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(54) A method for forming a dye image.

(57) A color dye image forming method is disclosed. In the method a silver halide light sensitive material comprising a paper support laminated with polyolefin layers on both side and a photographic layer comprising at least one silver halide emulsion layer provided on the support. The polyolefin layer provided on the emulsion coating side of the support contains titanium oxide particles in an amount of not less than 14 % by weight of the polyolefin and has a roughness in terms of arithmetical mean deviation of the profile SRa calculated by the following equation of not more than 0.1 µm, and the photographic layer contains gelatin in an amount of not more than 7.5 g/m^2;

$$SRa = \frac{1}{SA}\int_0^{Lx}\int_0^{Ly} \left| f\ (x,y) \right| dx,\ dy$$

wherein Lx is the length of measured area in the direction of X axis; Ly is the length of measured area in the direction of Y axis, S_A is the measured area, $S_A = Lx \times Ly$,
$S_A = 25mm^2$ and $Lx = Ly = 5mm$.

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FIELD OF THE INVENTION

The present invention relates to a method of forming an image with use of a silver halide color photographic light-sensitive material, and more particularly to an image forming method capable of simply easily providing color prints having excellent sharpness and gloss.

BACKGROUND OF THE INVENTION

A silver halide photographic light-sensitive material (hereinafter may be merely called 'light-sensitive material'), provides an excellent image quality and has a high sensitivity, but it is demanded that the image quality be still further improved. Important factors determining the image quality include sharpness, which causes a print image to look clear and solid, and gloss, which is effective to cause the print image to look fine and high-grade.

The support of a photographic paper for color pint-making use is a reflective support having on each of both sides thereof a polyolefin-coat layer, which has a large influence upon the above-mentioned sharpness and gloss.

As a means to improve the sharpness there is a method of increasing the density of titanium oxide particles contained in the polyolefin-coat layer on the silver halide emulsion-coating side of the support, and examples of the method include those described in JP O.P.I. Nos. 275246/1987, 156439/1991 and 156444/1991, but these methods have the disadvantage that they increase unevenness and nonuniformity of emulsion coating.

For improving the gloss it is effective to increase the surface smoothness of the support as described in JP O.P.I. Nos. 234251/1988, 83086/1990, 93640/1990, 97942/1990, 216139/1990 and 281251/1990, but it has been found that the method was liable to cause nonuniform coating trouble in the initial stage of the emulsion coating.

The above initial-stage coating trouble was later found out to be solvable by decreasing the amount of gelatin in the coating solution as a result of various investigations, but this method still had another disadvantage that it causes the density of a print image to largely change in a relatively short-period storage of it after printing.

On the other hand, every manufacturer producing light-sensitive materials is urged to provide its product to customers at a lower price, so that the productivity improvement of light-sensitive materials is essential.

A light-sensitive material manufacturer is proceeding with various measures for higher production efficiency, but among these measures, increasing the rate of coating photographic component layers such as silver halide emulsion layers and the like on a support contributes directly to its productivity improvement, so that the use of a highly-increased-speed coating is urgently needed.

It is, however, diffcult to make a uniform, rapid coating of a layer with no trouble; streak defects, coating mottles, unequal coverage and the like are liable to appear, which are a hindrance to increasing the coating rate.

The demand for large-format prints has lately been expanding. Even minor coating defects that have so far been out of the question, since they can become conspicuous in the case of large-format prints, come into serious quality question. Such the coating characteristic is known to be largely affected by the composition of a silver halide emulsion coating liquid or by the quality of a support used. Under such circumstances, worsening of nonuniform coating trouble is absolutely not allowed, and therefore overall improvement of the above problem is essential.

On the other hand, the procedure of collecting and processing color negative films to make color prints with use of color photographic papers, the so-called 'DPE', was conventionally carried out in large-scale photo-finishing laboratories (called large labs), but the DPE has lately been conducted mostly by small-scale photo-finishers (called minilabs) in order to streamline the collection and delivery system.

These minilabs naturally had a strong demand for speeding up and simplifying the processing procedures. As one of means to meet the demand, the use of high-silver-chloride-content color papers for rapid processing has already been developed to such an extent as to dominate the market.

For the rest of the means, simplification of the processing steps and alleviation of the control thereof, it is very effective to use the bleach-fix process in common for both color negative film and color paper or to separate the bleaching solution and fixer solution components of the color paper bleach-fix bath; various investigations have so far been made on the above problem, which will soon make them a practical reality. However, it has now been found that these methods have the serious disadvantage that they cause conspicuous stain to appear on the light-sensitive material after running processing, particularly after a relatively short-period storage of the processed light-sensitive material, which is a stumbling block to the practical use thereof

SUMMARY OF THE INVENITON

It is an object of the invention to provide a method for the formation of a dye image which makes it possible to easily obtain color prints which are excellent in the image sharpness as well as in the print gloss.

The above object of the invention is accomplished by a method for forming a dye image comprising the steps of

imagewise exposing a silver halide color photographic light-sensitive material to light,
developing the light-sensitive material with a color developer,
fixing the developed light-sensitive material with a fixing solution, and
stabilizing the fixed light-sensitive material with a stabilizing solution.

In the above, the light-sensitive material comprises a paper support for photographic paper having polyolefin layers each provided on both sides of the support and a photographic layer comprising at least one silver halide emulsion layer provided on a surface of the support. The polyolefin layer provided on the surface of the support on which the emulsion layer to be provided contains titanium oxide particles in an amount of not less than 14% by weight of the polyolefin in the layer, and the surface of this polyolefin layer has a roughness expressed by arithmetical mean deviation of the profile SR_A calculated by the following equation of not more than 1.0 μm. The photographic layer contains gelatin in an amount of not more than 7.5 g/m^2.

$$SRa = \frac{1}{S_A} \int_0^{Lx} \int_0^{Ly} \left| f(x,y) \right| dx,\ dy$$

wherein Lx is the length of measured area in the direction of X axis; Ly is the length of measured area in the direction of Y axis; and S_A is the measured area, S_A = Lx X Ly, S_A = 25mm^2, and Lx = Ly = 5mm.

DETAILED DESCRIPTION OF THE INVENTION

In the invention, the central surface roughness (SRa) of a support can be measured and determined by using, e.g., a surface roughness analyser SE-3AK, manufactured by Kosaka Research Institute.

The material usable as the paper support according to the invention is one selected from among materials generally used; those produced from natural pulps such as sulfite-bleached soft wood pulp (NBKP), sulfite-bleached hard wood pulp (LBKP), alkali sulfite bleached soft wood pulp (NBSP) and alkali sulfite bleached hard wood pulp (LBSP), which may be used in combination. When used in combination, the preferred proportion of broadleaf tree pulp/needle-leaf tree pulp is from 95/5 to 60/40. Further, the above natural pulp may be used in combination with straw pulp, esparto pulp or bamboo pulp, and also, if necessary, with synthetic fibers. The thickness of the paper used depends on the purpose for which the paper is used, but is normally, in basis weight of 50 to 250g/m^2.

The paper preferably has its strength such as waterproofness increased by adding thereto various additives, e.g., sizing agents such as an alkylketene dimer fatty acid salt, rosin, maleated rosin, an alkenylsuccinate, an alkylsuccinate and a polysuccharide, which each may be used in an amount of 0.2 to 2% of that of the pulp used.

As a dry paper strength-increasing agent there may be used cationized starch, cationized polyacrylamide, anionized polyacrylamide, carboxy-modified vinyl alcohol and the like.

As a wet paper strength-increasing agent there may be used melamine resin, urea resin, epoxidized polyamide resin, and the like.

As a fixing agent there may be used polyvalent metal salts such as aluminum sulfate and aluminum chloride, and a cationic polymer such as cationized starch.

The paper may, if necessary, contain a white pigment, such as clay, talc, calcium carbonate, titanium oxide or barium sulfate.

In general, the pulp has its surface tub sized or press sized by using a liquid containing various water-soluble polymer additives.

For example, as the water-soluble polymer additive there may be used cationized starch, polyvinyl alcohol, carboxymodified polyvinyl alcohol, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, polyacrylamide or gelatin.

An inorganic electrolyte such as Sodium chloride or sodium sulfate; a hygroscopic material such as glycerol or polyethylene glycol; a pH adjusting agent such as hydrochloric acid, sodium hydroxide or sodium carbonate; and other additives such as dyes, a brightening agent, an antistatic agent, a defoaming agent, and the like, may be used in combination.

The pulp, after being appropriately beaten and adding as needed the above additives thereto, becomes a pulp slurry, which, by means of a paper machine such as Fourdrinier machine, is formed into a paper layer and the layer is then dried and subjected to super calender treatment. Before or after this drying process, the surface of the paper is subjected to sizing treatment.

The support according to the invention is one obtained by coating a polyolefin resin on both sides of the paper obtained in the above manner.

Examples of the polyolefin resin used include α-olefin homopolymers such as polyethylene, polypropylene, etc., and mixtures of such various polymers; the particularly preferred polyolefin is a high-density polyethylene, a low-density polyethylene or a mixture thereof. These polyolefins are not restricted in the molecular weight, but those having a molecular weight of 20,000 to 200,000 may be generally used. The thickness of the polyolefin resin coat layer is not limited either, but is normally about 15 to 50μm.

The titanium oxide used in the polyolefin coat layer of the invention may or may not undergo surface treatment with aluminum hydroxide, alcohol or surfactant. The above white pigment is used in an amount of not less than 14% by weight, preferably 15 to 18% by weight of the polyolefin resin of the polyolefin resin coat layer on the photographic emulsion-coating side of the reflective support.

The SRa of the support of the invention is not more than 1.0μm, preferably 0.05 to 0.09μm. Preparation of a support having a SRa of not more than 1.0μm is carried out by single or combined use of methods for (1) increasing the thickness of the resin coat layer, (2) increasing compression pressure at the time of resin coating, (3) increasing the machine calender pressure in order to improve the surface flatness of the paper support, (4) adjusting the pulp fiber length, void rate, average fiber width and average fiber thickness which form the paper, and (5) application of a single sided glossed paper obtained by bringing one side of a wet-state paper into close contact with a heated mirror surface dryer.

The silver halide grain contained in the emulsion layer in the invention preferably has a silver chloride content of not less than 90 mol%, a silver bromide content of not more than 10 mol%, and a silver iodide content of not more than 0.5 mol%, and more preferably is a silver chloride having a silver bromide content of 0.1 to 1 mol%.

The silver halide grains of the invention may be used alone or used in a mixture with other silver halide grains different in the composition; may also be mixed with silver halide grains having a silver chloride content of less than 90 mol%.

When two or more different emulsions are mixed, in a silver halide emulsion layer containing silver halide grains having a silver chloride content of not less than 90 mol%, the silver halide grains having a silver chloride content of not less than 90 mol% accounts for preferably not less than 60% by weight and more preferably not less than 80% by weight of the whole silver halide grains contained in the emulsion layer. The silver halide grain may be of either a uniform structure with the same composition from the inside through the outside or a not-uniform structure with difference in the composition between the inside and the outside of the grain. If the inside and the outside of the grain are different in the composition, the composition may change continuously or discontinuously.

The grain diameter of the silver halide grain, although not restricted, is preferably 0.2 to 1.6μm and more preferably 0.25 to 1.2μm in consideration of rapid processing, sensitivity and other photographic characteristics. The grain diamter can be determined according to one of various methods well-known to those skilled in the art.

The grain diameter distribution of the silver halide grains of the invention may be either of the polydisperse type or monodisperse type. Preferably the silver halide grains are monodisperse silver halide grains whose grain diameter distribution's coefficient of variation is not more than 0.22, and more preferably not more than 0.15, wherein the coefficient of variation is a coefficient showing the broadness of a grain diameter distribution, which is defined by

$$\text{Coefficient of variation} = \frac{\text{Standard deviation of grain diameter distribution}}{\text{Average grain diameter}}$$

The silver halide grains of the invention may be prepared according to any one of an acidic method, neutral method or ammoniacal method. The grains may be grown at a time or grown after preparing seed grains.

The reaction between a water-soluble silver salt and a water-soluble halide may take place in any one of the normal precipitation process, reverse precipitation process and double-jet process or a process in combination thereof, but the silver halide is preferably one obtained in the double-jet process. As one form of the double-jet process there may be used the pAg-controlled double-jet process described in JP O.P.I. No. 48521/1979.

Further, a solvent for silver halide, such as thioether, may be used if necessary.

The silver halide grain used may be in any arbitrary form. A preferred example of the grain form is a cubic grain having {100} planes as its crystal surfaces. The grain may also be in a octahedral, tetradecahedral or dodecahetral crystal form, and further may be a grain having twin planes.

The silver halide used may be either of grains in a single crystal form or a mixture of grains in various crystal forms.

The silver halide grain may have metallic ions incorporated into its inside and/or its surface by adding thereto a cadmium salt, zinc salt, lead salt, thalium salt, iridium salt including its complex salt, rhodium salt including its complex salt or ion salt including its complex salt in the grain forming process and/or the grain growing process, and also may have a reduction sensitization nucleus provided to its inside and/or its surface by being placed in an appropriate reductive atmosphere.

The silver halide emulsion to be used in the invention, after completion of the growth of the silver halide, may have its useless water-soluble salts either removed therefrom or allowed to remain thereinside.

The silver halide grain may be of either the type of forming a latent image mainly on its surface or the type of forming a latent image thereinside; preferably it is of the type of forming a latent image mainly on its surface.

The silver halide emulsion is chemically sensitized in the usual manner: a sulfur sensitization method, which uses an active gelatin or a compound containing sulfur, capable of reacting with silver ions; a selenium sensitization method, which uses a selenium compound: a reduction sensitization method, which uses a reductive material; and a noble-metallic sensitization method, which uses a gold compound or other noble-metallic compound, may be used alone or in combination.

