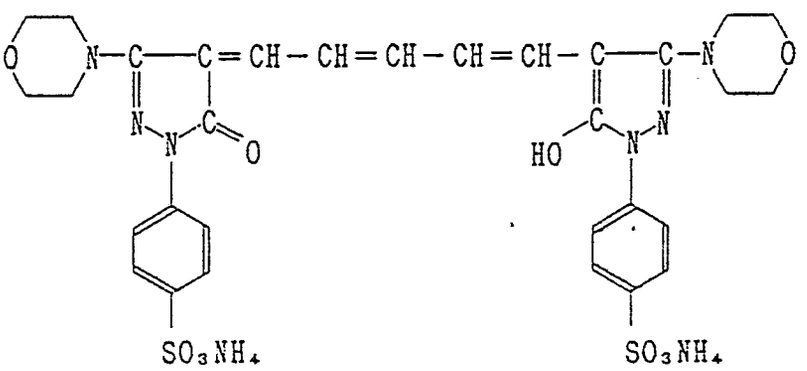
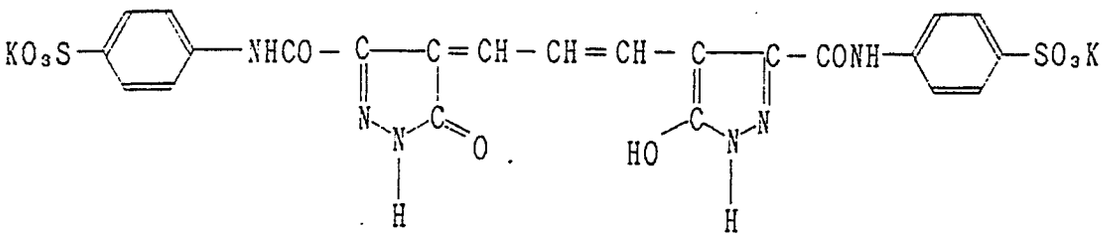
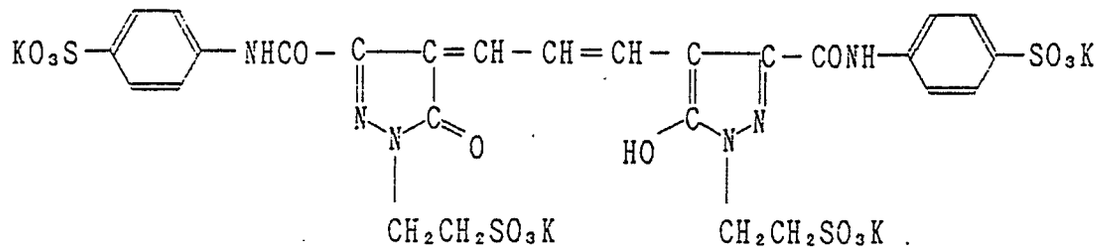


(II - 28)



(II - 29)



In the formula (AI - III), r represents an integer of 1 to 3, W represents an oxygen atom and a sulfur atom, L represents a methine group, Rf_{31} to Rf_{34} each represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a heterocyclic group, of which at least one is substituent other than a hydrogen atom. The methine group represented by L can include those as described in the item of the formula (AI -II).

The alkyl group represented by Rf_{31} to Rf_{34} may include the same alkyl groups as mentioned for Rf_6 and Rf_6' in the item of the formula (AI - II), and said alkyl groups may include various substituents to be introduced into the groups of a sulfo, a carboxy, a hydroxy, an alkoxy, an alkoxycarbonyl, a cyano and a sulfonyl. The aryl gropu represented by Rf_{31} to Rf_{34} may be preferably a phenyl group, and the substituent to be introduced onto the phenyl group may include vairous ones mentioned as the substituent to be introduced into the groups of Rf_6 and Rf_6' in the item of the formula (AI - II), and it is desired to have at least one of the sulfo group, a carboxy group, a sulfamoyl group on the aromatic ring.

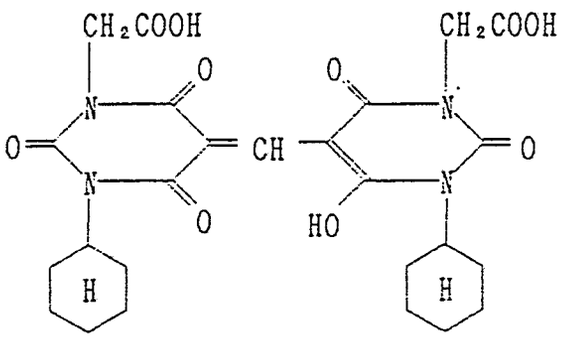
The aralkyl group represented by Rf_{31} to Rf_{34} may be preferably a benzyl group a phenethyl group, and the substituent to be introduced into the heterocyclic group may include the same substituents on the aryl group of Rf_{31} to Rf_{34} as described above.

The group represented by Rf_{31} to Rf_{34} may be preferably an alkyl group or an aryl group, and further the barbituric acid and the thiobarbituric acid represented by the formula (AI -III) should desirably have at least one of a carboxy group, a sulfo group and a sulfamoyl group within one molecule, preferably of the symmetric type.

Typrical specific examples of the compounds represented by the above formula (AI - III) are shown below, but the present invention is not limited by these at all.

(Exemplary compounds)

(Ⅲ－1)



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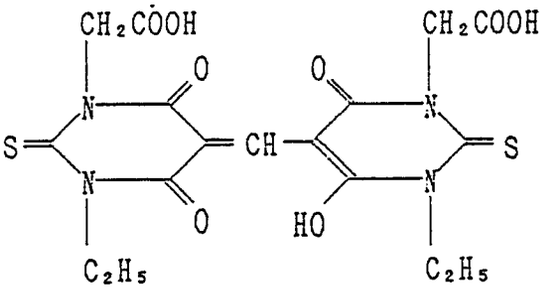

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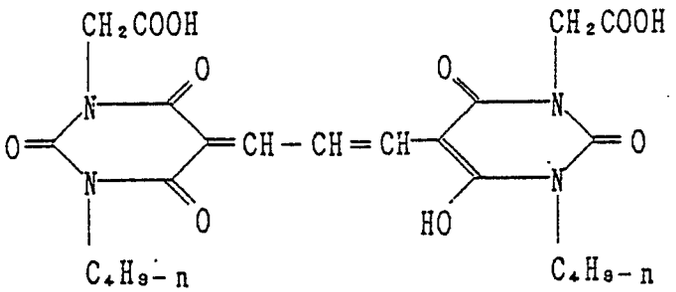

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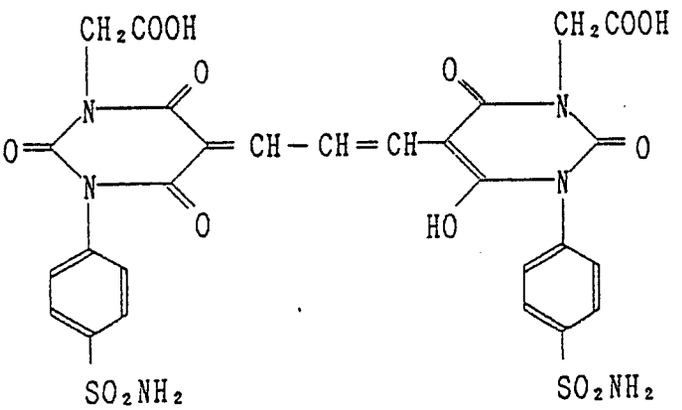

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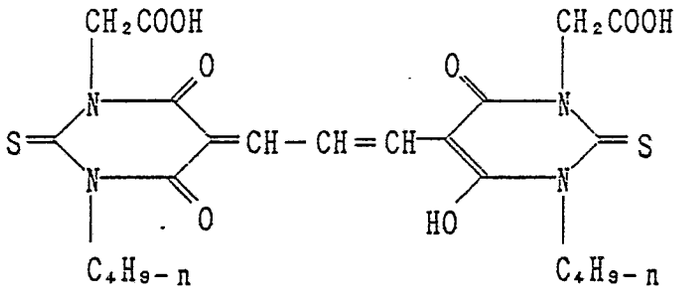

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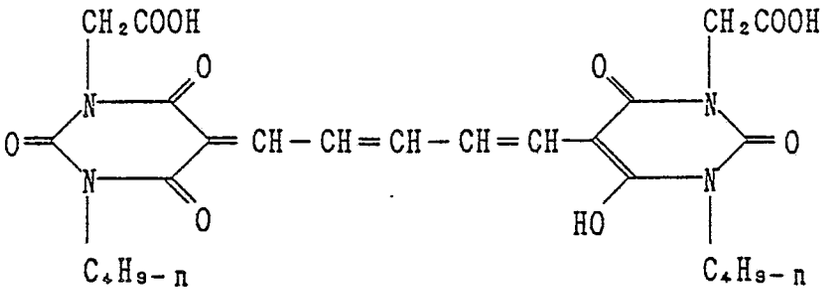

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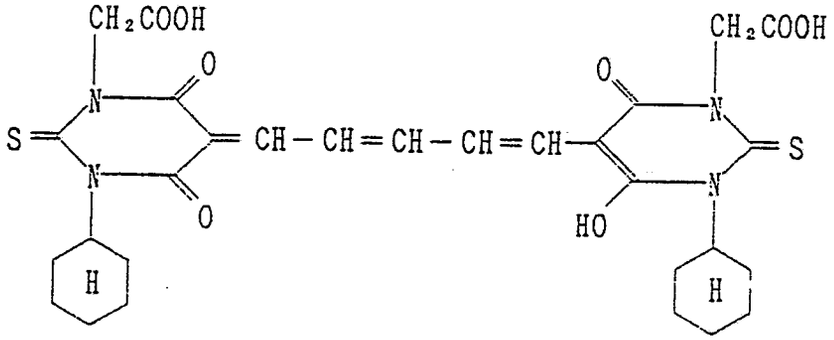
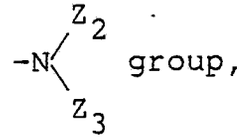


In the formula (AI - IV), *l* represents an integer of 1 or more, L represents a methine group, Rf_{41} has the same meaning as Rf_6 and Rf_6' in the formula (AI - II), preferably an alkyl group and an aryl group, which aryl group should desirably have at least one sulfo group.

Rf_{42} can introduce all of the substituents shown for Rf_7 and Rf_7' in the formula (AI - II), preferably selected from an alkyl group, a carboxyl group, an alkoxycarbonyl group, a carbamoyl group, a ureido group, an acylamino group, an imide group and a cyano group.

Rf_{43} represents $-OZ_1$ group or



where Z_1, Z_2 and Z_3 each representa hydrogen atom, an alkyl group, Z_2 and Z_3 being either the same or different or bonded together to form a ring.

The alkyl group represented by Z_1, Z_2 and Z_3 may include, for example, a methyl group, an ethyl group, a butyl group, a hydroxyalkyl group (e.g., a hydroxyethyl group, etc.), an alkoxyalkyl group (e.g., a β-ethoxyethyl group, etc.), a carboxyalkyl group (e.g., a β-carboxyethyl group, etc.), an alkoxycarbonylalkyl group (e.g., a β-ethoxycarbonylethyl group, etc.), a cyanoalkyl group (e.g., a β-diaminoethyl group, etc.), a sulfoalkyl group (e.g., a β-sulfoethyl group, a γ-sulfopropyl group, etc.) and the like.

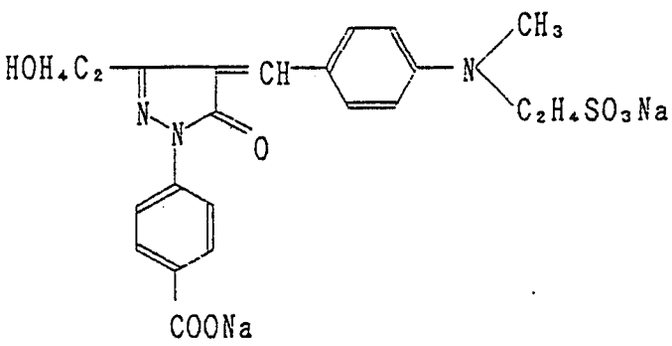
Z_2 and Z_3 may be bonded together to form a 5-or 6-membered ring, specifically a morpholino group, a piperidino group, a pyrrolidino group, etc.

Rf_{44} represents a hydrogen atom, an alkyl group, a chlorine atom, an alkoxy group, and the alkoxy group may be exemplified by a methoxy group, an ethoxy group, etc.

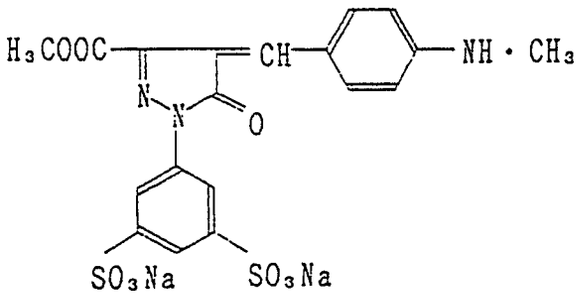
Typical specific examples of the above formula (AI - IV) are shown below, but the present invention is not limited by these at all.

(Exemplary compounds)

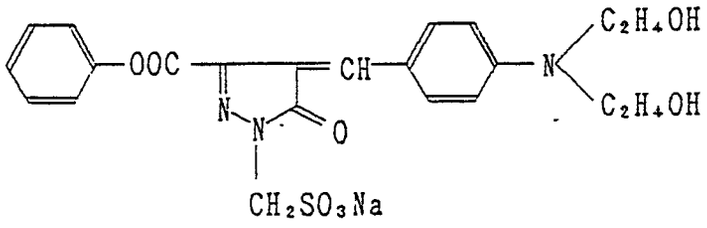
(IV − 1)



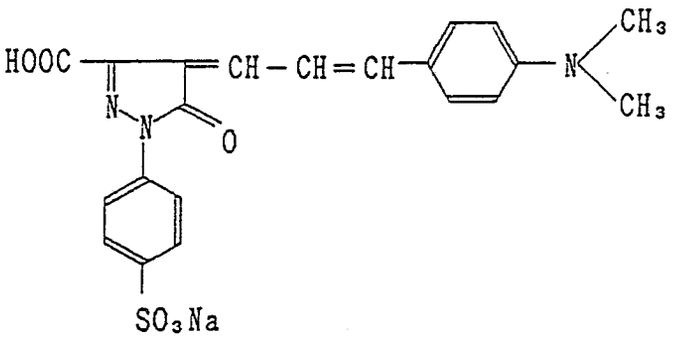
(IV − 2)



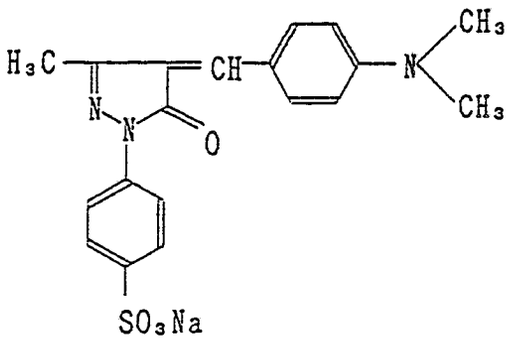
(IV − 3)



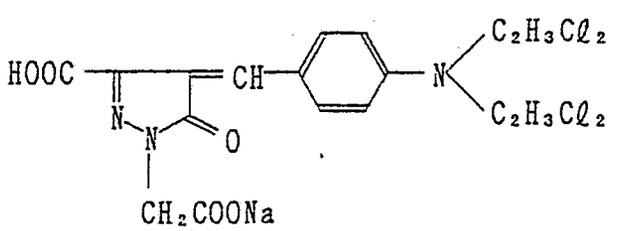
(Ⅳ－4)



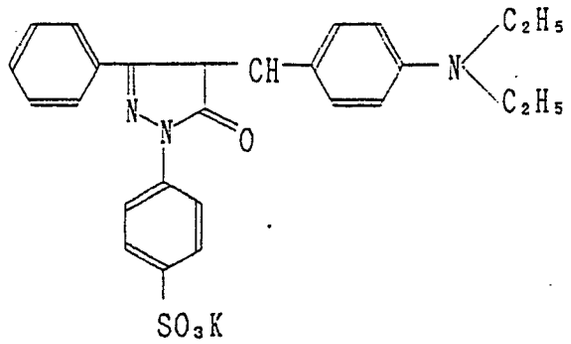
(Ⅳ－5)



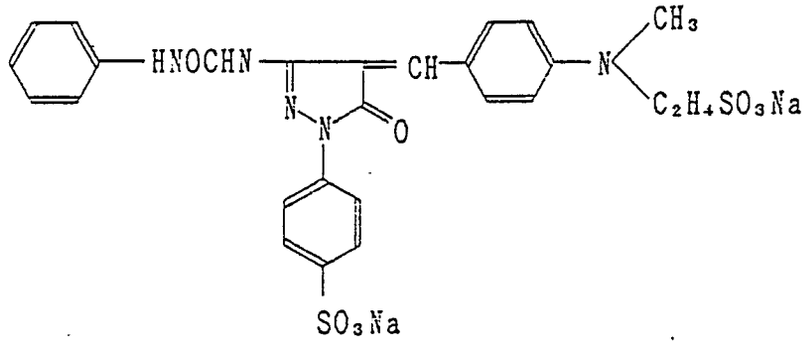
(Ⅳ－6)



(IV - 7)



(IV - 8)



The compounds represented by the above formula (AI - II), (AI - III) or (AI - IV) can be synthesized according to the synthetic methods as described in U.S. Patents No. 3,575,704, No. 3,247,127, No. 3,540,887 and No. 3,653,905, Japanese Provisional Patent Publications No. 85130/1973, No. 99620/1974, No. 111640/1984, No. 111641/1984 and No. 17083/1984.

The AI dye according to the present invention has the property of being decolored in the photographic development processing bath by the presence of hydroxylamine.

The AI dye of the present invention can be used as the irradiation prevention dye contained in the light-sensitive silver halide emulsion, or alternatively as the filter dye or the halation preventive dye contained in the non-sensitive hydrophilic colloid layer. Also, two or more kinds of the dyes of the present invention may be used in combination depending ont he purpose of use or also combined with other dyes. The dye according to the present invention can be contained in the light-sensitive silver halide emulsion layer or other hydrophilic colloid layers easily according to conventional methods. Generally, the dye or an organic or inorganic alkali salt of the dye can be dissolved in water to make up an aqueous dye solution with an appropriate concentration, which is then added into a coating solution, followed by coating according to a known method to incorporate the dye in the photographic material. The amount of these dyes contained, which may differ depending on the purpose of use, is generally 1 to 800 mg coated per 1 m^2 of area of the photographic material.

In addition to the AI dye of the present invention, further other dyes may be used in combination. Examples of dyes available in combination may include the pyrazoloneoxonol dyes disclosed in U.S. Patent No. 2,274,782; the diarylazo dyes disclosed in U.S. Patent No. 2,956,879; the styryl dyes or the butadienyl dyes disclosed in U.S. Patents No. 3,423,207 and No. 3,384,487; the merocyanine dyes disclosed in U.S. Patent No. 2,527,583; the merocyanine dyes and oxonol dyes disclosed in U.S. Patents No. 3,486,897, No. 3,652,284 and No. 3,718,472; the enaminohemioxonol dyes disclosed in U.S. Patent No. 3,796,661; and the dyes disclosed in G.B. Patents No. 584,609 and No. 1,177,429; Japanese Provisional Patent Publications No. 85130/1973; No. 99620/1974 and No. 114420/1974; and U.S. Patents No. 2,533,472, No. 3,148,187, No. 3,177,078, No. 3,247,127, No. 3,540,887, No. 3,575,704 and No. 3,653,905.

Hydroxylamine in the present invention is ordinarily used in the form of a salt such as hydrochloride, sulfate, p-toluenesulfonate, oxalate, phosphate, acetate, etc.

The color developing solution to be used in the present invention as mentioned above has a

hydroxylamine concentration generally of, for example, 0.05 g/liter or higher, more preferably 0.07 g/liter to 4 g/liter, particularly preferably 0.2 g/liter to 4 g/liter.

In the silver halide emulsion of the present invention, for the purpose of preventing fogging during the preparation steps, storage or photogrpahic processing of the light-sensitive material or maintaining stably the photographic performance, during chemical aging, on completion of chemical aging and/or after completion of chemical aging, until coating of the silver halide emulsion, compounds known as anti-foggants or stabilizers known in the field of photography can be added.

As the binder (or protective colloid) in the silver halide emulsion of the present invention, gelatin may be advantageously used, but hydrophilic colloids such as gelatin derivatives, graft polymers of graft with other polymers, other proteins, sugar derivatives, cellulose derivatives, synthetic hydrophilic polymeric materials such as polymers or copolymers can be also used.

The photographic emulsion layer and other hydrophilic colloid layers in the light-sensitive material by use of the silver halide emulsion of the present invention (hereinafter called the light-sensitive material of the present invention) can be hardened by cross-linking the binder (or protective colloid) molecules and by use of one or more kinds of film hardener for enhancing film strength. The film hardener can be added in an amount which can effect film hardening to the extent which requires no addition in the processing solution, but it is also possible to add a film hardener in the processing solution.

In the silver halide emulsion layer and/or other hydrophilic colloid layers in the light-sensitive material of the present invention, a plasticizer can be added for enhancement of flexibility.