In the invention, as a chemical sensitizer there may be used, for example, a chalcogen sensitizer, a general term for sulfur sensitizers, selenium sensitizers and tellurium sensitizers. For photographic use, sulfur sensitizers and selenium sensitizers are suitable. Examples of the sulfur sensitizer include thiosulfates, allylthiocarbazide, thiourea, allylisothiocyanate, cystine, p-toluenethiosulfonates, rhodanine.

The adding amount of a sulfur sensitizer depends largely on various conditions such as pH, temperature and silver halide grain size, but as a standard it is preferably 10^{-7} to 10^{-1} mol per mol of silver halide.

A selenium sensitizer may be used in place of the sulfur sensitizer. Examples of the selenium sensitizer include aliphatic isoselenocyanates such as allyisoselenocyanate, selenoureas, selenoamides, selenocarboxylates and esters thereof, selenophosphates, and selenides such as diethyl selenide, diethyl diselenide.

Further, a reduction sensitizer may also be used. Any reducing agent may be used without restriction, but preferred examples of the reduction sensitizer include stannous chloride, thiourea dioxide, hydrazine and polyamine, which may be used in combination with a non-gold noble metallic compound such as a palladium compound.

The silver halide grain used in the invention preferably contains a gold compound. The gold compound suitably usable in the invention may be of a gold's oxidation number of either +1 or +3, and thus a variety of gold compounds may be used, typical examples of which include chloroaurates such as potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, pyridyltrichlorogold, gold sulfide and gold selenide.

The gold compound may be used so as to sensitize the silver halide or so as substantially not to contribute to sensitizing the silver halide.

The adding amount of the gold compound depends upon various conditions, but as a standard, it is 10^{-8} to 10^{-1} mol, preferably 10^{-7} to 10^{-2} mol per mol of silver halide. The compound may be added at any point of time, such as during the silver halide grain formation, during the physical ripening, during or after the chemical ripening in the emulsion preparation process.

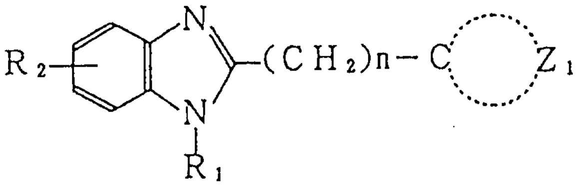
The emulsion used in the invention may be spectrally sensitized to desired wavelength regions by using sensitizing dyes known to those skilled in the art. Such sensitizing dyes may be used alone or in combination. Further, in combination with such sensitizing dyes there may be incorporated into an emulsion a supersensitizer which in itself has no spectral sensitization effect or does substantially not absorb visible light, but serves to intensify the sensitization effect of sensitizing dyes.

As for gelatin applicable to the invention, there may be used lime-treated gelatin, acid-treated gelatin, and the enzyme-treated gelatin described in Bull. Soci. Sci. Phot. Japan, No.16, p.30 (1966). Further, a hydrolyzed product or enzyme-decomposed product of gelatin may also be used.

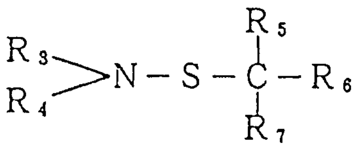
The coating weight of gelatin of the photographic layer of the light-sensitive material of the invention is not more than 7.5g/m^2, more preferably 6.5 to 7.2g/m^2.

At least one of the layers of the color light-sensitive material of the invention contains preferably at least one compound selected from among the compounds represented by the following Formulas I, II, III, IV, V and VI

Formula I

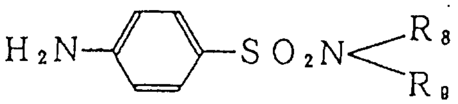


Formula II



$$\begin{matrix} R_3 \\ R_4 \end{matrix}\!\!>N-S-\overset{\overset{\displaystyle R_5}{|}}{\underset{\underset{\displaystyle R_7}{|}}{C}}-R_6$$

Formula III



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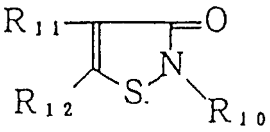
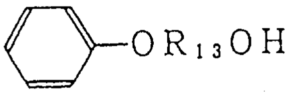
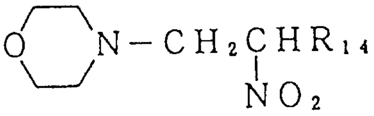


Formula V



Formula VI



$$O\langle\ \rangle N-CH_2\underset{\underset{\displaystyle NO_2}{|}}{C}HR_{14}$$

In Formulas I to IV, R_1 represents a hydrogen atom, an alkyl group or an aryl group; R_2 is a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a nitro group, a carboxyl group, a sulfo group, a sulfamoyl group, a hydroxyl group, an alkoxy group or a thiazolyl group; Z_1 is a group of non-metallic atoms necessary to form a thiazoline ring; R_3 and R_4 each represent an alkyl group, an aryl group, a -COR group or a $-SO_2N(R')(R'')$ group, wherein R, R' and R" each are an alkyl or aryl group provided that R_3 and R_4 may form a ring together with the nitrogen atom; R_5, R_6 and R_7 each are a halogen atom or an alkyl group; R_8 and R_9 each are a hydrogen atom, an alkyl group, an aryl group or a nitrogen-containing heterocyclic group; R_{10} is a hydrogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, a heterocyclic group, an alkylcarbamoyl gropup, an arylcarbamoyl group, an alkylsulfamoyl group or a arylsulfamoyl group; and R_{11} and R_{12} each represent a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, a cyano group, an alkylthio group, an arylthio group, an alkylsulfonyl group, an alkylsulfonyloxy group or a heterocyclic group, provided that R_{11} and R_{12} together may form a ring.

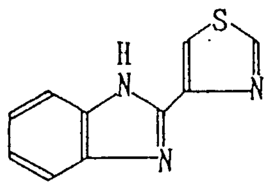
In Formula V, R_{13} is an alkylene group or an arylene group. In Formula VI, R_{14} is a lower alkyl group having 1 to 5 carbon atoms, preferably methyl or ethyl.

The substitutable groups represented by R_1 to R_{13} in above include those having further substituents.

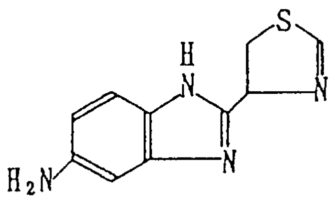
Those compounds represented by Formulas I through VI are known compounds, which include the compounds described in JP O.P.I. Nos. 27424/1979, 157244/1982, 84237/1984, 226344/1984, 263938/1985 and 233743/1986.

The following are typical examples of the compounds represented by Formulas I through VI, which are usable in the invention, but the invention is not limited by the examples.

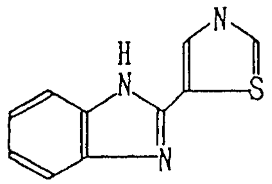
I − 1



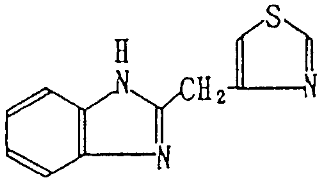
I − 2



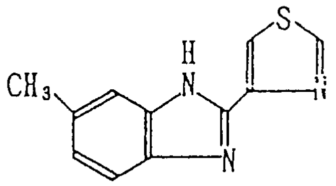
I − 3



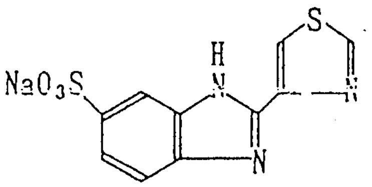
I − 4



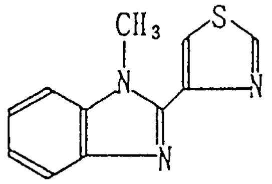
I − 5



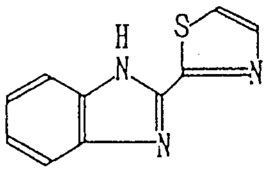
I − 6



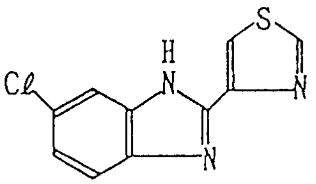
I − 7



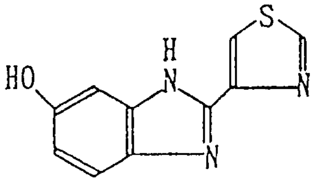
I − 8



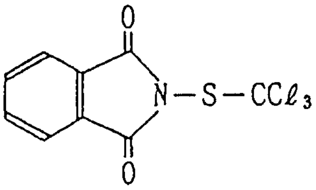
I − 9



I − 10



II − 1



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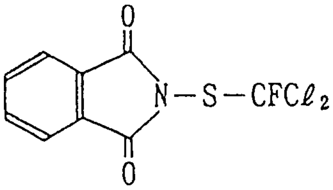
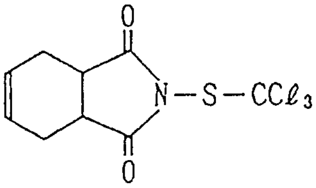


II − 3



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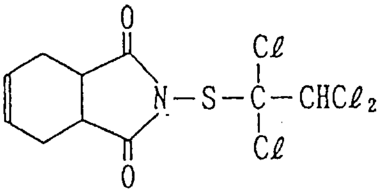

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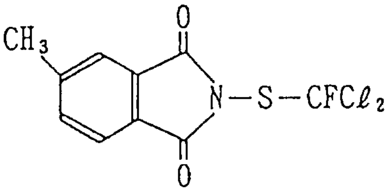
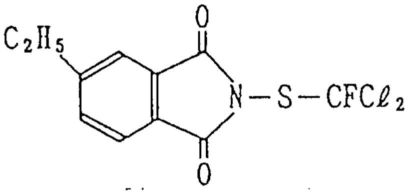
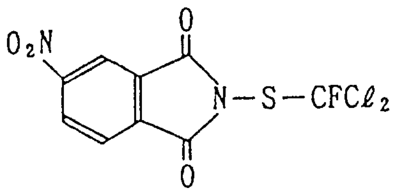


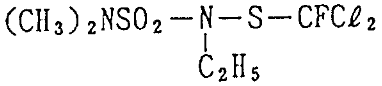
II − 6



II − 7

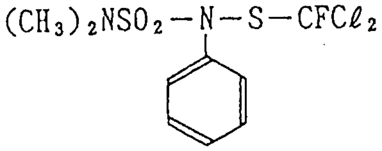


II − 8



$(CH_3)_2NSO_2-\underset{C_2H_5}{\underset{|}{N}}-S-CFCl_2$

II − 9



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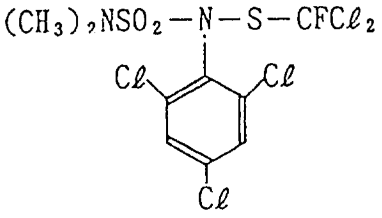

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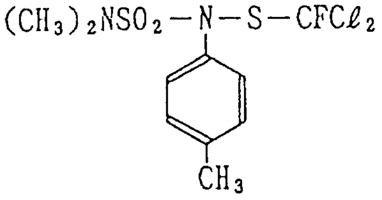

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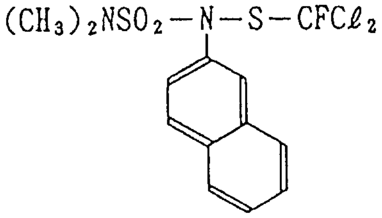

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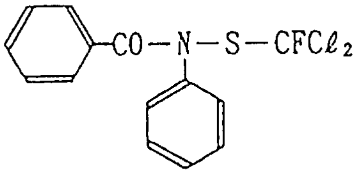

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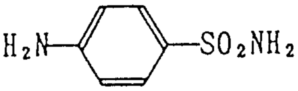

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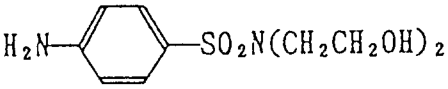

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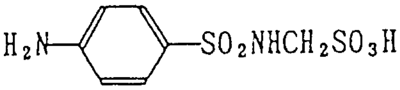

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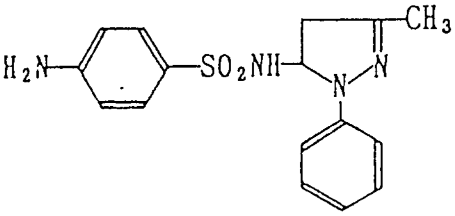

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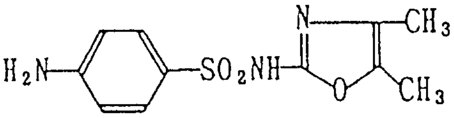

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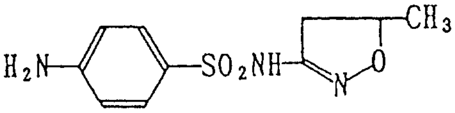

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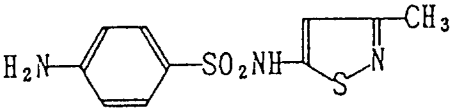

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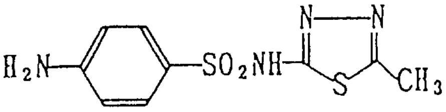

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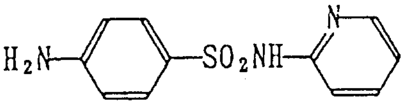

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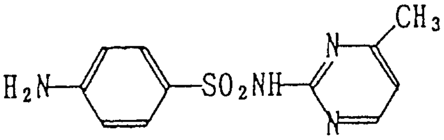

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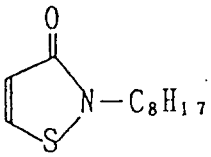

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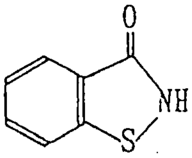