In the photographic emulsion layer and other hydrophilic colloid layers in the light-sensitive material of the present invention, a dispersion (latex) of a water insoluble or difficultly soluble synthetic copolymer can be contained.

In the emulsion layer in the light-sensitive material of the present invention, in the color development processing, a dye forming coupler which undergoes coupling reaction with the oxidized product of an aromatic primary amine developing agent (e.g., a p-phenylenediamine derivative, an aminophenol derivative, etc.) to form a dye is used. Said dye forming couplers are ordinarily selected so as to form dyes which absorb sensitive spectral lights of the emulsion layers for the respective emulsion layers, and a yellow dye forming coupler is used in the blue-sensitive emulsion layer, a magenta dye forming coupler in the green-sensitive emulsion layer, and a cyan dye forming coupler in the red-sensitive emulsion layer. However, depending on the purpose, a light-sensitive silver halide color photographic material can be also prepared in a manner different from the above combinations.

These dye forming couplers may be either tetravalent type which requires 4 molecules of silver ions to be reduced for formation of one molecule of dye or divalent type which requires only 2 molecules of silver ions to be reduced. In the color forming coupler, it is possible to incorporate compounds capable of releasing photographically useful frag ment such as development accelerators, bleaching accelerators, developers, silver halide dissolving agents, tone controllers, film hardeners, fogging agents, antifoggants, chemical sensitizers, spectral sensitizers, and sensitivity reducers. Colored couplers having the effect of color correction for these color forming coulers, or DIR couplers which release development inhibitor with development to improve sharpness or graininess of image may be also used in combination. In this case, the DIR coupler should be preferably one which forms a dye of the same type as the dye formed from the color forming coupler used in the same emulsion layer, but different dyes may be also formed when turbidity of the color is not conspicuous. In place of DIR compound capable of undergoing the coupling reaction with the oxidized product of a developing agent to form a colorless compound simultaneous with release of a development inhibitor may be also used.

A colorless coupler which undergoes the coupling reaction with the oxidized product of an atomatic primary amine developing agent but does not form a dye can be also used in combination with the color forming coupler.

The support to be used for the light-sensitive material of the present invention may include flexible reflective supports such as papers, synthetic papers laminated with α-olefin polyer (e.g., polyethylene, polypropylene, ethylene/butene copolyer), etc.; films comprising semi-synthetic or synthetic polymers such as cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate, polyamide, etc.; flexible supports of these films provided with reflective layers; glasses; metals; earthenwares, etc.

The light-sensitive material of the present invention can be exposed by use of an electromagnetic wave in the spectral region to which the emulsion layers constituting the light-sensitive have sensitivities. As the light source, all of the light sources known in the art may be available, including natural light (sunlight), tungsten lamp, fluorescent lamp, mercury lamp, xenon arc lamp, carbon arc lamp, xenon flash lamp, cathode ray tube flying spot, various laser beam, fluorescent diode light, electron beam, X-ray, lights

emitted from phosphors excited by gamma-ray, alpha-ray, etc.

EXAMPLES

The present invention is described in detail below by referring to Examples, by which the present invention is not limited at all.

Example 1

On a resin-coated paper support, the respective layers shown below were successively applied from the support side to prepare a sample.

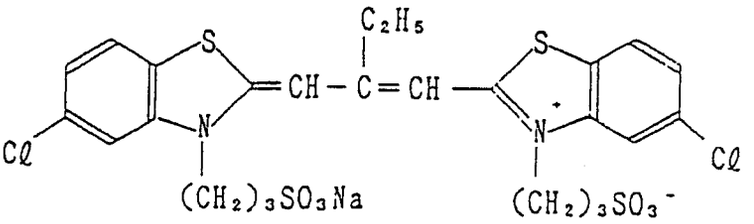
Layer 1 ... Cyan forming red-sensitive silver halide emulsion layer

According to the method shown in Japanese Provisional Patent Publication No. 127548/1980, an internal latent image type silver halide emulsion was prepared. More specifically, 175 ml of a 2.1 mole aqueous solution of potassium chloride containing 10 g of gelatin and 175 ml of a 2 mole aqueous solutoin of silver nitrate were added at the same time over 10 minutes while being controlled at 60 °C. After physical aging for 10 minutes, 200 ml of a 2 mole aqueous solution of potassium bromide was added, followed further by physical aging for 10 minutes. Subsequently, after removal of water-soluble halides by washing with water, 10 g of gelatin was added, and the total amount was made up to 500 ml by addition of water. The silver chloride shell was coated by adding at the same time 100 ml of a 2 mole aqueous silver nitrate and 100 ml of a 2.1 mole aqueous solution of potassium chloride at 60 °C to the conversion type silver chlorobromide emulsion over 5 minutes, and then washed with water to obtain a silver chlorobromide core/shell emulsion containing 61 mole % of silver bromide.

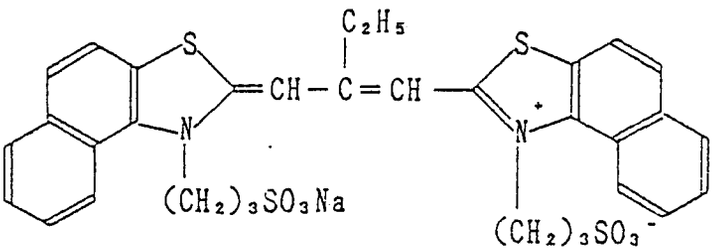
As the cyan coupler, 70 g of 2,4-dichloro-3-methyl-6-[α-(2,4-di-tert-amylphenoxy)butyramido]phenol (Cyan coupler C -1), 2 g of 2,5-di-tert-octylhydroquinone, 50 g of dibutyl phthalate and 140 g of ethyl acetate were mixed and dissolved, and the resultant solution was added into a gelatin solution containing sodium isopropylnaphthalene sulfonate to be dispersed by emulsification.

Subsequently, the dispersion was added to the above emulsion previously spectrally sensitized with the dyes (a) and (b) shown below, 1 g of potassium 2,5-dihydroxy-4-sec-octadecylbenzene sulfonate was added, followed by addition of bis(vinylsulfonylmethyl)ether as the film hardener, and the mixture was applied to a silver quantity f 400 mg/m^2 and a coupler quantity of 460 mg/m^2.

Dye (a):



Dye (b):



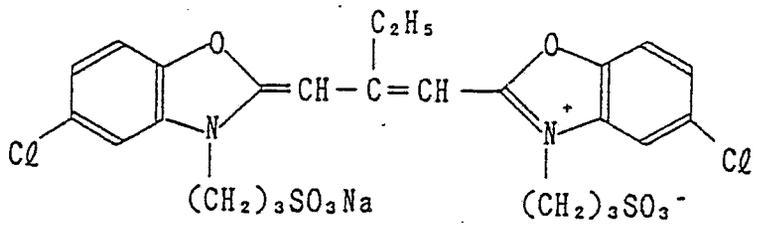
Layer 2 ... Intermediate layer:

A 2.5 % of gelatin solution (100 ml) containing 5 g of gray colloidal silver and 10 g of 2,5-di-tert-octylhydroquinone dispersed in dibutyl phthalate was coated to a colloid silver quantity of 400 mg/ml.

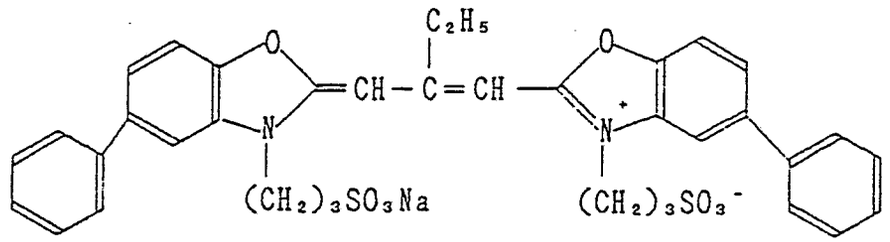
Layer 3 ... Magent forming green-sensitive silver halide emulsion layer:

As the magenta coupler, 40 g of 1-(2,4,6-trichlorophenyl)-3-(2-chloro-5-octadecylsuccinimidoanilino)-5-pyrazolone, 1 g of 2,5-di-tert-octylhydroquinone (Magenta coupler M - 1), 75 g of dioctyl phthalate and 30 g of ethyl acetate were mixed and dissolved, and the resultant solution was added into a gelatin solution containing sodium isopropylnaphthalene sulfonate to be dispersed by emulsification. Subsequently, the dispersion was added to the above emulsion previously spectrally sensitized with the dyes (c) and (d) shown below, 1 g of potassium 2,5-dihydroxy-4-sec-octadecylbenzene sulfonate was added, followed by addition of bis(vinylsulfonylmethyl)ether as the film hardener, and the mixture was coated to a silver quantity of 400 g/m^2 and a coupler quantity of 400 mg/m^2.

Dye (c):



Dye (d):



Layer 4 ... Yellow filter layer:

A 2.5 % gelatin solution containing 5 g of yellow colloid silver and 5 g of 2,5-di-tert-octylhydroquinone dispersed in dibutyl phthalate was coated to a colloid silver quantity of 200 mg/m^2.

Layer 5 ... Yellow forming blue-sensitive silver halide emulsion layer:

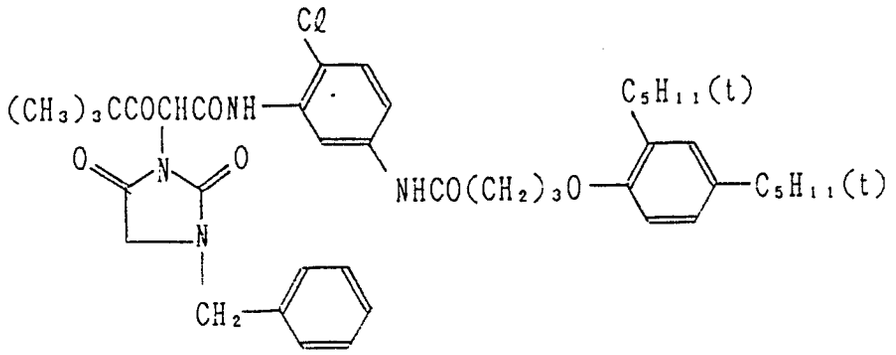
As the yellow coupler, 80 g of α-[4-(1-benzyl-2-phenyl-3,5-dioxo-1,2,4-triazolidinyl)]-α-pyvalyl-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)butylamido]acetanilide (Yellow coupler Y - 1), 1 g of 2,5-di-tert-octylhydroquinone, 80 g of dibutyl phthalate and 200 g of ethyl acetate were mixed and dissolved, and the resultant solution was added into a gelatin solution containing sodium isopropylnaphthalene sulfonate to be dispersed by emulsification. Subsequently, the dispersion was added to the above emulsion, 1 g of potassium 2,5-dihydroxy-4-sec-octadecylbenzene sulfonate was added, followed by addition of bis-(vinylsulfonylmethyl)ether as the film hardener, and the mixture was coated to a silver quantity of 380 mg/m^2 and a coupler quantity of 530 mg/m^2.

Layer 6 ... Protective layer

This layer was coated to a gelatin quantity of 200 mg/m^2.

In the respective layers, saponin was contained as the coating aid to prepare Sample I.

(Y - 1)



Next, according to the method described in Japanese Patent Publication No. 7772/1971, the three kinds of silver chlorobromide emulsions A, B and C shown below were prepared, chemically sensitized respectively with the use of sodium sulfate penta hydrate, and 4-hydroxy-1,3,3a,7-tetrazaindene was added as the stabilizer:

A: containing 80 mole % of silver bromide;

B: containing 70 mole % of silver bromide; and

C: containing 80 mole % of silver bromide.

For B, the above dyes (c) and (d) were further added to give a green-sensitive silver chlorobromide emulsion (B').

For C, the above dyes (c) and (d) were further added to give a red-sensitive silver chlorobromide emulsion (C').

On a paper support laminated on both surfaces with a polyethylene, the respective layers shown below were successively provided by coating.

Layer 1 ... a layer containing 1.2 g/m^2 of gelatin, 0.32 g/m^2 of (calculated on silver, hereinafter the same) of a blue-sensitive silver chlorobromide emulsion (containing 80 mole % of silver bromide) (A) and 0.80 g/m^2 of a yellow coupler (Y -1) dissolved in 0.50 g/m^2 of dioctyl phthalate.

Layer 2 ... an intermediate layer comprising 0.70 g/m^2 of gelatin.

Layer 3 ... a layer containing 1.25 g/m^2 of gelatin, 0.25 g/m^2 of a green-sensitive silver chlorobromide emulsion (containing 70 mole % of silver bromide) (B') and 0.62 g/m^2 of a magenta coupler (M - 1) dissolved in 0.30 g/m^2 of dioctyl phthalate.

Layer 4 ... an intermediate layer comprising 0.20 g/m^2 of gelatin.

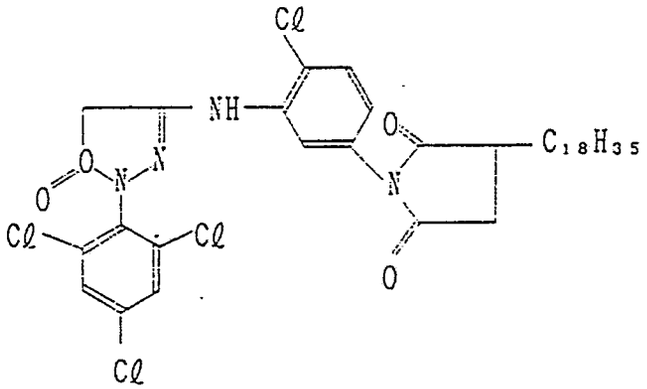
Layer 5 ... a layer containing 1.20 g/m^2 of gelatin, 0.30 g/m^2 of a red-sensitive silver chlorobromide emulsion (containing 80 mole % of silver bromide) (C') and 0.45 g/m^2 of a cyan coupler (C - 1) dissolved in 0.20 g/m^2 of dioctyl phthalate.

Layer 6 ... a layer containing 1.00 g/m^2 of gelatin, and 0.30 g/m^2 of a UV-ray absorber dissolved in 0.20 g/m^2 of dioctyl phthalate.

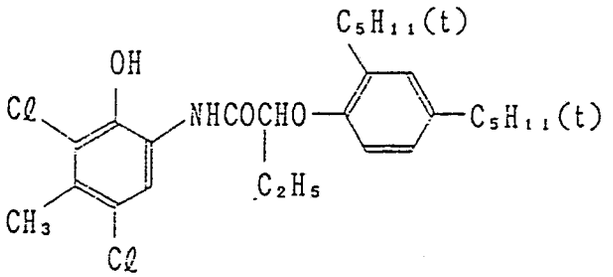
Layer 7 ... a layer containing 0.50 g/m^2 of gelatin.

As the film hardener, 2,4-dichloro-6-hydroxy-s-triazine sodium was added in the layers 2, 4 and 7 each in an amount of 0.017 g per 1 g of gelatin.

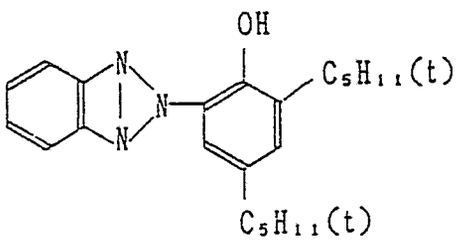
(M - 1)



(C - 1)



(UV - 1)



As described above, Sample II of color paper (negative-type light-sensitive silver halide color photographic material) was prepared.

The above Sample I and Sample II were cut into widths of 82 mm, and the Sample I was given uniform image exposure by an automatic color paper printer with the use of a positive obtained by camera photographing of a color reversal film with ASA100, followed by color development, while the Sample II was given uniform image exposure by an automatic color printer with the use of a negative obtained by camera photographing of a color negative film with ASA100, and each sample was tested by use of an automatic developing machine shown in Fig. 1.

Fig. 1 is a schematic illustration showing one example of sutomatic developing machine which can be used for processing of the present invention, and as shown in the Figure, the main automatic developing machine 1 is constituted of a paper feeding section2, a photographic processing section 3 and a drying section 4.

The light-sensitive silver halide photographic material 5 which is a sample according to the present example is formed in a roll and housed in a dark box 6. The light-sensitive silver halide photographic material 5 withdrawn from the dark box 6 was subjected to development processing at the photographic processing section 3 while being conveyed by a series of rollers rotating in pressure contact therewith.

In the present example, the photographic processing section 3 is constituted of four processing tanks, namely a development processing tank 7, a bleach-fixing processing tank 8 and stabilizing tanks 9 and 9'. The stabilizing tanks 9 and 9' are two-tank countercurrent system. On the other hand, the exposure device 11 is detected by the sensor 13 when an internal latent image type direct positive sensitive material is used as the light-sensitive silver halide photographic material, and fog exposure can be given during develop-

ment processing by lighting on the fluorescent lamp 12, but no fog exposure is given when a negative-type sensitive material is used.

The exposed light-sensitive silver halide photographic material 5 is subjected to processing in the respective processing tanks for predetermined periods of time in the photographic processing section 3, then delivered to the drying section 4 to be dried therein and thereafter cut by a cutting member 14 into predetermined lengths before discharged out of the device.

In the Figure, 15 is a waste-solution storage section and 16 is a supplemental solution storage section.

The processing conditions are as follows:

Processing conditions

Processing step	Processing temperature	Processing time
1. Color development (note 1)	38 °C	2 minutes
2. Bleach-fixing	35 °C	50 seconds
3. Stabilizing	32 °C	1 minute

(note 1) Whole surface exposure was set so that irradiation was effected for 10 seconds after the sample was introduced into the color developing solution.

As the processing solutions, the processing solutions having the compositions shown below were used.

(Color developing solution)

Benzyl alcohol	16 ml
Ethylene glycol	16 ml
Hydroxylamine derivative indicated in Table 1	5 g
3-Methyl-4-amino-N-ethyl-N-(ß-methanesulfonamidoethyl)aniline sulfate	5.7 g
3-Methyl-4-amino-N-ethyl-N-hydroxyethylaniline sulfate	2 g
Potassium carbonate	25 g
Potassium sulfite (50 % solution)	6 ml
Potassium bromide	1.0 g
Polyphosphoric acid (TPPS)	3.0 g
Water	added to 1 liter (pH 10.2)

(Supplemental color developing solution)

Benzyl alcohol	20 ml
Ethylene glycol	20 ml
Hydroxylamine derivative indicated in Table 1	5 g
3-Methyl-4-amino-N-ethyl-N-(ß-methanesulfonamidoethyl)aniline sulfate (CD - 3)	6.8 g
3-Methyl-4-amino-N-ethyl-N-hydroxyethylaniline sulfate (CD - 4)	2.4 g
Potassium carbonate	25 g
Potassium sulfite (50 % solution)	7.5 ml
Polyphosphoric acid (TPPS)	4.0 g

(made up to one liter with water and adjusted to pH 10.60 with potassium hydroxide or sulfuric acid)

(Bleach-fixing solution)

Iron (III) ammonium ethylenediamine-tetraacetate	70 g
Ammonium sulfite	5.0 g
Ammonium thiosulfate	150 g
Aqueous ammonia (28 %)	10 ml

(made up to one liter with water and adjusted to pH 7.5 with acetic acid or aqueous ammonia)

(Supplemental bleach-fixing solution)

Iron (III) ammonium ethylenediamine-tetraacetate	80 g
Ammonium sulfite	10 g
Ammonium thiosulfate	180 g
Aqueous ammonia (28 %)	10 ml

(made up to one liter with water and adjusted to pH 7.0 with acetic acid or aqueous ammonia)

(Stabilizing solution and supplemental stabilizing solution) 2-Methyl-4-isothiazolin-3-one 0.01 g
1-Hydroxyethylidene-1,1-diphosphonic acid 1.5 g
(made up to one liter with water and adjusted to pH 7.0 with potassium hydroxide)

The supplemental color developing solution is supplemented in an amount of 3.2 ml per 100 cm^2 of the light-sensitive material, and the supplemental bleach-fixing solution in an amount of 3.2 ml per 100 cm^2 of the light-sensitive material. Also, the supplemental stabilizing solution is supplemented in an amount of 3.2 ml per 100 cm^2 of the light-sensitive material. The stabilizing solution is made the two-tank countercurrent system and supplemented to the final tank. In the processing line 1, Sample I is continuously processed until the total amount of the supplemental color developing solution becomes two-fold amount of the color developing tank (hereinafter referred to as 2-round), while in the processing line 2, Sample II is subjected to 2-round continuous processing, and in the processing line 3, 2-round continous processing was performed while processing alternatively 3 m^2 of Sample I and 3 m^2 of Sample II.

For observation of photographic characteristics, Sample I and Sample II subjected to wedge exposure were processed at the processing initiation time and completion of 2-round of the respective lines.

The maximum density and the minimum density of yellow (Y) of the samples obtained by processing are shown in Table 1.