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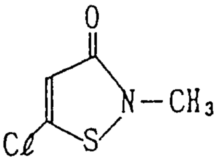

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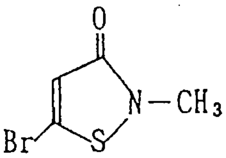

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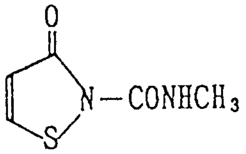

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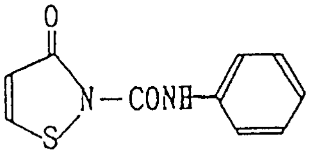

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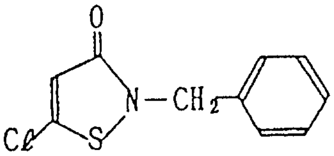

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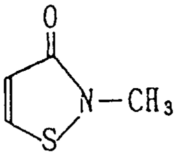

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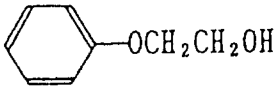

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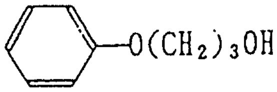

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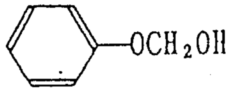
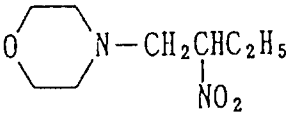
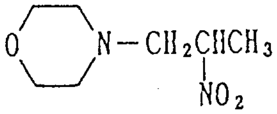


VI - 1



VI - 2

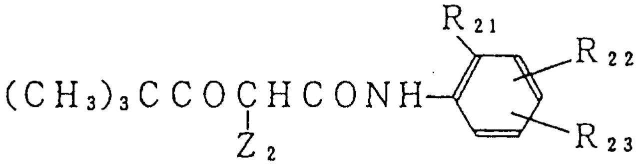


Any of the above compounds represented by Formulas I to VI may be added to any photographic component layers, but is added preferably to non-light-sensitive layers when taking into account photographic characteristics such as fog and sensitivity. The adding point of time of the above compound is during the preparation of a colloid emulsion for photographic component layers, which compound is capable of preventing the emulsion from being decomposed by bacteria, mould, etc., after the addition.

Of the compounds represented by Formula I through VI, preferred are those represented by Formulas I, II and IV and more preferred are those of Formulas I and IV. The adding amount thereof to photographic component layers is preferably $5x10^{-7}$ to $2x10^{-3}$ mol, and more preferably $5x10^{-6}$ to $5x10^{-4}$ mol per m^2. In incorporating the compound into the light-sensitive material, the compound is added preferably in the form of a solution or emulsified liquid after being dissolved in a solvent such as water, methanol, ethanol, ethylene glycol, diethylene glycol, triethylene glycol, benzyl alcohol, ethanolamine, diethanolamine or triethanolamine.

Known acylacetanilide couplers are usable as the yellow dye-forming coupler for the invention. Among them benzoylacetanilide and pivaloylacetanilide compounds are advantageous; particularly those represented by the following Formula Y-I are suitable for the invention.

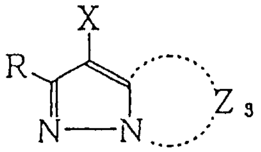
Formula Y-I



wherein R_{21} is a halogen atom or an alkoxy group; R_{22} is a hydrogen atom, a halogen atom or a substitutable alkoxy group; R_{23} is a substitutable acylamino group, an alkoxycarbonyl group, an alkylsulfamoyl group, an arylsulfamoyl group, an arylsulfonamido group, an alkylureido group, an arylureido group, a succinimido group, an alkoxy group or an aryloxy group; and Z_2 is a group capable of splitting off upon its coupling reaction with the oxidation product of a color developing agent.

Any of various magenta couplers may be used as the magenta coupler for the invention. Among them, those represented by the following Formula M-1 are suitably used.

Formula M-1



wherein Z_3 is a group of non-metallic atoms necessary to form a nitrogen-containing heterocyclic ring which may have a substituent; X represents a hydrogen atom or a substituent capable of splitting off upon the reaction with the oxidation product of a color developing agent; and R is a hydrogen atom or a substituent.

In Formula M-1, the substituent represented by R is not restricted, but is typically an alkyl group, aryl group, anilino group, acylamino group, sulfonamido group, alkylthio group, arylthio group, alkenyl group, cycloalkyl group, halogen atom, cycloalkenyl group, alkynyl group, heterocyclic group, sulfonyl group, sulfinyl group, phosphonyl group, acyl group, carbamoyl group, sulfamoyl group, cyano group, alkoxy group, aryloxy group, heterocyclic oxy group, siloxy group, acyloxy group, carbamoyloxy group, amino group, alkylamino group, imido group, ureido group, sulfamoylamino group, alkoxycarbonylamino group, aryloxycarbaonylamino group, alkoxycarbonyl group, aryloxycarbonyl group, heterocyclic thio group, spiro compound residue or organic hydrocarbon compound residue.

The preferred scope and examples of the substituent represented by R, the group represented by X, capable of splitting off upon the reaction with the oxidation product of a color developing agent, the nitrogen-containing heterocyclic ring formed by Z, and the substituent which the ring formed by Z may have, and the preferred extent of the magenta couplers represented by Formula (M-I) are the same as those described in European Patent Publication No. A-0327272, pp 23 to 52.

Examples of the above compound include the exemplified compounds M-1 to M-61 described in European Patent Publication No. A-0273712, pp.6 to 21 and Compounds Nos. 1 to 223 described in European Patent Publication No. A-0235913. pp.36 to 92.

For the synthesis of these couplers reference can be made to Perkin, the Journal of the Chemical Society, 2047-2052 (1977); U.S. Patent No. 3,725,067; and JP O.P.I. Nos. 99437/1984, 42045/1983, 162548/1984, 171956/1984, 33552/1985, 43659/1985, 172982/1985, 190779/1985, 209457/1987 and 307453/1988.

The above couplers may be used in combination with different other magenta couplers. They may be used in an amount of normally 1×10^{-3} mol to 1 mol, and preferably 1×10^{-2} mol to 8×10^{-1} mol per mol of silver halide.

Typically usable as the cyan dye-forming coupler for the invention are phenol or naphthol four-equivalent or two-equivalent-type cyan dye-forming couplers, and the most preferred among them are 2-acylamino-5-alkylphenol and 2,5-diacylaminophenol couplers.

Into the color light-sensitive material of the invention may be incorporated various photographic additives, examples of which include UV absorbents such as benzophenon and benzotriazole compounds; antistain agents such as hydroquinone derivatives; surfactants such as sodium alkylnaphthalenesulfonate, sodium alkylbenzenesulfonate, sodium alkylsuccinatesulfonate and polyalkylene glycol; water-soluble antiirradiation dyes such as azo, styryl, triphenylmethane, oxonol and anthraquinone compounds; hardeners such as halogeno-s-triazine. vinylsulfone, acryloyl, ethyleneimine, N-methylol and epoxy compounds and water-soluble aluminum salts; physical property-improving agents for coated layers such as glycerol, aliphatic polyhydric alcohols, polymer dispersions (latex), solid or liquid paraffin and colloidal silica; and brightening agents such as diaminostilbene compounds, and various oil-soluble coating materials.

The photographic layers of the light-sensitive material of the invention comprise emulsion layers and, if necessary, other layers such as a subbing layer, intermediate layer, yellow filter layer, UV absorbent layer, protective layer and antihalation layer.

Incorporation of photographically useful hydrophobic compounds such as dye-forming compounds and image stabilizers into the light-sensitive material can be carried out in accordance with various methods such as the solid dispersing method, latex dispersing method and oil-in-water emulsification dispersing method; an appropriate one of the methods may be selected according to the chemical structure of a hydrophobic compound to be used.

The oil-in-water-type emulsification dispersing method includes various ways for dispersing hydrophobic compounds; normally, a hydrophobic compound is dissolved in a high-boiling organic solvent having a boiling point of higher than 150 ° C, if necessary, in combination with a low-boiling and/or water-soluble organic solvent, and the solution is emulsifiedly dispersed with the aid of a surfactant in a hydrophilic binder such as an aqueous gelatin solution by a dispersing means such as a stirrer, homogenizer, colloid mill, flow-jet mixer, supersonic device or the like, and then the obtained dispersion is added to a hydrophilic colloid layer. A process for removing the low-boiling solvent at the time of dispersing may be inserted.

In the invention, the color developing agent used in a color developer includes those known compounds widely used in various color photographic processes, such as aminophenol and p-phenylenediamine derivatives. These compounds are used generally in the form of salts such as hydrochlorides or sulfates because they, when in such the salt form, are more stable than in the free state. Any of these compounds is used in a concentration of preferably about 0.1g to about 30g, more preferably about 1g to about 15g per liter of a color developer solution.

Examples of the aminophenol developing agent include o-aminophenol, p-aminophenol, 5-amino-2-hydroxytoluene, 2-amino-3-hydroxytoluene and 2-hydroxy-3-amino-1,4-dimethylbenzene.

The most useful aromatic primary amine color developing agents are N,N-dialkyl-p-phenylenediamine compounds, in which the alkyl group and phenyl group may be substituted by arbitrary substituents. Those particularly useful among the compounds are N,N-diethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine hydrochloride, N,N-dimethyl-p-phenyl-enediamine hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)-toluene, N-ethyl-N-β-methansulfonamidoethyl-3-methyl-4-aminoaniline sulfate, N-ethyl-β-hydroxyethylaminoaniline, 4-amino-3-methyl-N,N-diethylaniline, and 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluene sulfonate.

In addition to the above developing agent, the developer that applies to processing the color light-sensitive material of the invention may contain known developer component compounds, including alkali agents such as sodium hydroxide or sodium carbonate, alkali metal thiocyanate, alkali metal halide, benzylalcohol, water softener, and thickener.

Development of the light-sensitive material is made at a temperature of preferably not lower than 15 ° C, and more preferably 30 ° C to 45 ° C, and at a pH of not less than 7, and generally about 10 to about 13.

Developing time, although not restricted, is preferably not longer than 3 minutes. The effect of the invention comes even more excellent in the case of processing in a short time, the so-called rapid processing; a great effect can be obtained where processing time is 90 seconds or less, particularly in the case of 30 seconds or less.

The light-sensitive material of the invention, when containing in its hydrophilic colloid layers a color developing agent as it is or in the form of a precursor thereof, can be processed in an alkaline activator bath.

The color developing agent precursor is a compound capable of producing a color developing agent under an alkaline condition, and examples of the precursor include aromatic aldehyde derivative-Schiff's base-type precursors, multivalent metallic ion complex precursors, phthalic acid imide derivative precursors, phosphoric acid amide derivative precursors, sugar-amine reaction product precursors and urethane-type precursors.

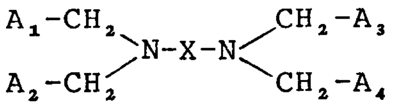
The aromatic primary amine color developing agent or its precursor, when used in an activator solution, needs to be added thereto in so much an amount that alone can carry out sufficient color formation. The amount depends largely upon the kind of the light-sensitive material used, but is preferably 0.1 to 5 mols, and more preferably 0.5 to 3 mols per mol of silver halide. These color developing agents or precursors thereof may be used alone or in combination.

The color developing agent or its precursor, in order to be incorporated into the light-sensitive material, may be added in the form of a solution of it dissolved in an appropriate solvent such as water, methanol, ethanol or acetone; in the form of an emulsified dispersion made from a solution of it dissolved in a high-boiling solvent such as dibutyl phthalate, dioctyl phthalate or tricresyl phosphate; or in the form of being impregnated in a latex polymer as described in Research Disclosure No. 14850.

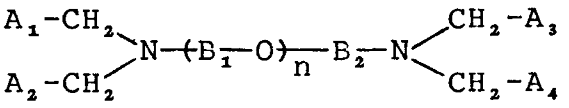
In the present invention, the color light-sensitive material is subjected to color developing, followed by bleaching and fixation.

In the invention, a ferric complex salt of an organic acid represented by Formula A or B is used as a bleaching agent for the bleaching solution.

Formula A



Formula B



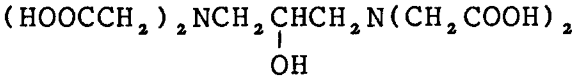
In Formula A, A_1 to A_4 may be either the same or different and each represent $-CH_2OH$, $-COOM$ or $-PO_3M_1M_2$; wherein M, M_1 and M_2 each are a hydrogen atom, an alkali metal such as sodium or potassium, or an ammonium group; and X is a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms, such as propylene, butylene or pentamethylene, wherein the substituent thereto includes a hydroxyl group, an alkyl group having 1 to 3 carbon atoms, such as methyl, ethyl or propyl.

In Formula B, A_1 to A_4 are as defined in Formula A; n is an integer of 1 to 8; and B_1 and B_2 may be either the same or different and each represent a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms, such as ethylene, propylene, butylene or pentamethylene, in which the substituent thereto includes the same groups as those defined for X in Formula A.

The following are the preferred examples of the compounds represented by Formulas A and B.