Table 1

Experimental No.	Processing line	Hydroxylamine derivatives (5 g/l)	Sample I (yellow density)				Sample II (yellow density)			
			Processing initiation time		2-round		Processing initiation time		2-round	
			Maximum density	Minimum density	Maximum density	Minimum density	Maximum density	Minimum density	Maximum density	Minimum density
1 (Comparative)	1	—	2.13	0.13	2.10	0.13	2.45	0.08	2.43	0.08
2 (Comparative)	2	—	2.10	0.12	2.08	0.13	2.44	0.07	2.42	0.07
3 (Comparative)	3	—	2.12	0.12	1.90	0.16	2.45	0.08	2.44	0.07
4 (This invention)	3	(1)	2.11	0.12	2.09	0.13	2.46	0.07	2.45	0.08
5 (This invention)	3	(2)	2.10	0.12	2.10	0.12	2.47	0.06	2.44	0.07
6 (This invention)	3	(6)	2.11	0.13	2.09	0.13	2.46	0.07	2.44	0.07
7 (This invention)	3	(13)	2.12	0.12	2.11	0.13	2.46	0.06	2.43	0.06
8 (This invention)	3	(16)	2.13	0.12	2.07	0.12	2.48	0.07	2.44	0.07
9 (This invention)	3	(17)	2.12	0.13	2.11	0.12	2.45	0.06	2.42	0.06
10 (This invention)	3	(18)	2.11	0.12	2.06	0.13	2.46	0.06	2.44	0.07
11 (This invention)	3	(20)	2.13	0.12	2.12	0.13	2.45	0.08	2.43	0.07
12 (This invention)	3	(23)	2.14	0.12	2.09	0.12	2.47	0.07	2.46	0.08

As is apparent from Table 1, in Sample II, there is substantially no abnormality such as lowering in the maximum dye density of yellow accompanied with continuous processing or increase of yellow stain in all of the processing lines, but abnormality particularly in the processing lines 3 is great in Sample I. However, it can be understood that lowering in the maximum dye density of yellow and increase of yellow stain can be prevented by addition of the compound of the present invention.

Example 2

Into the second layer in Sample I of Example 1 was added 10 mg/m^2 of the exemplary AI dye (II - 9), into the third layer 10 mg/m^2 of (II - 8), and similarly into the second layer of Sample II 10 mg/m^2 of (II - 8) and into the fifth layer 10 mg/m^2 of (II - 9), and the same evaluation as in Example 1 was conducted for tests No. 1, 2, 3, 4, 6, 7, 9 and 11.

However, here, in place of yellow dye density, the maximum densities of magenta and cyan dyes were measured. The results are shown in Table 2.

Table 2

Experimental No.	Processing line	Hydroxylamine derivatives (5 g/l)	Sample I (magenta, cyan density)				Sample II (magenta, cyan density)			
			Processing initiation time		2-round		Processing initiation time		2-round	
			Magenta density	Cyan density	Magenta density	Cyan density	Magenta density	Cyan density	Magenta density	Cyan density
13 (Comparative)	1	—	2.25	2.26	2.16	2.21	2.33	2.22	2.31	2.21
14 (Comparative)	2	—	2.21	2.24	2.18	2.23	2.34	2.21	2.32	2.20
15 (Comparative)	3	—	2.23	2.27	2.03	2.01	2.33	2.23	2.31	2.23
16 (This invention)	3	(1)	2.21	2.25	2.18	2.24	2.32	2.21	2.32	2.22
17 (This invention)	3	(6)	2.24	2.26	2.20	2.23	2.35	2.22	2.31	2.21
18 (This invention)	3	(13)	2.23	2.24	2.21	2.21	2.33	2.24	2.31	2.24
19 (This invention)	3	(17)	2.22	2.25	2.20	2.24	2.34	2.21	2.30	2.23
20 (This invention)	3	(20)	2.23	2.23	2.19	2.20	2.35	2.22	2.32	2.21

As is apparent from Table 2, as compared with Sample II, the maximum densities of magenta and cyan dyes are remarkable lowered particularly in the processing line 3, but it can be understood that addition of the compound of the present invention brings about improvements to great extent.

In this example, when (II - 16), (II - 17), (II - 22) and (II - 23) were used in place of the exemplary compound (II - 8) of Al dye, and (II - 10), (II - 12), (II - 13) and (II - 19) in place of the exemplary compound (II - 9), substantially the same results were obtained.

Example 3

By using Samples I and III employed in Example 1, the same processing treatments were repeated as in Example 1 and the same evaluation as in Example 1 was conducted.

However, here, in place of hydroxylamine sulfate in the color developing solution and the supplemental color developing solution, hydroxylamines as shown in Table 3 were employed in amounts shown in Table 3.

The supplemental color developing solution is supplemented in an amount of 2.0 ml per 100 cm^2 of the light-sensitive material. Also, the color development is carried out at a processing temperature of 40 °C since the development level is inactive at 2-round.

Also, additives in the color developing solution and the supplemental color developing solution, and amounts thereof are shown in Table 3.

Table 3

Experimental No.	Processing line	Hydroxylamines	Additives	Sample I (maximum density) Yellow density	
				Processing initiation time	2-round
21	3	13 (5g/l)	—	2.11	1.97
22	3	13 (5g/l)	Triethanolamine (10g/l)	2.13	2.09
23	3	13 (5g/l)	PAI - 1 (1 g/l)	2.12	2.09
24	3	17 (5g/l)	—	2.11	1.95
25	3	17 (5g/l)	Triethanolamine (10g/l)	2.11	2.07
26	3	17 (5g/l)	PAI - 1 (1 g/l)	2.12	2.10
27	3	20 (5g/l)	—	2.12	1.94
28	3	20 (5g/l)	Triethanolamine (10g/l)	2.13	2.10
29	3	20 (5g/l)	PAI - 1 (1 g/l)	2.14	2.12

Table 3 (Contd)

Experimental No.	Processing line	Hydroxylamines	Additives	Sample I (maximum density) Yellow density: Processing initiation time	Sample I (maximum density) Yellow density: 2-round
30	3	1 (5g/l)	—	2.14	1.95
31	3	1 (5g/l)	Triethanol-amine (10g/l)	2.13	2.11
32	3	1 (5g/l)	PAI - 1 (1 g/l)	2.13	2.10
33	3	13 (6g/l) 1 (2g/l)	—	2.14	1.98
34	3	13 (6g/l) 1 (2g/l)	Triethanol-amine (10g/l)	2.13	2.09
35	3	13 (6g/l) 1 (2g/l)	PAI - 1 (1 g/l)	2.13	2.10
36	3	Hydroxyl-amine sul-fate(3g/l)		2.13	1.95
37	3	Hydroxyl-amine sul-fate(3g/l)	Triethanol-amine (10 g/l)	2.13	2.10
38	3	Hydroxyl-amine sul-fate(3g/l)	PAI - 1 (1 g/l)	2.14	2.11

As is apparent from Table 3, by using various hydroxylamine derivatives in place of hydroxylaime sulfate, while lowering of the maximum dye density of yellow in Sample I becomes large, it can be understood that addition of the additives of a poly(alkylamine) or an alkanolamine effectively prevents the lowering of the maximum dye density of yellow.

Example 4

Sample IV was prepared in the same manner as in Sample I in Example 1 except that, in Layer 1, 10 mg/m^2 of the exemplary compound (II - 9) of Al dye was added in addition to 1 g of potassium 2,5-dihydroxy-4-sec-octadecylbenzene sulfonate and, in Layer 3, 15 mg/m^2 of the exemplary compound (II - 8) of Al dye was added in addition to 1 g of potassium 2,5-dihydroxy-4-sec-octadecylbenzene sulfonate in addition to 1 g of potassium 2,5-dihydroxy-4-sec-octadecylbenzene sulfonate.

Further, into the second layer in Sample II of Example 1 was added 15 mg/m^2 of the exemplary

compound (II - 8) of AI dye, and into the fourth layer in Sample II of Example 1 was added 10 mg/m^2 of the exemplary compound (II - 9) of AI dye, to prepare Sample V, and the same evaluation as in Example 1 was conducted with the processing conditions as in Example 1 except for using hydroxylamine sulfate in the color developing solution and the supplemental color developing solution with an amount shown in Table 5.

In the processing line 1, Sample IV is continuously processed until the total amount of the supplemental color developing solution becomes two-fold amount of the color developing tank during 10 days (hereinafter referred to as 2-round), while in the processing line 2, Sample V is subjected to 2-round continuous processing during 10 days, and in the processing line 3, 2-round continuous processing was performed during 10 days while processing alternatively 3 m^2 of Sample IV and 3 m^2 of Sample V.

For observation of photographic characteristics, Sample IV and Sample V subjected to wedge exposure were processed at the processing initiation time and completion of 2-round of the respective lines.

The maximum density and the minimum densities of magenta (M) and cyan (C) of the samples obtained by processing are shown in Table 4.

Table 4

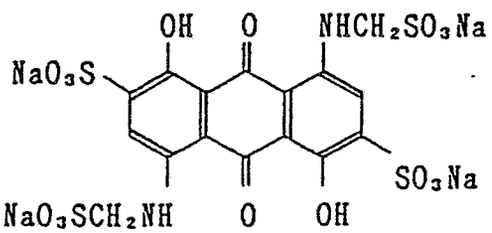
Experimental No.	Processing line	Hydroxylamine sulfate (g/l color devel. soln.)	Sample IV				Sample V			
			Processing initiation time		2-round		Processing initiation time		2-round	
			Magenta density	Cyan density	Magenta density	Cyan density	Magenta density	Cyan density	Magenta density	Cyan density
39 (Comparative)	1	—	2.24	2.25	2.15	2.18	2.32	2.20	2.31	2.19
40 (Comparative)	2	—	2.23	2.26	2.17	2.18	2.33	2.22	2.33	2.21
41 (Comparative)	3	—	2.23	2.25	2.02	2.05	2.33	2.21	2.31	2.20
42 (Comparative)	3	0.01	2.22	2.24	2.06	2.09	2.32	2.21	2.31	2.21
43 (Comparative)	3	0.03	2.22	2.23	2.11	2.14	2.32	2.21	2.30	2.20
44 (This invention)	3	0.05	2.21	2.23	2.18	2.20	2.32	2.21	2.31	2.20
45 (This invention)	3	0.1	2.21	2.22	2.19	2.21	2.31	2.21	2.30	2.19
46 (This invention)	3	1.0	2.19	2.19	2.18	2.19	2.30	2.20	2.29	2.19
47 (This invention)	3	5.0	2.17	2.19	2.17	2.19	2.29	2.19	2.29	2.18
48 (This invention)	3	10.0	2.15	2.18	2.15	2.18	2.28	2.18	2.27	2.17

As is apparent from Table 4, in Sample IV, there is substanially no lowering in magenta and cyan maximum dye densities accompanied with continuous processing in all of the processing lines, but in Sample IV, lowering in density particularly in the processing line 3 is great. However, it can be understood that lowering in the maximum dye densities of magenta and cyan can be effectively prevented by addition of 0.05 g of hydroxylamine sulfate per liter of the color developing solution.

Example 5

The same evaluation as in Example 1 was conducted except for using AI dyes as shown in Table 5 in place of AI dyes (II -8) and (II - 9) used in Example 4.

Comparative AI - 1



Comparative AI - 2

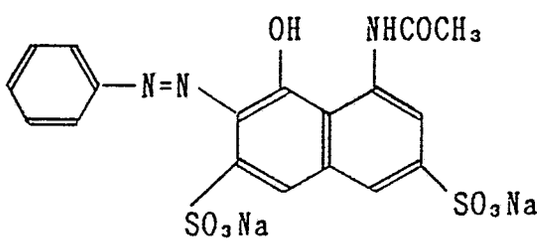


Table 5

Experimental No.	Processing line	Hydroxylamine sulfate (g/l color devel. soln.)	AI dye		Sample IV			
			II - 8 substitute	II - 9 substitute	Processing initiation time		2-round	
					Magenta density	Cyan density	Magenta density	Cyan density
49 (comparative)	3	3.0	Comparative AI - 2	Comparative AI - 1	2.18	2.19	2.04	2.06
50 (This invention)	3	3.0	II - 16	II - 10	2.18	2.20	2.17	2.18
51 (This invention)	3	3.0	II - 17	II - 12	2.20	2.22	2.19	2.20
52 (This invention)	3	3.0	II - 22	II - 13	2.19	2.20	2.17	2.19
53 (This invention)	3	3.0	II - 23	II - 19	2.18	2.21	2.17	2.19
54 (This invention)	3	3.0	I - 1	II - 19	2.20	2.21	2.20	2.20

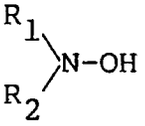
Table 5 (Contd)

Experimental No.	Processing line	Hydroxylamine sulfate (g/l color devel. soln.)	AI dye		Sample V			
			II - 8 substitute	II - 9 substitute	Processing initiation time		2-round	
					Magenta density	Cyan density	Magenta density	Cyan density
55 (comparative)	3	3.0	Comparative AI - 2	Comparative AI - 1	2.30	2.20	2.29	2.18
56 (This invention)	3	3.0	II - 16	II - 10	2.31	2.19	2.31	2.17
57 (This invention)	3	3.0	II - 17	II - 12	2.31	2.20	2.30	2.19
58 (This invention)	3	3.0	II - 22	II - 13	2.30	2.20	2.30	2.19
59 (This invention)	3	3.0	II - 23	II - 19	2.32	2.21	2.30	2.20
60 (This invention)	3	3.0	I - 1	II - 19	2.32	2.19	2.31	2.19

As is apparent from Table 5, in Sample IV, there can be seen lowering in maximum dye density in Comparative AI dye, but in the AI dye of the present invention, lowering in density can hardly be seen. Also, in Sample V, it can be understood that lowering in the maximum dye density accompanied with continuous processing can hardly be admitted.

Claims

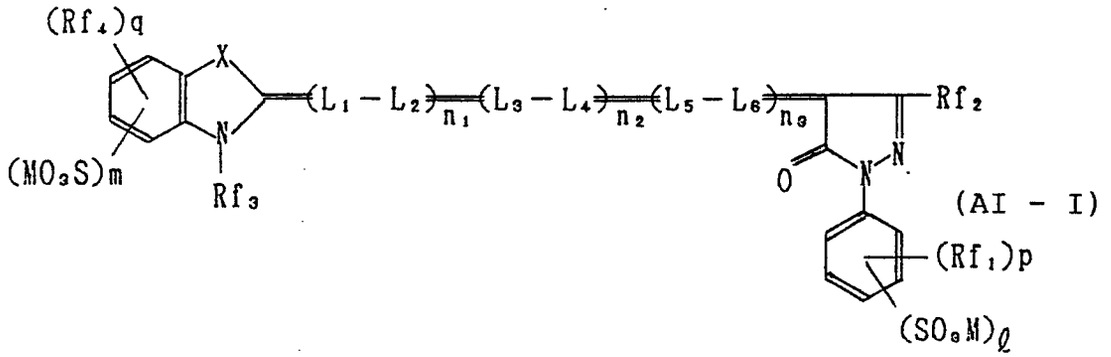
A method for common development processing of two kinds of light-sensitive silver halide photographic material which comprises the step of development processing an internal latent type direct positive light-sensitive silver halide photographic material and a negative-type light-sensitive silver halide photographic material in the same development processing bath, and the step of applying whole surface exposure on said internal latent type direct positive light-sensitive silver halide photogrpahic material during development processing of said internal latent type direct positive light-sensitive silver halide photographic material, characterized in that said developing processing solution contains a compound represented by the formula (A) shown below:



(A)

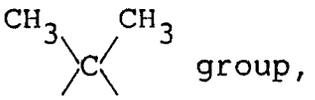
wherein R_1 and R_2 each represent hydrogen atom or an alkyl group having 1 to 5 carbon atoms which may have a substituent or may be combined with each other to form a heterocyclic ring.

2. The method according to Claim 1, wherein said internal latent type direct positive light-sensitive silver halide photographic material and said negative-type light-sensitive silver halide photographic material contains at least one of AI dye selected from the group consisting of the compounds represented by the formulae (AI - I), (AI - I'), (AI - II), (AI - III) and (AI - IV) shown below:

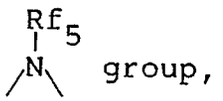


(AI - I)

wherein X represents a chalcogen atom,

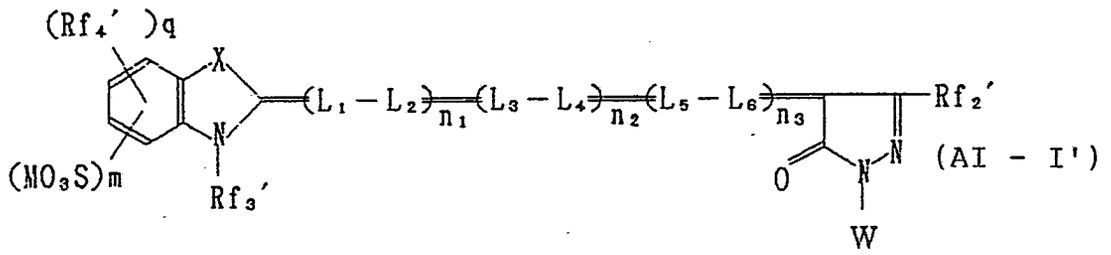


group,



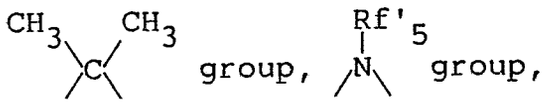
group,

L_1, L_2, L_3, L_4, L_5 and L_5 each represent a methine group; Rf_5 represents an alkyl group or an aryl group; Rf_1 represents a substitutable group; Rf_2 represents an aryl group, a heterocyclic group, an amino group, an acylamino group, an imide group, a ureido group, a carboxyl group, an alkoxycarbonyl group, a carbamoyl group, an alkoxy group, an aryloxy group, a hydroxy group, an alkyl group or a cyano group; Rf_3 represents an alkyl group; Rf_4 represents a substitutable group; M represents a hydrogen atom or a cation; l represents 0,1 or 2; m represents 0, 1 or 2; n_1, n_2 and n_3 each represent 0 or 1; p represents an integer of 0 to 5; and q represents an integer of 0 to 4; provided that $l + m \neq 0$,

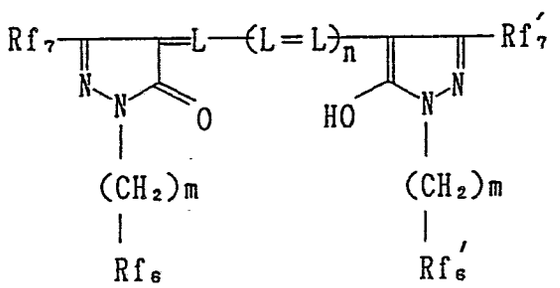


(AI - I')

wherein W represents a hydrogen atom, an alkyl group or a heterocyclic group; Rf_2' represents an alkyl group, an aryl group, a heretocyclic group, an amino group, an acylamino group, an imide group, a ureido group, a carboxy group, an alkoxycarbonyl group, a carbamoyl group, an aryloxy group, an alkoxy group, a hydroxy group or a cyano group; Rf_3' represents an alkyl group; Rf_4' represents a substitutable group; X represents a chalcogen atom,

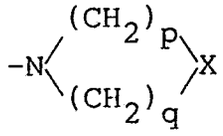


L_1, L_2, L_3, L_4, L_5 and L_5 each represent a methine group; Rf_5' represents an alkyl group or an aryl group; M represents a hydrogen atom or a cation; m represents 0, 1 or 2; n_1, n_2 and n_3 each represent 0 or 1; and q represents an integer of 0 to 4,

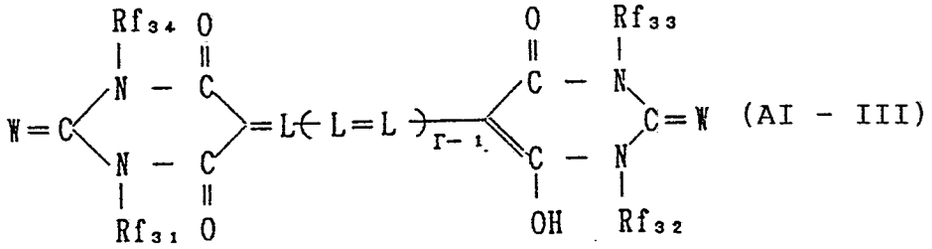


(AI - II)

wherein Rf_6 and Rf_6' each represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; Rf_7 and Rf_7' each represent a hydroxy group, an alkoxy group, a substituted alkoxy group, a cyano group, a trifluormethyl group, $-COORf_8$, $-CONHRf_8$, $-NHCORf_8$, an amino group, a substituted amino group, substituted with a alkyl group having 1 to 4 carbon atoms or a cyclic amino group represented by:

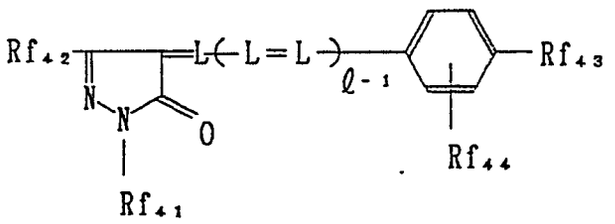


(where p and q each represent 1 or 2, and X represents an oxygen atom, a sulfur atom or $-CH_2$-group); Rf_8 represents a hydrogen atom, an alkyl group or an aryl group; L represents a methine group; n represents 0, 1, 2; and m represents 0 or 1,



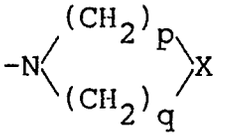
(AI - III)

wherein r represents an integer of 1 to 3; W represents an oxygen atom or a sulfur atom; L represents a methine group; Rf_{31} to Rf_{34} each represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a heterocyclic group, of which at least one is a substituent other than the hydrogen atom,

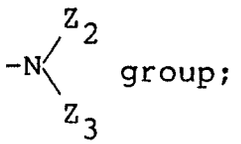


(AI - IV)

wherein l represents an integer of 1 or 2; L represents a methine group; Rf_{41} represents an alkyl group, an aryl group or a heterocyclic group; Rf_{42} represents a hydroxy group, an alkyl group, an alcoxy group, a substituted alkoxy group, a cyano group, a trifluormethyl group, -COORf$_8$, -CONHRf$_8$, -NHCORf$_8$, an amino group, a substitituted amino group substituted with an alkyl group having 1 to 4 carbon atoms, or a cyclic amino group represented by:



(where p and q each represent 1 or 2, and X represents an oxygen atom, a sulfur atom or -CH_2-group); Rf$_8$ represents a hydrogen atom, an alkyl group or an aryl group; Rf_{43} represents -OZ_1 group or a group:



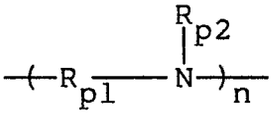
Z_1, Z_2 and Z_3 each represent a hydrogen atom or an alkyl group, Z_2 and Z_3 may be either the same or different, or can be bonded together to form a ring; Rf_{44} represents a hydrogen atom, an alkyl group, a chlorine atom or an alkoxy group.