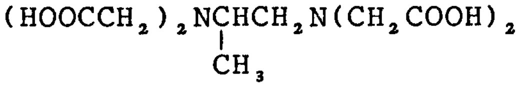
A-1 $(HOOCCH_2)_2N(CH_2)_3N(CH_2COOH)_2$

A-2



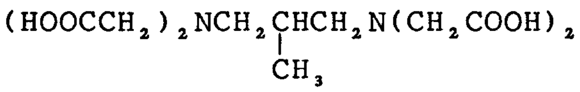
$(HOOCCH_2)_2NCH_2\underset{OH}{\underset{|}{C}}HCH_2N(CH_2COOH)_2$

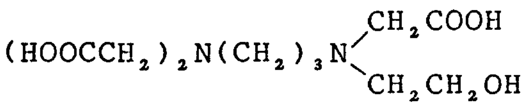
A-3



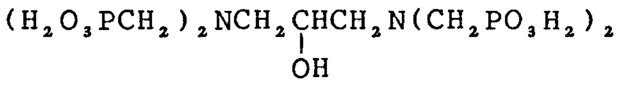
$(HOOCCH_2)_2N\underset{CH_3}{\underset{|}{C}}HCH_2N(CH_2COOH)_2$

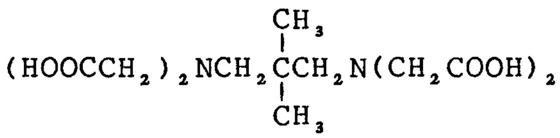
A-4 $(HOOCCH_2)_2N(CH_2)_4N(CH_2COOH)_2$

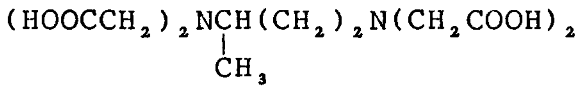
A-5 
$(HOOCCH_2)_2NCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2N(CH_2COOH)_2$

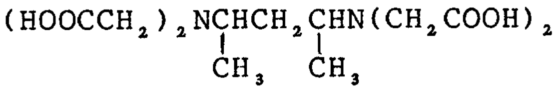
A-6 
$(HOOCCH_2)_2N(CH_2)_3N\begin{matrix}\diagup CH_2COOH \\ \diagdown CH_2CH_2OH\end{matrix}$

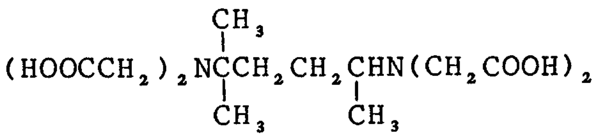
A-7 $(H_2O_3PCH_2)_2N(CH_2)_3N(CH_2PO_3H_2)_2$

A-8 
$(H_2O_3PCH_2)_2NCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2N(CH_2PO_3H_2)_2$

A-9 
$(HOOCCH_2)_2NCH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_2N(CH_2COOH)_2$

A-10 
$(HOOCCH_2)_2N\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_2N(CH_2COOH)_2$

A-11 
$(HOOCCH_2)_2N\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HN(CH_2COOH)_2$

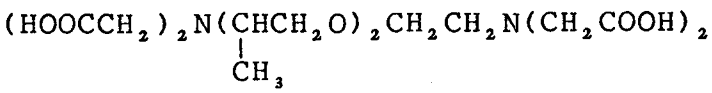
A-12 
$(HOOCCH_2)_2N\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HN(CH_2COOH)_2$

B-1 $(HOOCCH_2)_2N(CH_2CH_2O)_2CH_2CH_2N(CH_2COOH)_2$

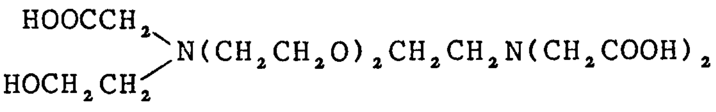
B-2 $(HOOCCH_2)_2NCH_2CH_2OCH_2CH_2N(CH_2COOH)_2$

B-3 $(HOOCCH_2)_2N(CH_2CH_2O)_3CH_2CH_2N(CH_2COOH)_2$

B-4 $(HOOCCH_2)_2N(CH_2CH_2CH_2O)_2CH_2CH_2CH_2N(CH_2COOH)_2$

B-5 
$(HOOCCH_2)_2N(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_2CH_2CH_2N(CH_2COOH)_2$

B-6 $(H_2O_3PCH_2)_2N(CH_2CH_2O)_2CH_2CH_2N(CH_2PO_3H_2)_2$

B-3 
$\begin{matrix}HOOCCH_2\diagdown \\ HOCH_2CH_2\diagup\end{matrix}N(CH_2CH_2O)_2CH_2CH_2N(CH_2COOH)_2$

As the ferric complex salts of these compounds of A-1 through A-12 and B-1 to B-7 there may be arbitrarily used sodium salts, potassium salts or ammonium salts of these ferric complex salts. From the invention's object and solubility point of view, the ammonium and potassium salts of these ferric complex salts are preferably used.

Of the above exemplified compounds the most preferably usable in the invention are compounds A-1, A-3, A-4, A-5, A-9, B-1, B-2 and B-7.

The ferric complex salt of the organic acid represented by Formula A or B is preferably contained in a concentration of not less than 0.1 mol, more preferably not less than 0.2 mol and most preferably 0.2 to 1.5 mols per liter of a bleaching solution.

In the bleaching solution, an additional bleaching agent may be used in combination with the above compound represented by Formula A or B. Examples of the combinedly usable bleaching agent include ferric complex salts with ammonium, sodium, potassium and triethanolamine salts of the following acids:

A'-1 Ethylenediaminetetraacetic acid
A'-2 Trans-1,2-cyclohexanediaminetetraacetic acid
A'-3 Dihydroxyethyl glycinate
A'-4 Ethylenediaminetetrakismethylenephosphonic acid
A'-5 Nitrilotrismethylenephosphonic acid
A'-6 Diethylenetriaminepentakismethylenephosphonic acid
A'-7 Diethylenetriaminepentaacetic acid
A'-8 Ethylenediaminediorthohydroxyphenylacetic acid
A'-9 Hydroxyethylethylenediaminetriacetic acid
A'-10 Ethylenediaminedipropionic acid
A'-11 Ethylenediaminediacetic acid
A'-12 Hydroxyethyliminodiacetic acid
A'-13 Nitrilotriacetic acid
A'-14 Nitrilotripropionic acid
A'-15 Triethylenetetraminehexaacetic acid
A'-16 Ethylenediaminetetrapropionic acid

An organic acid ferric complex salt may be used as it is, i.e., in the complex salt form, or in a solution a ferric ion complex salt may be formed by using a ferric salt such as ferric sulfate, ferric chloride, ferric acetate, ferric-ammonium sulfate, ferric phosphate, and aminopolycarboxylic acid or a salt thereof. When used in the complex salt form, either a single complex salt or two or more kinds of complex salt may be used. Further, where a ferric salt and an aminopolycarboxylic acid are used to form a complex salt in a solution, one or more kinds of ferric salt may be used, and also one or more kinds of aminopolycarboxylic acid may be used. In both cases, the aminopolycarboxylic acid may be used in excess of the amount necessary to form an ferric ion complex salt.

The above ferric salt ion complex salt-containing bleaching bath may contain additional complex salts of non-ferric metal ions such as of cobalt, copper, nickel and zinc.

The bleaching solution, when containing the imidazole and its derivative described in JP O.P.I. No. 295258/1989 or at least one of the exemplified compounds represented by the Formulas [I] to [IX] in the same publication, can exhibit its effect for rapid processing.

In addition to the above bleaching accelerators, those which may also be used in the invention are the exemplified compounds described in pp.14 to 30 of JP O.P.I. No. 123459/1987 the exemplified compounds described in pp.22 to 25 of JP O.P.I. No. 17445/1988 and the exemplified compounds described in JP O.P.I. Nos. 95630/1978 and 28426/1978.

The above bleaching accelerators may be used alone or in combination; the adding amount thereof is preferably about 0.01 to 100g, more preferably 0.05 to 50g and most preferably 0.05 to 15g per liter of a bleaching bath.

For preparing a bleaching solution, the bleaching accelerator may be added as it is, but is generally in advance dissolved in water, an alkali or organic acid, if necessary, with an organic solvent such as methanol, ethoanol or acetone, to be added in the form of a solution.

The bleach solution has a pH of preferably not more than 5.5, more preferably 2.5 to 5.5, wherein the pH is of the bleaching solution at the time of processing a light-sensitive material, which can be definitely distinguished from that of a bleacher replenisher.

The bleaching solution is used at a temperature of preferably 20°C to 50°C, and more preferably 25°C to 45°C.

The bleaching time for color photographic paper is preferably not longer than 40 seconds, more preferably not longer than 30 seconds, and most preferably not longer than 25 seconds, which makes the effect of the invention conspicuous also in rapid processing. The bleaching time herein means the duration between the moment when the leading end of a light-sensitive material begins to dip into the bleaching solution and the moment when the leading end gets out of the same solution.

The bleaching solution usually contains a halide such as ammonium bromide, potassium bromide or sodium bromide, and may also contain a brightening agent, defoaming agent and surfactant.

In the process of the invention, the replenisher to the bleaching solution is preferably comprised partially or wholly of an overflow of a bleaching solution that was once used in processing a different-type color light-sensitive material. That is, where bleaching baths A and B are used for two processing systems, respectively, a bleaching solution overflow from the bleaching bath A is utilized as a replenisher to the bleaching bath B. Light-sensitive materials to be processed in the bleaching baths A and B needs to be of types different from each other; for example, color negative film and color paper; color negative film or color paper and color reversal film or paper; color negative films different in the silver chloride concentration, silver bromide concentration or sensitivity; color papers different in the silver chloride concentration, silver bromide concentration or sensitivity, and the like; thus various combinations can be considered, but the combination of color negative film with color paper is particularly preferred in the embodiment of the invention.

The preferred replenishing amount to the bleaching solution is preferably not more than 50 ml/m^2, more preferably not more than 30 ml/m^2 for color photographic paper, and preferably not more than 180 ml/m^2, more preferably not more than 140 ml/m^2 for color negative film; the less the replenishing amount, the more conspicuous does the effect of the invention appear.

In the invention, in order to increase the activity of the bleaching bath, air- or oxygen-blow-in may be made inside the processing bath or inside the replenisher storage tank therefor, or else an appropriate oxidation agent such as hydrogen peroxide, a bromate or a persulfate may be discretionarily added thereto.

Suitably usable as the fixing agent for the fixing solution in the fixing process that follows the bleaching process are thiosulfates and/or thiocyanates. The adding amount of the thiosulfate is preferably not less than 0.4 mol/liter, and that of the thiocyanate is preferably not less than 0.5 mol/liter.

Besides the fixing agent, the fixation bath may also contain a pH buffer comprised of a single salt or two or more salts such as boric acid, borax, potassium hydroxide, sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, acetic acid, sodium acetate, ammonium hydroxide.

It is preferable that the solution further contain a large amount of an alkali halide or ammonium halide, e.g., rehalogenating agents such as potassium bromide, sodium bromide, sodium chloride, ammonium bromide. The solution may also contain discretionary amounts of compounds known as additives for ordinary fixer solutions.

In the fixing solution, the ammonium ion should account for preferably not more than 50 mol%, more preferably not more than 20 mol%, and most preferably 0 to 20 mol% of the whole cations, which is considered a preferred embodiment because it enables to prevent possible stain that appears when fixation is made directly after bleaching, and also because it uses a reduced amount of ammonium ions to thereby meet low-pollution requirements. However, reduction in ammonium ions affects the fixing capacity, so that it is a more preferred embodiment to use in combination a thiocyanate in a concentration of 0.5 mol to 3.0 mols per liter or a thiosulfate in a concentration of preferably 0.4 mol or more, more preferably 1.0 mol or more, and most preferably 1.2 to 2.5 mols per liter of the solution.

The replenishing amount to the fixing bath is preferably 120 ml or less, more preferably 20 to 1000 ml, and most preferably 50 to 800 ml per m^2 of a light-sensitive material.

The pH range of the fixing solution is preferably 4 to 8.

To the fixing solution may be added a compound represented by the formula [FA] or one of the exemplified compounds thereof described in JP O.P.I. No. 295258/1989, p.15; the use of that fixing bath provides an additional effect that it significantly curbs a sludge possibly produced when processing a small quantity of light-sensitive materials over a long period of time. The adding amount of the compound having the formula [FA] is preferably 0.1 to 200g per liter of a fixing solution.

In the fixing solution, there may be used a sulfite or a sulfite-releasing compound, examples of which include potassium sulfite, sodium sulfite, ammonium sulfite, ammonium hydrogensulfite, potassium hydrogensulfite, sodium hydrogensulfite, potassium metabisulfite, sodium metabisulfite and ammonium metabisulfite. Further, the fixing solution may also contain a compound represented by the formula [B-1] or [B-2] described in JP O.P.I. No.295258/1989, p.16.

The concentration of the sulfite or sulfite-releasing compound in the fixing solution is preferably at least 0.05 mol, more preferably 0.08 to 0.65 mol, further preferably 0.10 to 0.50, and most preferably 0.12 to 0.40 mol per liter of the fixing bath.

The fixing time in the fixing solution is arbitrary, but is preferably not longer than 6 minutes and 30 seconds, more preferably 5 seconds to 4 minutes and 20 seconds, and most preferably 10 seconds to 3 minutes and 20 seconds.

In the processing method of the invention, it is a preferable embodiment to provide a forcible stirring or agitation to the bleaching bath and fixing bath because it makes the invention not only more effective but also highly adaptable to rapid processing. The forcible stirring or agitation herein, unlike the usual circulation of a solution, implies providing an appropriate means for making forced stirring or agitation of the bath. As for the forcible stirring means there may be employed those means described in JP O.P.I. Nos. 206343/1989 and 295258/1989.

In the invention, setting the time required for each cross-over run between the color-developing bath and the bleaching bath and between other baths to within 10 seconds, preferably within 7 seconds, although outside the effect of the invention, is effective in reducing the bleaching fog, and further, the use of a duckhill valve to decrease the amount of the solution carried-in by a light-sensitive material is also a favorable embodiment in practicing the invention.

The fixing process according to the invention is followed by washing or stabilization treatment, but is preferably by a stabilization treatment in a stabilizing solution.

It is preferable for the object of the invention to have the stabilizing solution contain a chelating agent having a chelating stability constant of not less than 8. The chelating stability constant herein means the constant generally known by L. G. Sillen and A. E. Martell, 'Stability Constants of Metal-ion Complexes, published from The Chemical Society, London (1964), and by S. Chaberek and A. E. Martell, 'Organic Sequestering Agents, Wiley (1959).

Examples of chelating agents having a chelating stability of 8 or more to ferric ions (Fe^{3+}) include organic carboxylic acid chelating agents, organic phosphoric acid chelating agents, inorganic phosphoric acid chelating agents and polyhydroxy compounds.

The using amount of the chelating agent is preferably 0.01 to 50g, and more preferably 0.05 to 20g per liter of the stabilizing solution.

Preferred compounds as additives to the stabilizing solution include ammonium compounds, which may be provided in the form of ammonium salts of various inorganic compounds; these may be used alone or in combination. The adding amount of the ammonium compound is preferably 0.001 to 1.0 mol, more preferably 0.002 to 2.0 mols per liter of the stabilizing solution.

Further, it is preferable to have the stabilizing solution contain a sulfite. Any sulfite, organic or inorganic, may be used as long as it releases a sulfite ion, but preferably usable is an inorganic salt, examples of which include sodium sulfite, potassium sulfite, ammonium sulfite, ammonium hydrogensulfite, potassium hydrogensulfite, sodium hydrogensulfite, sodium metabisulfite, potassium metabisulfite, ammonium metabisulfite and hydrosulfite. Any of these sulfites is added in an amount to make a concentration of preferably at least $1x10^{-3}$ mol, more preferably $5x10^{-3}$ to 10^{-1} mol per liter of the stabilizing solution, particularly for antistain effect. The sulfite may be added directly to the stabilizing solution, but is preferably added to a replenisher to the stabilizing bath.

Those generally known as additives except the above compounds to the stabilizing solution include polyvinylpyrrolidones (PVP K-15, K-30, K-90); organic salts such as citrates. acetates, succinates, oxalates and maleates; pH adjusting agents such as phosphates, borates, hydrochloric acid and sulfuric acid; fungicides such as phenol derivatives, catechol derivatives, imidazole derivatives, triazole derivatives, thiabendazole derivatives, organic halide compounds and other fungicides known as the slime-control agent for use in the paper-pulp industry; and further, brightening agents, surface active agents, preservatives and metallic salts such as of Bi, Mg, Zn, Ni, Al, Sn, Ti and Zr. These compounds may be used alone or in combination.

A light-sensitive material, after being processed in the stabilizing solution, requires no washing treatment at all. However, the light-sensitive material may, if necessary, be discretionarily subjected to a short-time rinse or surface washing with only a slight amount of water.

In the invention, there may be used a stabilizing solution subjected to ion-exchange resin treatment to have its calcium ion content and magnesium ion content reduced to 5 ppm or less, and further, there may be used a method for incorporating the foregoing fungicide and halogen ion-releasing compound into this stabilizing solution.

The pH range of the fixing solution of the invention is preferably 5.5 to 10.0. The pH adjusting agent to be contained in the stabilizing solution can be any of generally known alkali agents or acidic agents.

The processing temperature range in the stabilizing bath is preferably 15 to 70°C, and more preferably 20 to 55°C. The processing time is preferably not longer than 120 seconds, more preferably 3 to 90 seconds and most preferably 6 to 50 seconds.

The amount of a replenisher to the stabilizing bath is preferably 0.1 to 50 times, and more preferably 0.5 to 30 times the carry-in amount per unit area of a light-sensitive material from the preceding fixing bath.

The stabilizing bath is preferred to be comprised of a plurality of baths, preferably not less than 2 baths and not more than 6 baths, more preferably 2 to 3 baths, and most preferably 2 baths in a counter-current system, i.e., a system in which a liquid supply is made to the subsequent bath and overflow is made from the preceding bath.

EXAMPLES

Example 1

A 20% amount of sulfite bleached soft wood pulp (NBSP) beaten by a refiner up to Canadian standard freeness (JIS P-8121-76) of 250 ml and an 80% amount of sulfite bleached hard wood pulp (LBSP) beaten in the same manner up to the same freeness of 280 ml were mixed to be used as a raw material for manufacturing paper.

Additives for paper making were added in the following proportions by weight to the absolute dry weight of the pulp.

Cationized starch	2.0 %
Alkylketene dimer resin	0.4 %
Anionic polyacrylamide resin	0.1 %
Polyamidopolyamine-epichlorohydrin resin	0.7 %
pH adjusted to 7.5 with sodium hydroxide.	

The above additives-containing material was subjected to Fourdrinier-paper-machine treatment, and then to size-press and machine-calender treatments, whereby a paper having a weight of 170g/m^2, bulk density of 1.0 and a moisture of 8% was produced. As the press sizing solution agent, a 5% sizing liquid prepared by dissolving carboxyl-modified PVA and sodium chloride in a proportion of 2:1 in water was used and coated in a coating weight of 2.2g/m^2 on both sides of the paper.

Both sides of the obtained paper were subjected to corona discharge treatment, and then on the obverse side was formed by an extrusion coating method a 35µm-thick polyolefin resin coat layer comprising high-density polyethylene (S.G. = 0.94, MI = 6.8) containing anatase-type titanium dioxide in a concentration as given in Table 1, while on the reverse side was formed by an extrusion coating method a polyethylene resin coat layer containing no titanium dioxide, and the thus obtained product was pressed against a cleaning roller having a smooth surface at 20 °C, whereby a photographic paper support having a SRa value as shown in Table 1.

Table 1

Sample No.	Support		Gelatin						Preservative	Processing condition
	Titanium dioxide	SRa	Layer							
			5	4	3	2	1	whole		
1 (Comp.)	12%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	—	B
2 (Comp.)	15%	1.20	1.2	0.9	1.2	1.1	1.2	7.2	—	B
3 (Comp.)	15%	0.08	1.4	0.9	1.4	1.2	1.3	7.8	—	B
4 (Inv.)	15%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	—	B
5 (Inv.)	15%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	V-1(0.002)	B
6 (Inv.)	15%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	VI-1(0.002)	B
7 (Inv.)	15%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	IV-3(0.002)	B
8 (Inv.)	18%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	—	B
9 (Inv.)	21%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	—	B
10 (Inv.)	15%	1.0	1.2	0.9	1.2	1.1	1.2	7.2	—	B
11 (Inv.)	15%	0.06	1.2	0.9	1.2	1.1	1.2	7.2	—	B
12 (Inv.)	15%	0.08	1.3	0.9	1.3	1.2	1.2	7.5	—	B
13 (Inv.)	15%	0.08	1.1	0.7	1.1	1.0	1.0	6.5	—	B
14 (Comp.)	15%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	—	A
15 (Comp.)	12%	0.08	1.2	0.9	1.2	1.1	1.2	7.2	—	A
16 (Comp.)	15%	1.20	1.2	0.9	1.2	1.1	1.2	7.2	—	A
17 (Comp.)	15%	0.08	1.4	0.9	1.4	1.2	1.3	7.8	—	A

On the thus prepared support were coated layers having the compositions shown in Tables 2 and 3 in accordance with a continuous simultaneous multilayer slide hopper coating method, whereby multilayer color light-sensitive material Samples 1 to 17 were prepared. The coating liquids were prepared as follows:

Coating liquid for Layer 1

Twenty-six point seven grams of yellow coupler Y-1, 10.0g of dye image stabilizer ST-1, 6.67g of ST-2 and 0.67g of additive HQ-1 were dissolved in 6.67g of a high-boiling solvent DNP with 60 ml of ethyl acetate, and this solution was emulsifiedly dispersed by means of a supersonic homogenizer into 220ml of an aqueous 10% gelatin solution containing 7ml of 20% surfactant SU-1 to thereby prepare a yellow coupler dispersion. The obtained dispersion was mixed with a blue-sensitive silver halide emulsion (containing 10g of silver) prepared under the hereinafter described conditions, whereby a coating liquid for Layer 1 was prepared.

Coating liquids for Layers 2 to 7 also were prepared in similar manner to the liquid for Layer 1. As hardeners, H-1 was added to Layers 2 and 4, and H-2 to Layer 7. As coating aids, surfactants SU-2 and SU-3 were added to each coating liquid to adjust its surface tension.

Table 2

Layer	Composition	Added amt(g/m^2)
Layer 7 (protective layer)	Gelatin Antistain agent HQ-2 Antistain agent HQ-3 Antistain agent HQ-4 Antistain agent HQ-5 DIDP Fungicide (Table 1)	1.20 0.002 0.002 0.004 0.02 0.01 (Table 1)
Layer 6 (UV absorbing layer)	Gelatin UV absorbent UV-1 UV absorbent UV-2 UV absorbent UV-3 Antistain agent HQ-5 DNP PVP Antiirradiation dye AI-2 Antiirradiation dye AI-4	0.40 0.10 0.04 0.16 0.04 0.45 0.03 0.02 0.01
Layer 5 (Red-sensitive layer)	Gelatin Red-sensitive silver chlorobromide emulsion Em-R Cyan coupler C-1 Cyan coupler C-2 Dye image stabilizer ST-1 Antistain agent HQ-1 HBS-1 DOP	Table 1 0.21 0.17 0.25 0.20 0.01 0.40 0.40

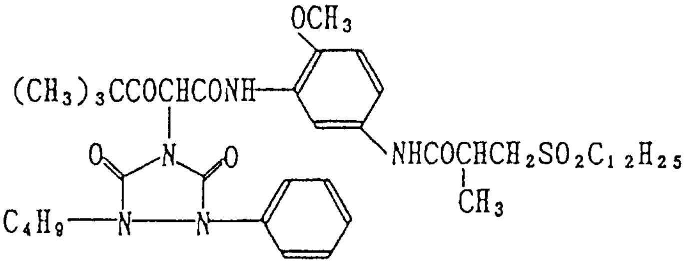
Table 3

Layer	Composition	Added amt(g/m^2)
Layer 4 (UV absorb-ing layer)	Gelatin	Table 1
	UV absorbent UV-1	0.28
	UV absorbent UV-2	0.09
	UV absorbent UV-3	0.38
	Antistain agent HQ-5	0.10
	DNP	0.80
Layer 3 (Green-sensitive layer)	Gelatin	Table 1
	Green-sensitive silver chlorobromide emulsion Em-G	0.17
	Magenta coupler M-1	0.35
	Dye image stabilizer ST-3	0.20
	Dye image stabilizer ST-4	0.17
	DIDP	0.13
	DBP	0.15
	Antiirradiation dye AI-1	0.01
Layer 2 (Intermediate layer)	Gelatin	Table 1
	Antistain agent HQ-2	0.03
	Antistain agent HQ-3	0.03
	Antistain agent HQ-4	0.05
	Antistain agent HQ-5	0.23
	DIDP	0.20
Layer 1 (Blue-sensitive layer)	Gelatin	Table 1
	Blue-sensitive silver chlorobromide emulsion Em-B	0.26
	Yellow coupler Y-1	0.80
	Dye image stabilizer ST-1	0.30
	Dye image stabilizer ST-2	0.20
	Antistain agent HQ-1	0.02
	Antiirradiation dye AI-3	0.01
	DNP	0.40
Support	Polyethylene-laminated paper	

The additives used in the above layers are collectively shown below:

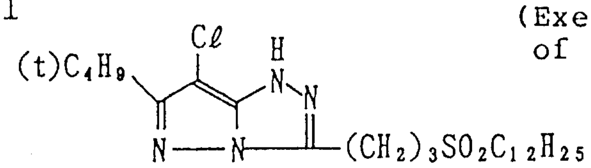
DBP:	Dibutyl phthalate
DOP:	Dioctyl phthalate
DNP:	Dinonyl phthalate
DIDP:	Di-i-decyl phthalate
PVP:	Polyvinylpyrrolidone
HQ-1:	2,5-di-t-octylhydroquinone
HQ-2:	2,5-di-sec-dodecylhydroquinone
HQ-3:	2,5-di-sec-tetradecylhydroquinone
HQ-4:	2-sec-dodecyl-5-sec-tetradecylhydroquinone
HQ-5:	2,5-di-(1,1-dimethyl-4-hexyloxycarbonylbutyl)-hydroquinone
HBS-1:	1-methyl-4-(4-dodecylphenyl)sulfamoylbenzene
SU-1:	Sodium tri-i-propylnaphthalenesulfonate
SU-2:	Sodium di-(2-ethylhexyl)sulfosuccinate
SU-3:	Sodium di-(2,2,3,3,4,4,5,5-octafluoropentyl)-sulfosuccinate
H-1:	Tetra(vinylsulfonylmethyl)methane
H-2:	Sodium 2,4-dichloro-6-hydroxy-s-triazine

Y − 1

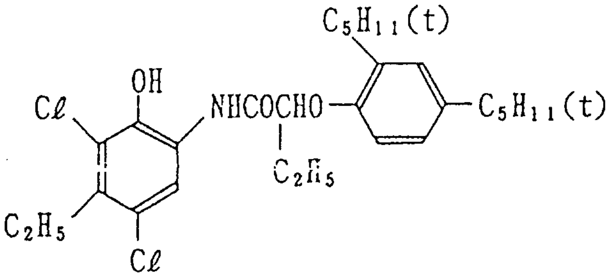


M - 1

(Exemplified compound M-2 of Formula M-I)