3. The method according to Claim 1, wherein said compound represented by the formula (A) is a hydroxylamine.

4. The method according to Claim 3, wherein said hydroxylamine is containined in said developing solution in an amount of 0.05 g/liter or more.

5. The method according to Claim 3, wherein said developing solution contains at least one of a poly-(alkyleneimine) and an alakanolamine.

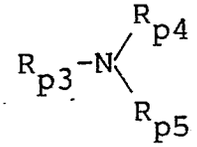
6. The method according to Claim 5, wherein said poly(alkyleneimine) is a compound represented by the formula:



(P - I)

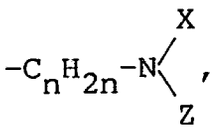
wherein R_{p1} represents an alkylene group having 1 to 6 carbon atoms; R_{p2} represents an alkyl group; and n is an integer of 500 to 20,000.

7. The method according to Claim 5, wherein said polyalkanolamine is a compound represented by the formula:



(P - II)

wherein R_{p3} represents a hydroxyalkyl group having 2 to 6 carbon atoms, R_{p4} and R_{p5} each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, a benzyl group or a formula:



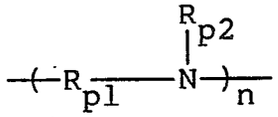
n in the above formula being an integer of 1 to 6, X and Z each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms or a hydroxyalkyl group having 2 to 6 carbon atoms.

8. The method according to Claim 2, wherein said compound represented by the formula (A) is a hydroxylamine.

9. The method according to Claim 8, wherein said hydroxylamine is containined in said developing solution in an amount of 0.05 g/liter.

10. The method according to Claim 8, wherein said developing solution contains at least one of a poly-(alkyleneimine) and an alakanolamine.

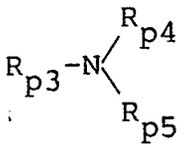
11. The method according to Claim 10, wherein said poly(alkyleneimine) is a compound represented by the formula:



(P - I)

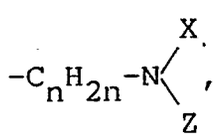
wherein R_{p1} represents an alkylene group having 1 to 6 carbon atoms; R_{p2} represents an alkyl group; and n is an integer of 500 to 20,000.

12. The method according to Claim 10, wherein said polyalkanolamine is a compound represented by the formula:



(P - II)

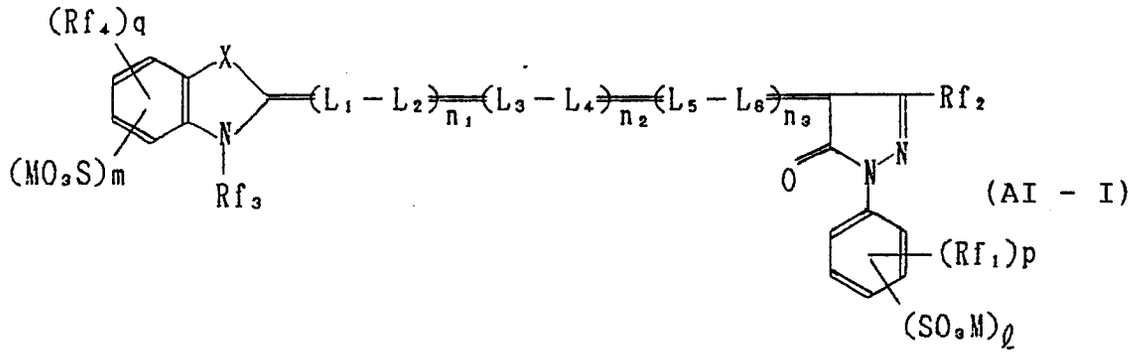
wherein R_{p3} represents a hydroxyalkyl group having 2 to 6 carbon atoms, R_{p4} and R_{p5} each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, a benzyl group or a formula:



n in the above formula being an integer of 1 to 6, X and Z each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms or a hydroxyalkyl group having 2 to 6 carbon atoms.

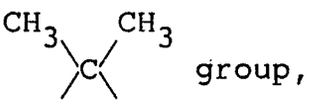
13. A method for common development processing of two kinds of light-sensitive silver halide photographic material which comprises the step of development processing an internal latent type direct positive light-sensitive silver halide photographic material and a negative-type light-sensitive silver halide photographic material in the same development processing bath, and the step of applying whole surface

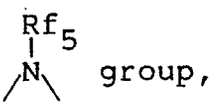
exposure on said internal latent type direct positive light-sensitive silver halide photogrpahic material during development processing of said internal latent type direct positive light-sensitive silver halide photographic material; said internal latent type direct positive light-sensitive silver halide photographic material and said negative-type light-sensitive silver halide photographic material contains at least one of AI dye selected from the group consisting of the compounds represented by the formulae (AI - I), (AI - I'), (AI - II), (AI - III) and (AI - IV) shown below:



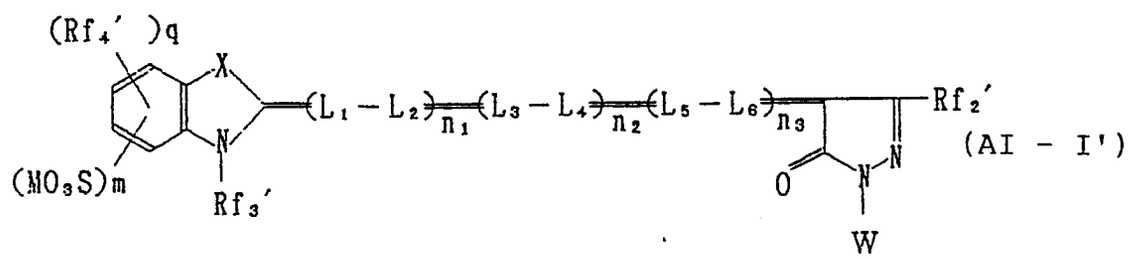
(AI - I)

wherein X represents a chalcogen atom,



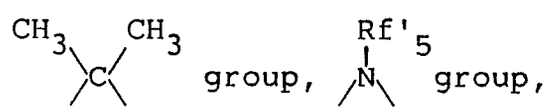


L_1, L_2, L_3, L_4, L_5 and L_5 each represent a methine group; Rf_5 represents an alkyl group or an aryl group; Rf_1 represents a substitutable group; Rf_2 represents an aryl group, a heterocyclic group, an amino group, an acylamino group, an imide group, a ureido group, a carboxyl group, an alkoxycarbonyl group, a carbamoyl group, an alkoxy group, an aryloxy group, a hydroxy group, an alkyl group or a cyano group, Rf_3 represents an alkyl group or a cyano group; Rf_3 represents an alkyl group; Rf_4 represents a substitutable group; M represents a hydrogen atom or a cation; l represents 0.1 or 2; m represents 0, 1 or 2; n_1, n_2 and n_3 each represent 0 or 1; p represents an integer of 0 to 5; and q represents an integer of 0 to 4; provided that $l + m \neq 0$,

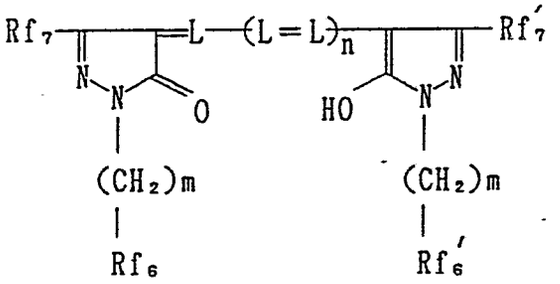


(AI - I')

wherein W represents a hydrogen atom, an alkyl group or a heterocyclic group; Rf_2' represents an alkyl group, an aryl group, a heterocyclic group, an amino group, an acylamino group, an imide group, a ureido group, a carboxy group, an alkoxycarbonyl group, a carbamoyl group, an aryloxy group, an alkoxy group, a hydroxy group or a cyano group; Rf_3' represents an alkyl group; Rf_4' represents a substitutable group; X represents a chalcogen atom,

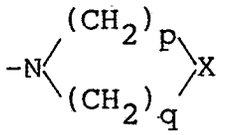


L_1, L_2, L_3, L_4, L_5 and L_5 each represent a methine group; Rf_5' represents an alkyl group or an aryl group; M represents a hydrogen atom or a cation; m represents 0, 1 or 2; n_1, n_2 and n_3 each represent 0 or 1; and q represents an integer of 0 to 4,

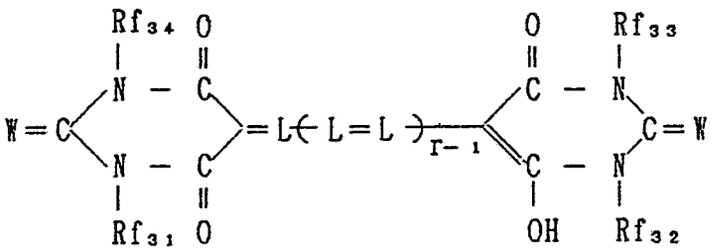


(AI - II)

wherein Rf_6 and Rf_6' each represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; Rf_7 and Rf_7' each represent a hydroxy group, an alkoxy group, a substituted alkoxy group, a cyano group, a trifluoromethyl group, $-COORf_8$, $-CONHRf_8$, $-NHCORf_8$, an amino group, a substituted amino group, substituted with a alkyl group having 1 to 4 carbon atoms or a cyclic amino group represented by:

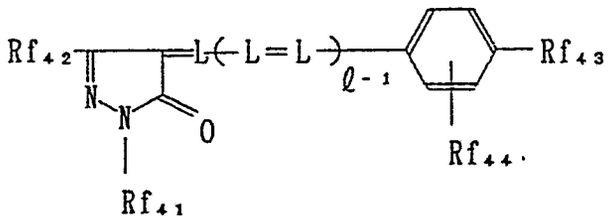


(where p and q each represent 1 or 2, and X represents an oxygen atom, a sulfur atom or $-CH_2$-group); Rf_8 represents a hydrogen atom; an alkyl group or an aryl group; L represents a methine group; n represents 0, 1, 2; and m represents 0 or 1,



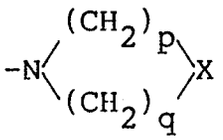
(AI - III)

wherein r represents an integer of 1 to 3; W represents an oxygen atom or a sulfur atom; L represents a methine group; Rf_{31} to Rf_{34} each represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a heterocylic group, of which at least one is a substituent other than the hydrogen atom,

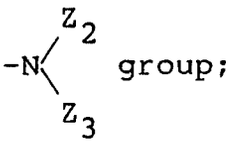


(AI - IV)

wherein l represents an integer of 1 or 2; L represents a methine group; Rf_{41} represents an alkyl group, an aryl group or a heterocyclic group; Rf_{42} represents a hydroxy group, an alkyl group, an alkoxy group, a substituted alkoxy group, a cyano group, a trifluoromethyl group, $-COORf_8$, $-CONHRf_8$, $-NHCORf_8$, an amino group, a substituted amino group substituted with an alkyl group having 1 to 4 carbon atoms, or a cyclic amino group represented by:



(where p and q each represent 1 or 2, and X represents an oxygen atom, a sulfur atom or -CH_2-group); Rf_8 represents a hydrogen atom, an alkyl group or an aryl group; Rf_{43} represents -OZ_1 group or a group:

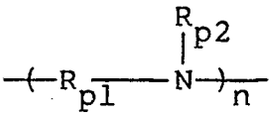


Z_1, Z_2 and Z_3 each represent a hydrogen atom or an alkyl group, Z_2 and Z_3 may be either the same or different, or can be bonded together to form a ring; Rf_{44} represents a hydrogen atom, an alkyl group, a chlorine atom or an alkoxy group; and said developing solution contains 0.05 g/liter of more of hydroxylamine.

14. The method according to Claim 13, wherein said hydroxylamine is contained said developing solution in an amount of 0.07 g/liter to 4 g/liter.

15. The method according to Claim 13, wherein said developing solution contains at least one of a poly(alkyleneimine) and an alkanolamine.

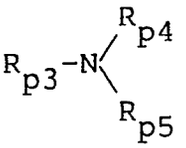
16. The method according to Claim 15, wherein said poly(alkyleneimine) is a compound represented by the formula:



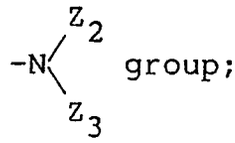
(P - I)

wherein R_{p1} represents an alkylene group having 1 to 6 carbon atoms; R_{p2} represents an alkyl group; and n is an integer of 500 to 20,000.

17. The method according to Claim 15, wherein said polyalkanolamine is a compound represented by the formula:



(P - II)



Z_1, Z_2 and Z_3 each represent a hydrogen atom or an alkyl group, Z_2 and Z_3 may be either the same or different, or can be bonded together to form a ring; Rf_{44} represents a hydrogen atom, an alkyl group, a chlorine atom or an alkoxy group.

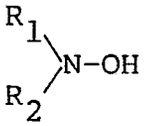
18. The method according to Claim 13, wherein said developing solution further contains a sulfite or a sulfite ion releasing compound.

19. The method according to Claim 18, wherein said sulfite of said sulfite ion releasing compound is selected from the group consisting of potassium sulfite, sodium sulfite, ammonium sulfite, sodium metabisulfite, potassium metabisulfite, sulfurous acid adduct of formaldehyde, sulfurous acid adduct of acetaldehyde and sulfurous acid adduct of glutaraldehyde.

20. The method according to Claim 19, wherein said sulfite of said sulfite ion releasing compound is contained in the range from 1.0×10^{-4} to 1.0×10^{-1} mole/liter of the color developing solution.

21. The method according to Claim 13, wherein said AI dye is the compound represented by the formula of (AI - 1) and (AI -2).

22. A method for common development processing of two kinds of light-sensitive silver halide photographic material which comprises the step of development processing an internal latent type direct positive light-sensitive silver halide photographic material and a negative-type light-sensitive silver halide photographic material in the same development processing bath, and the step of applying whole surface exposure on said internal latent type direct positive light-sensitive silver halide photogrpahic material during development processing of said internal latent type direct positive light-sensitive silver halide photographic material, characterized in that said developing processing solution contains a compound represented by the formula (A) shown below:



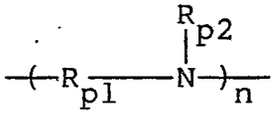
(A)

wherein R_1 and R_2 each represent hydrogen atom or an alkyl group having 1 to 5 carbon atoms which may have a substituent, provided that R_1 and R_2 cannot be hydrogen atoms at the same time.

23. The method according to Claim 22, wherein said compound is contained in an amount of 0.1 to 50 g/liter of the developing solution.

24. The method according to Claim 22, wherein said developing solution contains at least one of a poly-(alkyleneimine) and an alakanolamine.

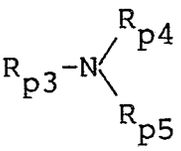
25. The method according to Claim 24, wherein said poly(alkyleneimine) is a compound represented by the formula:



(P - I)

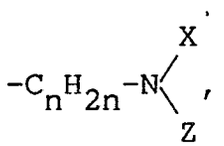
wherein R_{p1} represents an alkylene group having 1 to 6 carbon atoms; R_{p2} represents an alkyl group; and n is an integer of 500 to 20,000.

26. The method according to Claim 24, wherein said polyalkanolamine is a compound represented by the formula:



(P - II)

wherein R_{p3} represents a hydroxyalkyl group having 2 to 6 carbon atoms, R_{p4} and R_{p5} each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, a benzyl group or a formula:



n in the above formula being an integer of 1 to 6, X and Z each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms.

27. The method according to Claim 22, wherein said developing solution further contains a sulfite or a sulfite ion releasing compound.

28. The method according to Claim 22, wherein said sulfite of said sulfite ion releasing compound is selected from the group consisting of potassium sulfite, sodium sulfite, ammonium sulfite, sodium metabisulfite, potassium metabisulfite, sulfurous acid adduct of formaldehyde, sulfurous acid adduct of acetaldehyde and sulfurous acid adduct of glutaraldehyde.

20. The method according to Claim 22, wherein said sulfite of said sulfite ion releasing compound is contained in the range from 1.0×10^{-4} to 1.0×10^{-1} mole/liter of the color developing solution.

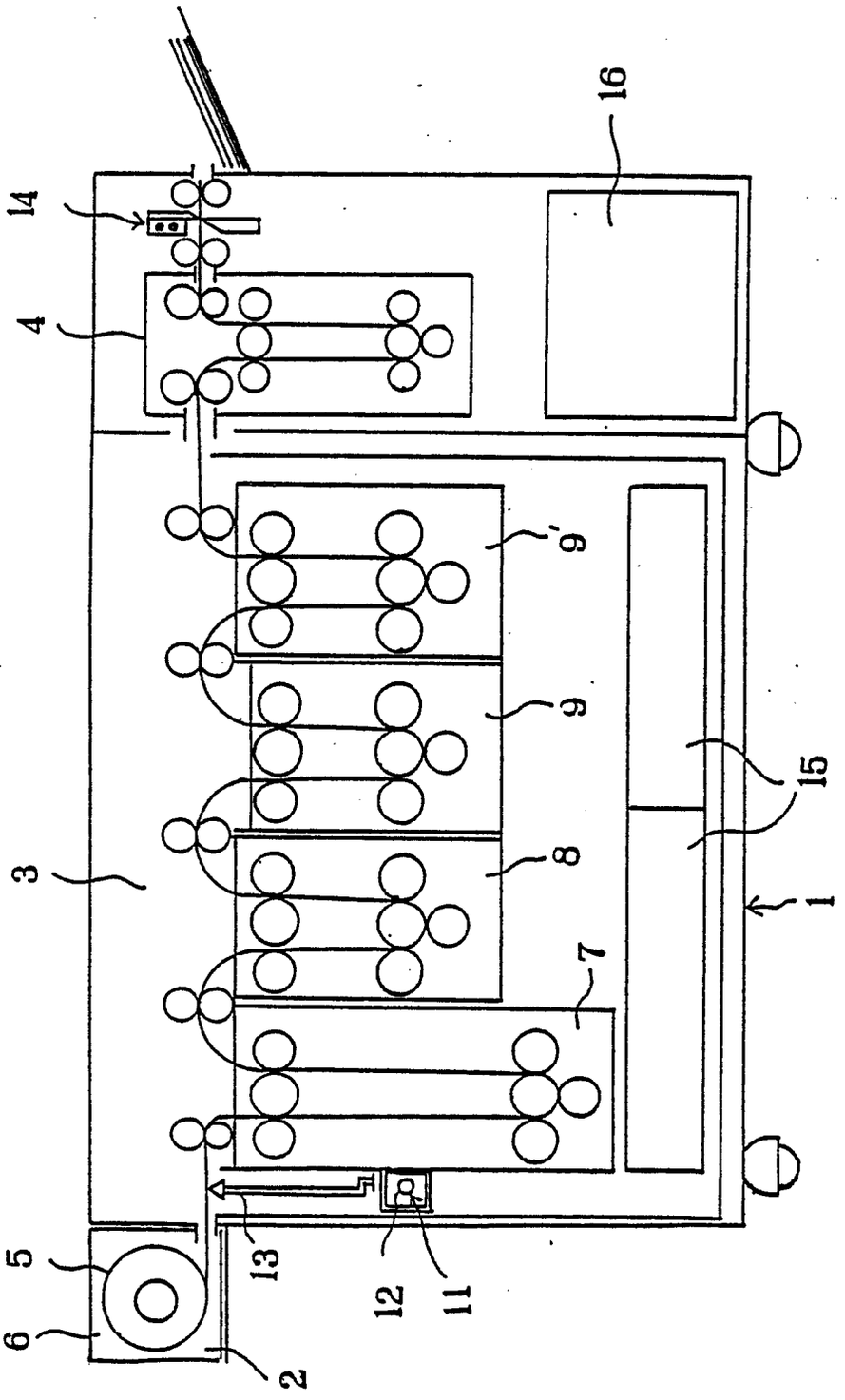


Fig. 1