C - 1



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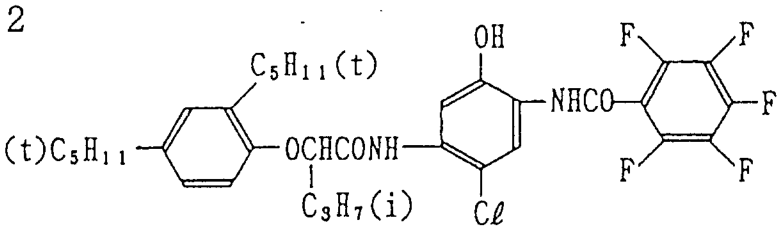
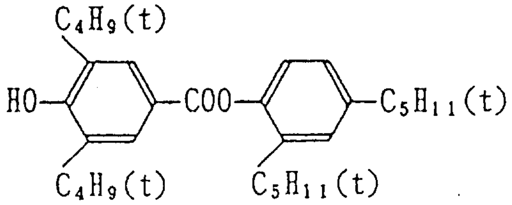
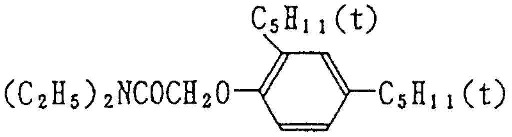


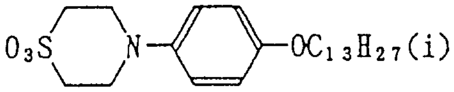
S T - 1



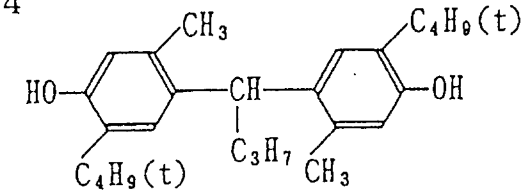
S T - 2



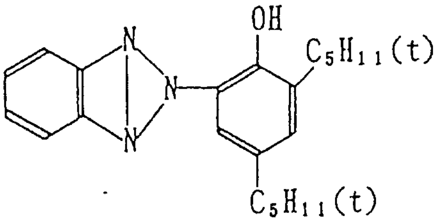
S T - 3



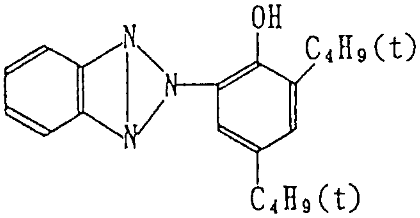
ST－4



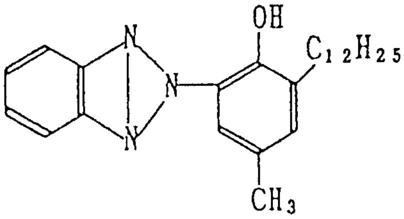
UV－1



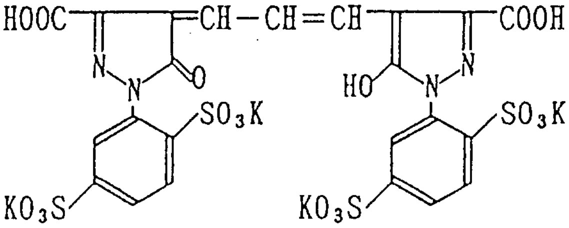
UV－2



UV－3



AI－1



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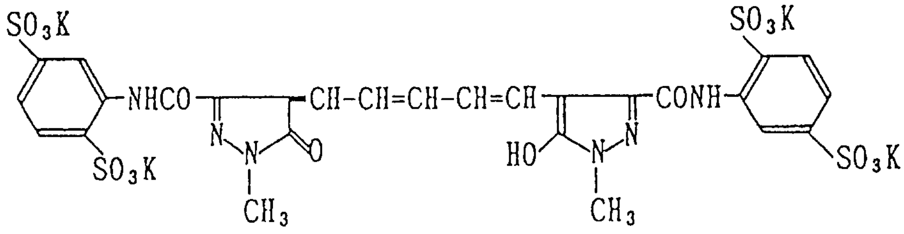

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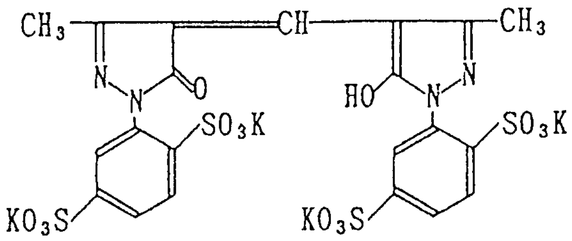
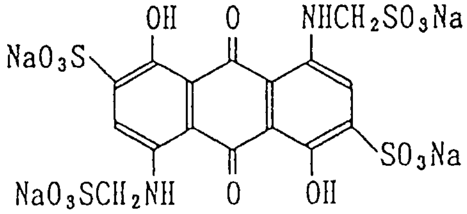


A I − 4



Preparation of blue-sensitive silver halide emulsion

The following Solution A and Solution B were simultaneously added spending 30 minutes to 1000 ml of an aqueous 2% gelatin solution kept at a temperature of 40 ° C with pAg and pH controlled to 6.5 and 3.0, respectively, and further the following Solution C and Solution D were simultaneously added spending 180 minutes thereto with pAg and pH controlled to 7.3 and 5.5, respectively, wherein the pAg control was conducted according to the method described in JP O.P.I. No. 45437/1984, and the pH control was made with use of an aqueous solution of sulfuric acid or sodium hydroxide.

Solution A	
Sodium chloride	3.42g
Potassium bromide	0.03g
Water to make	200 ml

Solution B	
Silver nitrate	10 g
Water to make	200 ml

Solution C	
Sodium chloride	102.7g
Potassium bromide	1.0g
Water to make	600 ml

Solution D	
Silver nitrate	300 g
Water to make	600 ml

After completion of the addition of the solutions, the emulsion was desalted by use of a 5% aqueous solution of Demol N, manufactured by Koa Atlas Co., and a 20% aqueous solution of magnesium sulfate, and mixed with a gelatin solution to obtain a monodisperse cubic emulsion EMP-1, which has an average grain size of 0.85 µm, a variation coefficient of 0.07 and a silver chloride content of 99.5 mol%.

The above emulsion EMP-1 was subjected to a 90-minute chemical ripening treatment at 50 °C with use of the following compounds, whereby a blue-sensitive silver halide emulsion Em-B was obtained.

Sodium thiosulfate	0.8mg/mol AgX
Chloroauric acid	0.5mg/mol AgX
Stabilizer STAB-1	$6x10^{-4}$ mol/mol AgX
Sensitizing dye BS-1	$4x10^{-4}$ mol/mol AgX
Sensitizing dye BS-2	$1x10^{-4}$ mol/mol AgX

Preparation of green-sensitive silver halide emulsion

A monodisperse cubic grains emulsion EMP-2, having an average grain size of 0.43µm, a coefficient of variation of 0.08 and a silver chloride content of 99.5 mol%, was obtained in the same manner as in EMP-1 except that the adding period of time of Solutions A and B and that of Solutions C and D were changed.

The emulsion EMP-2 was subjected to a 120-minute chemical ripening treatment at 55 °C with use of the following compounds, whereby a green-sensitive silver halide emulsion Em-G was obtained.

Sodium thiosulfate	1.5mg/mol AgX
Chloroauric acid	1.0mg/mol AgX
Stabilizer STAB-1	$6x10^{-4}$ mol/mol AgX
Sensitizing dye GS-1	$4x10^{-4}$ mol/mol AgX

Preparation of red-sensitive silver halide emulsion

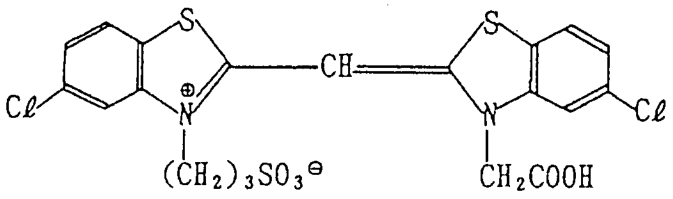
A monodisperse cubic grains emulsion EMP-3, having an average grain size of 0.50µm, a coefficient of variation of 0.08 and a silver chloride content of 99.5 mol%, was obtained in the same manner as in EMP-1 except that the adding period of time of Solutions A and B and that of Solutions C and D were changed.

EMP-3 was chemically ripened for 90 minutes at 60 °C with use of the following compounds, whereby a red-sensitive silver halide emulsion Em-R was obtained.

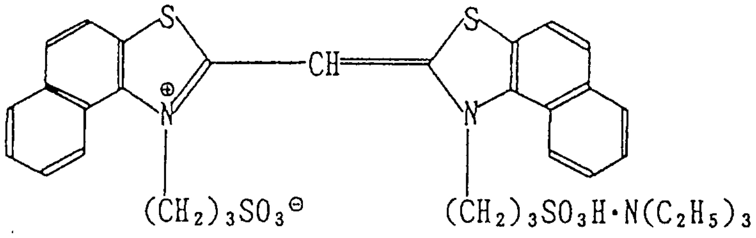
Sodium thiosulfate	1.8mg/mol AgX
Chloroauric acid	2.0mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye RS-1	1×10^{-4} mol/mol AgX

STAB-1: 1-(3-acetamidophenyl)-5-mercaptotetrazole

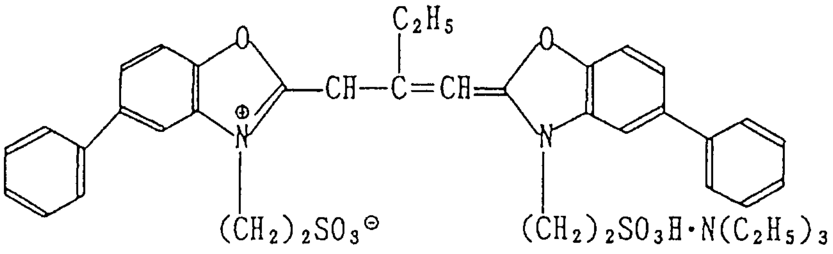
BS-1



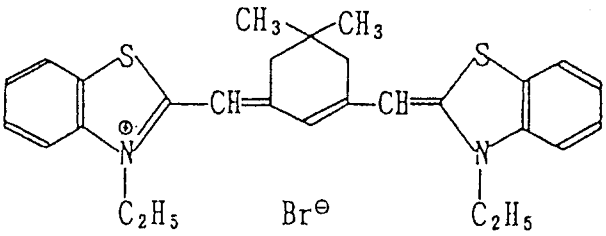
BS-2



GS-1



RS-1



Each of the prepared color paper samples shown in Table 1, after being exposed through an optical wedge, was subjected to running processing tests under the following conditions. The running tests were carried out by repeating the developing and replenishing procedures, spending 14 days, up to the time when the whole used color developer replenisher amounts to double the volume of the color developer bath.

Processing condition A

Processing step	Temperature	Time	Rep. amt*
(1) Color developing	35.0±0.3 ° C	45 seconds	160 ml
(2) Bleach-fixing	35.0±0.5 ° C	60 seconds	160 ml
(3) Stabilizing (Tribath cascade)	30 to 34 ° C	90 seconds	240 ml
(4) Drying	60 to 80 ° C	30 seconds	

*Replenishing amount: A value per m^2 of a light-sensitive material processed.

Color developer bath

Triethanolamine	10 g
Diethylene glycol	5 g
N,N-diethylhydroxylamine	5.0g
Potassium bromide	0.02g
Potassium chloride	2 g
Diethylenetriaminepentaacetic acid	5 g
Potassium sulfite	0.2g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate	5.2g
Potassium carbonate	25 g
Potassium hydrogencarbonate	5 g

Water to make 1000 ml

Adjust pH to 10.10 with use of potassium hydroxide or sulfuric acid.

Color developer replenisher

Triethanolamine	14.0g
Diethylene glycol	8.0g
N,N-diethylhydroxylamine	6.0g
Potassium chloride	1.3g
Diethylenetriaminepentaacetic acid	7.5g
Potassium sulfite	0.3g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate	7.8g
Potassium carbonate	30 g
Potassium hydrogencarbonate	1 g

Water to make 1000 ml

Adjust pH to 10.60 with use of potassium hydroxide or sulfuric acid.

Bleach-fix solution and replenisher thereto

Ferric ammonium ethylenediaminetetraacetate	100 g
Ethylenediaminetetraacetic acid	3.0g
Ammonium thiosulfate (70% solution)	150 g
Ammonium sulfite (40% solution)	51.0g
Use ammonia water or glacial acetic acid to adjust pH to 6.0, and add water to make the whole 1000 ml.	

Stabilizing solution and replenisher thereto

o-Phenylphenol	0.2g
Brightening agent, Uvitex CK (product of Ciba Geigy)	1.0g
Lead sulfate	0.5g
Ammonium sulfite (40% solution)	5.0 ml
1-Hydroxyethylidene-1,1-diphosphonic acid (60% solution)	5.0g
Ethylenediaminetetraacetic acid	1.5g
Benzoisothiazolin-3-one	0.2g
Use ammonia water or sulfuric acid to adjust pH to 7.8, and add water to make 1000 ml.	

Processing condition B

Processing step	Temperature	Time	Rep. amt. (ml/m^2)
(1) Color developing	35 °C	45 seconds	160
(2) Bleaching	38 °C	20 seconds	30
(3) Fixing	38 °C	20 seconds	30
(4) Stabilising*	30 °C	90 seconds	240
(5) Drying	60 to 80 °C	30 seconds	--

*Stabilizing: tribath cascade system.

Color developer

Diethylene glycol	15 g
Potassium bromide	0.02g
Potassium chloride	2.0g
Potassium sulfite (50% solution)	0.5 ml
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate	6 g
Diethylhydroxylamine (85% solution)	5 g
Triethanolamine	10 g
Potassium carbonate	30 g
Ethylenediaminetetraacetic acid	2 g
Brightening agent (PK-Conc, produced by Nippon Soda Co.)	2 g
Water to make 1000 ml Adjust pH to 10.15 with potassium hydroxide or sulfuric acid.	

Color developer replenisher

Diethylene glycol	17 g
Potassium chloride	3 g
Potassium sulfite (50% solution)	1.0 ml
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate	8.8g
Diethylhydroxylamine (85% solution)	7 g
Triethanolamine	10 g
Potassium carbonate	30 g
Ethylenediaminetetraacetic acid	2 g
Brightening agent (PK-Conc, produced by Nippon Soda Co.)	2.5g
Water to make 1000 ml Adjust pH to 11.0 with use of potassium hydroxide or sulfuric acid.	

Bleaching solution

Ferric sodium organic acid salt A-1	100 g
Ethylenediaminetetraacetic acid	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml
Water to make 1000 ml Adjust Ph to 7.0 with use of ammonium water or glacial acetic acid.	

Bleaching solution replenisher

Ferric sodium organic acid salt A-1	120 g
Ethylenediaminetetraacetic acid	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml
Water to make 1000 ml Adjust pH to 6.3 with use of ammonia water or glacial acetic acid.	

Fixing solution and replenisher thereto

Ammonium thiosulfate	180 g
Ammonium thiocyanate	120 g
Sodium metabisulfite	3 g
Ethylenediaminetetraacetic acid	0.8g
Water make 1000 ml Adjust pH to 6.5 with acetic acid or ammonia water.	

Stabilizing solution and replenisher thereto

o-Phenylphenol	0.15g
Zinc sulfate, heptahydrate	0.2g
Ammonium sulfite (40% solution)	5.0ml
1-Hydroxyethylidene-1,1-diphosphonic acid (60% solution)	2.5g
Ethylenediaminetetraacetic acid	2.0g
Brightening agent (Tinopal SFP, produced by Ciba Geigy)	2.0g
Ammonia water or sulfuric acid to adjust pH to 7.8, and water to make 1000 ml.	

The photographic characteristics of each sample subjected to the above running processing test were evaluated as follows.

Sharpness

Each sample was exposed by being brought into contact with a resolution chart to a white light and subjected to the above running processing to thereby form a chart image on the sample. The wedge section of the formed chart image was measured by means of a microphotometer with respect to its yellow, magenta and cyan color components to thereby evaluate the sharpness of the sample.

$$\text{Sharpness} = \frac{\text{Dmax} - \text{Dmin in the 3 lines/mm line pattern of print image}}{\text{Dmax} - \text{Dmin in the broad space section of print image}}$$

The evaluation was made on the basis of the average of the sharpness values of yellow, magenta and cyan images; the larger the average value, the more excellent the sharpness of the sample; 50% or above is excellent.

Glossiness

The entire area of each sample was exposed to a white light; then subjected to the running processing; and the processed sample's surface glossiness was visually evaluated.

A Clear, glass-surface-like, brilliant print surface with smooth support.
B Slightly blurred surface, but acceptable for practical use.
C Blurred, dim surface with unsmooth support.

Coating uniformity

Each sample was uniformly exposed through a color separation filter to a white light so that a grey density of about 1.0 can be obtained, then subjected to the running processing, and after that, the processed sample was visually evaluated with respect to the degree of its coating uniformity.

A The coated layer's thickness is uniform; no density unevenness appears even in solid density areas.
B The thickness is slightly not uniform, but acceptable for practical use.
C The thickness is not uniform to cause density unevenness, which is conspicuous in solid density areas, leading to degradation of image quality.

Short-term image preservability

Each sample was exposed through a color separation filter with an optical wedge to a white light, and subjected to the running processing. The processed image was measured with respect to its initial density right after the processing and also with respect to its density after three months of its storage under conditions of 23 °C/70%RH, and on the basis of the difference between both the densities, the short-term image preservability of each sample was evaluated.

Stain: Rated according to increase/decrease in the density measured using blue light

Less than 0.01 .... acceptable
0.01 or more ...... unacceptable

Image density: Rated according to changes in the density value obtained when measuring a density point of 1.0 in blue light.

Less than 0.05 .... acceptable
0.05 or more ...... unacceptable

The results are shown in Table 4.

Table 4

Sample No.	Sharp-ness(%)	Gloss	Coating uniformity	Short-term image preservability	
				Stain	Image density
1 (Comp.)	45	A	A	+0.024	+0.05
2 (Comp.)	52	C	A	+0.005	+0.05
3 (Comp.)	55	A	C	+0.021	+0.03
4 (Inv.)	56	A	A	+0.005	+0.04
5 (Inv.)	56	A	A	+0.004	+0.02
6 (Inv.)	55	A	A	+0.004	+0.02
7 (Inv.)	56	A	A	+0.005	+0.02
8 (Inv.)	60	A	A	+0.003	+0.04
9 (Inv.)	62	A	A	+0.003	+0.04
10 (Inv.)	54	B	A	+0.005	+0.04
11 (Inv.)	56	A	B	+0.005	+0.04
12 (Inv.)	55	A	B	+0.008	+0.02
13 (Inv.)	58	A	A	+0.003	+0.05
14 (Comp.)	56	A	A	+0.005	+0.09
15 (Comp.)	46	A	A	+0.008	+0.10
16 (Comp.)	52	C	A	+0.004	+0.10
17 (Comp.)	55	A	C	+0.007	+0.04

As is apparent from Table 4, the samples 4 to 13 for the invention are satisfactory in all the photographic characteristics.

Example 2

On a triacetyl cellulose film support were formed layers having the following compositions in order from the support side, whereby a multilayer color negative light-sensitive material samples were prepared.

The values shown in the following are the respective additives' adding amounts per m^2 except that silver halide and colloidal silver are shown in silver equivalents, while sensitizing dyes are in molar values per mol of silver contained in the same layer.

Layer 1: Antihalation layer	
Black colloidal silver	0.2g
UV absorbent UV-4	0.23g
High-boiling solvent Oil-1	0.18g
Gelatin	1.4g

Laer 2: First intermediate layer	
Gelatin	1.3g

Layer 3: Low-speed red-sensitive emulsion layer	
Silver iodobromide emulsion (average grain size: 0.4μm, AgI: 2.0 mol%)	1.0g
Sensitizing dye SD-1	1.8x10^{-5} mol
Sensitiaing dye SD-2	2.8x10^{-4} mol
Sensitizing dye SD-3	3.0x10^{-4} mol
Cyan coupler C-3	0.70g
Colored cyan coupler CC-1	0.066g
DIR compound D-1	0.03g
DIR compound D-3	0.01g
High-boiling solvent Oil-1	0.64g
Gelatin	1.2g

Layer 4: Medium-speed red-sensitive emulsion layer	
Silver iodobromide emulsion (average grain size: 0.7μm, AgI: 8.0 mol%)	0.8g
Sensitizing dye SD-1	2.1x10^{-5} mol
Sensitizing dye SD-2	1.9x10^{-4} mol
Sensitizing dye SD-3	1.9x10^{-4} mol
Cyan coupler C-3	0.28g
Colored cyan coupler CC-1	0.027g
DIR compound D-1	0.01g
High-boiling solvent Oil-1	0.26g
Gelatin	0.6g

Layer 5: High-speed red-sensitive emulsion layer	
Silver iodobromide emulsion (average grain size: 0.8μm, AgI: 8.0 mol%)	1.7 g
Sensitizing dye SD-1	1.9x10^{-5} mol
Sensitizing dye SD-2	1.7x10^{-4} mol
Sensitizing dye SD-3	1.7x10^{-4} mol
Cyan coupler C-3	0.05g
Cyan coupler C-4	0.10g
Colored cyan coupler CC-1	0.02g
DIR compound D-1	0.0025g
High-boiling solvent Oil-1	0.17g
Gelatin	1.2g

Layer 6: Second intermediate layer	
Gelatin	0.8g

Layer 7: Low-speed green-sensitive emulsion layer	
Silver iodobromide emulsion (average grain size: 0.4µm, AgI: 2.0 mol%)	1.1g
Sensitizing dye SD-4	6.8x10^{-5} mol
Sensitizing dye SD-5	6.2x10^{-4} mol
Magenta coupler M-2	0.54g
Magenta coupler M-3	0.19g
Colored magenta coupler CM-1	0.06g
DIR compound D-2	0.017g
DIR compound D-3	0.01g
High-boiling solvent Oil-2	0.81g
Gelatin	1.8g

Layer 8: Medium-speed green-sensitive emulsion layer	
Silver iodobromide emulsion (average grain size: 0.7µm, AgI: 8.0 mol%)	0.7g
Sensitizing dye SD-6	1.9x10^{-4} mol
Sensitizing dye SD-7	1.2x10^{-4} mol
Sensitizing dye SD-8	1.5x10^{-5} mol
Magenta coupler M-2	0.07g
Magenta coupler M-3	0.03g
Colored magenta coupler CM-1	0.04g
DIR compound D-2	0.018g
High-boiling solvent Oil-2	0.30g
Gelatin	0.8g

Layer 9: High-speed green-sensitive emulsion layer	
Silver iodobromide emulsion (average grain size: 1.0µm, AgI: 8.0 mol%)	1.7g
Sensitizing dye SD-6	1.2x10^{-4} mol
Sensitizing dye SD-7	1.9x10^{-4} mol
Sensitizing dye SD-8	3.4x10^{-6} mol
Magenta coupler M-2	0.09g
Magenta coupler M-4	0.04g
Colored magenta coupler CM-1	0.04g
High-boiling solvent Oil-2	0.31g
Gelatin	1.2g

Layer 10: Yellow filter layer	
Yellow colloidal silver	0.05g
Antistain agent SC-1	0.1g
High-boiling solvent Oil-2	0.13g
Gelatin	0.7g
Formalin scavenger HS-1	0.09g
Formalin scanvenger HS-2	0.07g

Layer 11: Low-speed blue-sensitive emulsion layer	
A mixture of Silver iodobromide emulsion (average grain size: 0.4µm, AgI: 2.0 mol%) and silver iodobromide emulsion (average grain size: 0.7µm, AgI: 8.0 mol%)	0.5g
Sensitizing dye SD-9	$5.2x10^{-4}$ mol
Sensitizing dye SD-10	$1.9x10^{-5}$ mol
Yellow coupler Y-2	0.65g
Yellow coupler Y-3	0.24g
DIR compound D-1	0.03g
High-boiling solvent Oil-2	0.18g
Gelatin	1.3g

Layer 12: High-speed blue-sensitive emulsion layer	
Silver iodobromide emulsion (average grain size: 1.0µm, AgI: 8.0 mol%)	1.0g
Sensitizing dye SD-9	$1.8x10^{-4}$ mol
Sensitizing dye SD-10	$7.9x10^{-5}$ mol
Yellow coupler Y-2	0.15g
Yellow coupler Y-3	0.05g
High-boiling solvent Oil-2	0.074g
Gelatin	1.30g
Formalin scavenger HS-1	0.05g
Formalin scavenger HS-2	0.12g

Layer 13: First protective layer	
Fine-grained silver iodobromide emulsion (average grain size: 0.08µm, AgI: 1.0 mol%)	0.4g
UV absorbent UV-4	0.07g
UV absorbent UV-5	0.10g
High-boiling solvent Oil-1	0.07g
High-boiling solvent Oil-3	0.07g
Formalin scavenger HS-1	0.13g
Formalin scavenger HS-2	0.37g
Gelatin	1.3g

Layer 14: Second protective layer	
Alkali-soluble matting agent (average particle size: 2µm)	0.13g
Methyl methacrylate (average particle size: 3µm)	0.02g
Lubricant WAX-1	0.04g
Gelatin	0.6g

In addition to the above compositions, coating aid SU-4, dispersion assistant SU-1, viscosity adjusting agent, hardeners H-2 and H-3, stabilizer ST-11, antifoggants AF-1 and two kinds of AF-2 having weight average molecular weights of 10,000 and 100,000, respectively, were added to the respective layers.

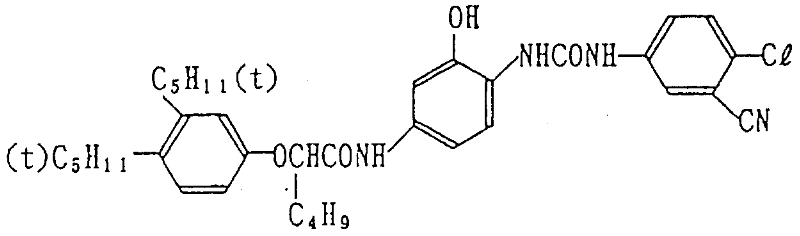
The emulsions used in the above sample were prepared in conventional manner similar to that of Example 1. Each emulsion was optimally subjected to gold/sulfur sensitization. The average grain size is the length of a side of a cube equivalent in the volume to an averaged grain.

The additives used in preparation of the above sample are as follows:

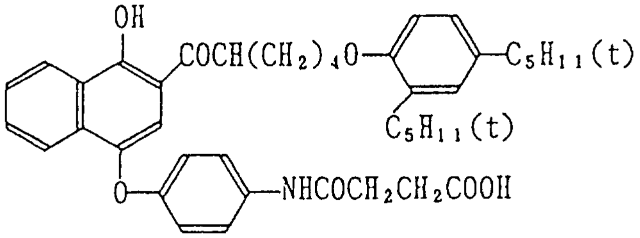
Oil-1: Dioctyl phthalate
Oil-2: Tricresyl phosphate
Oil-3: Dibutyl phthalate
SC-1: 2-sec-octadecyl-5-methylhydroquinone

SU-4: Sodium dioctyl sulfosuccinate
HS-1: 4-ureidohydantoin
HS-2: Hydantoin
H-3: Bis(vinylsulfonylmethyl) ether
ST-11: 4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene
AF-1: 1-Phenyl-5-mercaptotetrazole
AF-2: Poly-N-vinylpyrrolidone

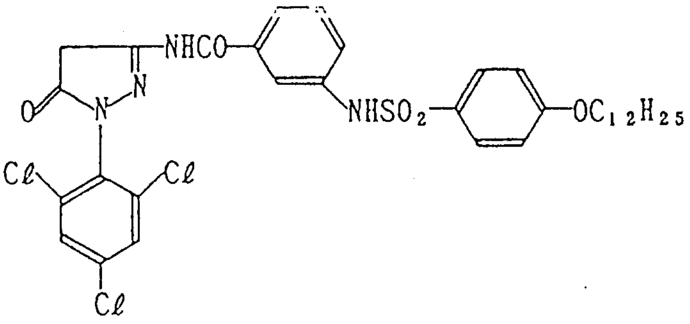
C - 3



C - 4



M - 2



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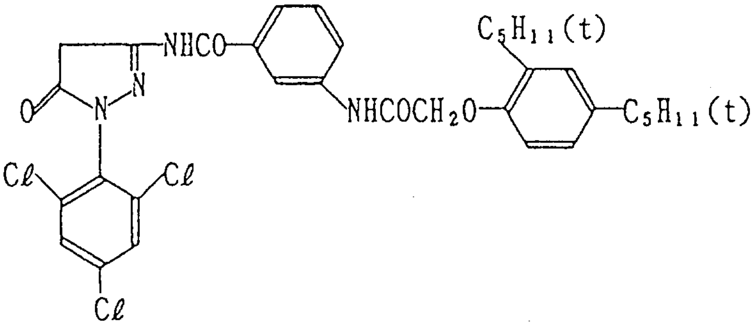
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C₅H₁₁(t)
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Cℓ
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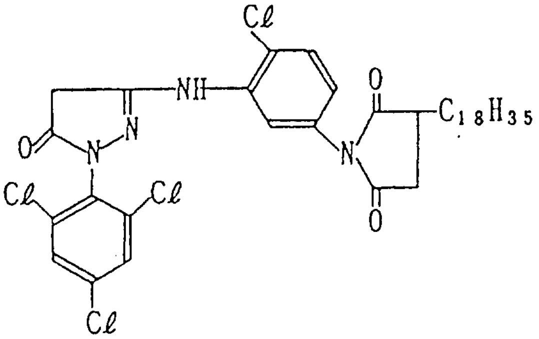
N
N

M − 4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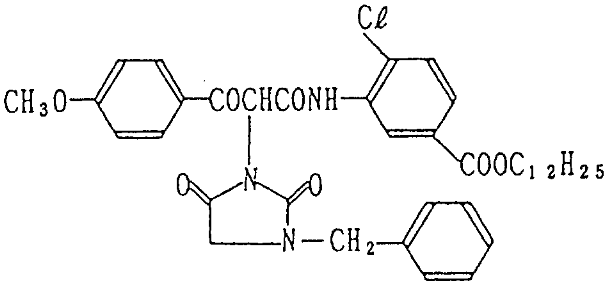
Y − 2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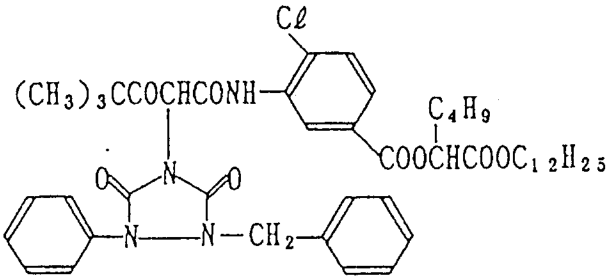
Y − 3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N
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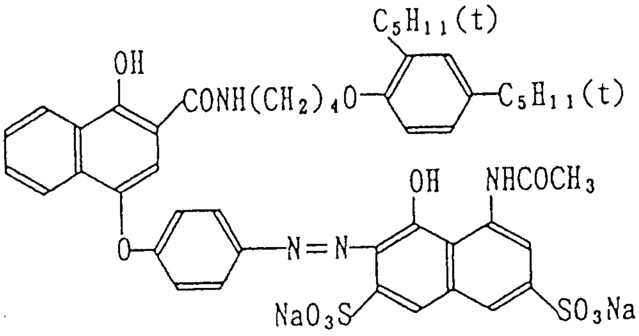
CC-1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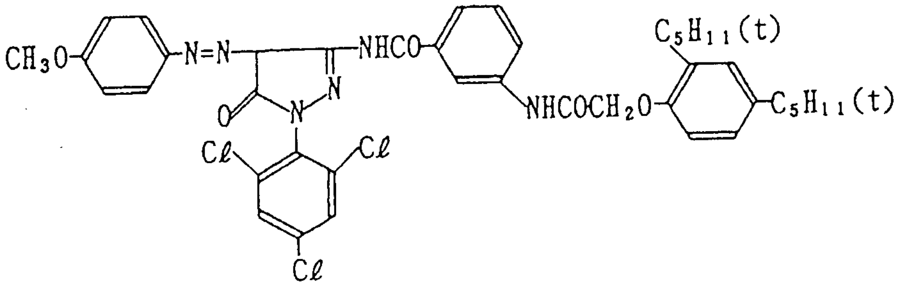
SO₃Na

CM-1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O
Cℓ
Cℓ
Cℓ
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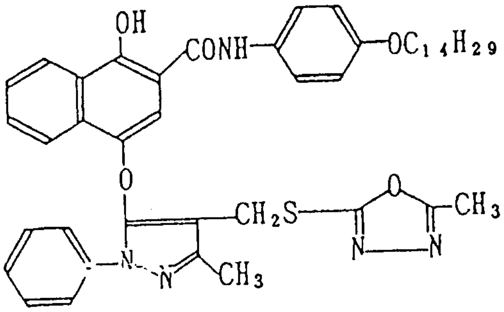
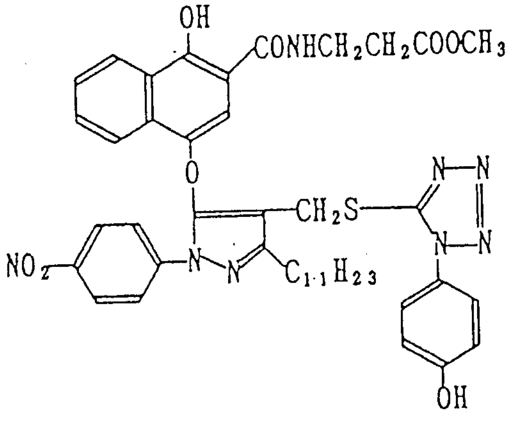
C₅H₁₁(t)

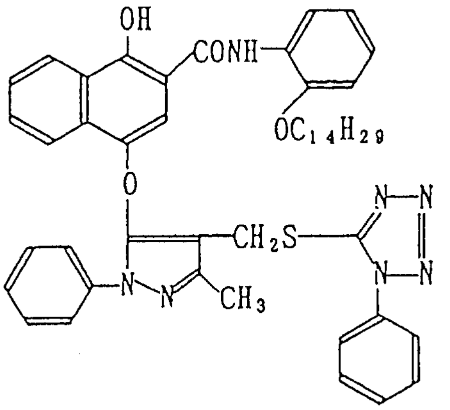
D-1


OH
CONH
OC₁₄H₂₉
O
CH₂S
O
CH₃
N
N
N
N
CH₃

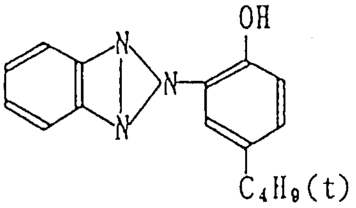
D-2


OH
CONHCH₂CH₂COOCH₃
O
CH₂S
N
N
N
N
NO₂
N
N
C₁₁H₂₃
OH

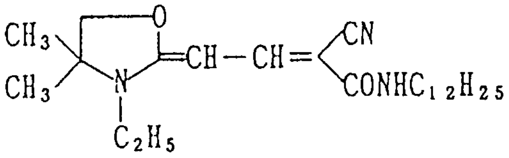
D − 3



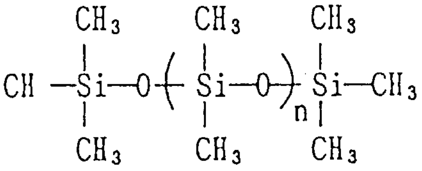
U V − 4



U V − 5



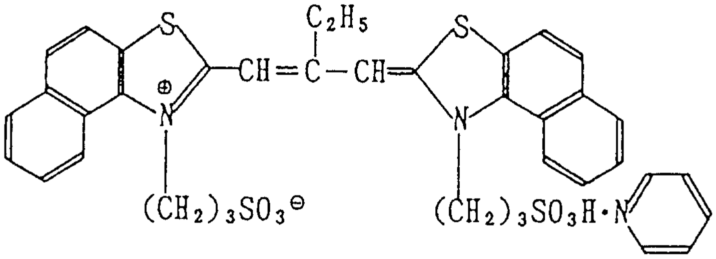
W A X − 1



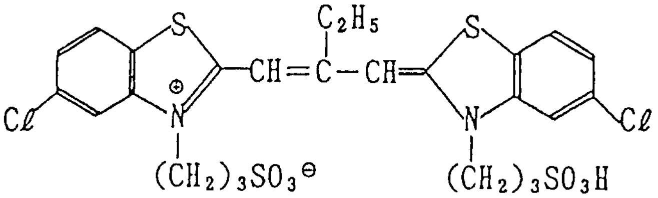
$$\mathrm{CH}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right)_n\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

Weight average molecular weight $\overline{Mw}$=30,000

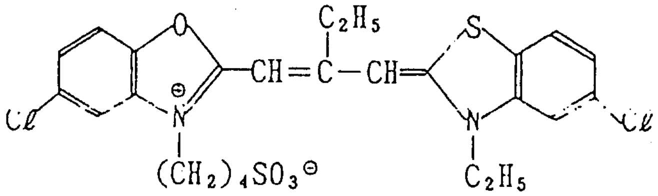
SD−1



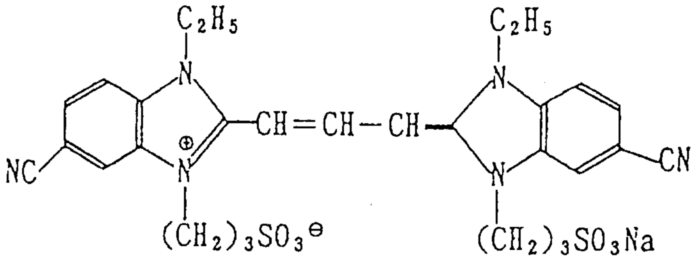
SD−2



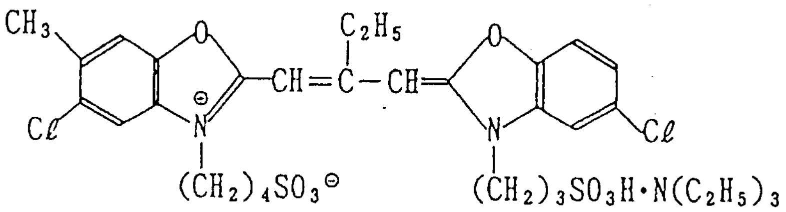
SD−3



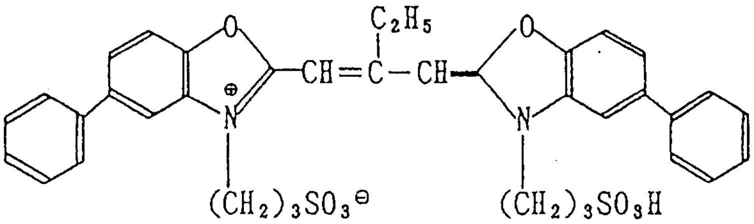
S−4



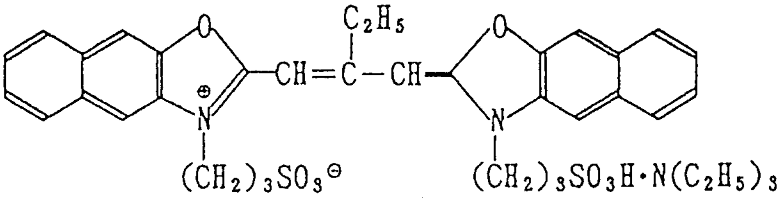
SD−5



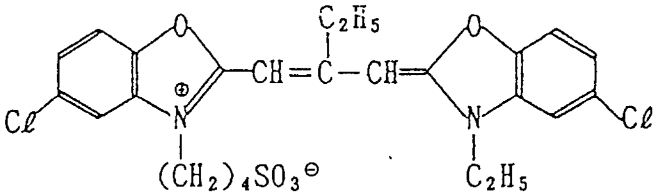
SD-6



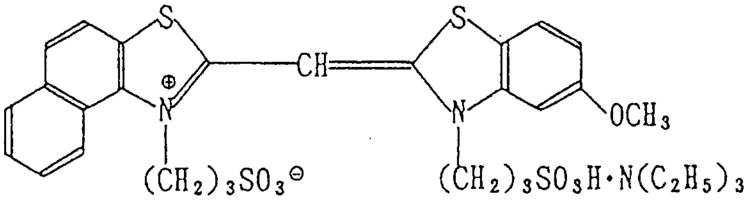
SD-7



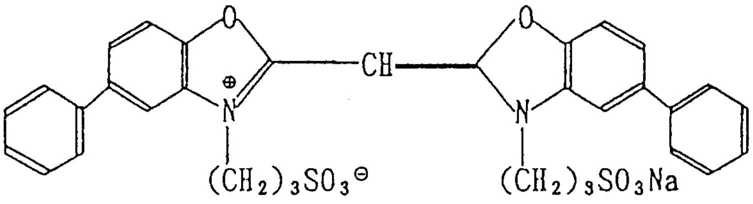
SD-8



SD-9



SD-10



The thus prepared sample was exposed through an wedge to white light, and processed under the following conditions:

Processing condition-C

Processing step	Time	Temperature	Rep. amt.*
Color developing	3 min. 15 sec.	38 ° C	536 ml
Bleaching	45 sec.	38 ° C	134 ml
Fixing	1 min. 30 sec.	38 ° C	536 ml
Stabilizing**	90 sec.	38 ° C	536 ml
Drying	1 min.	40 to 70 ° C	--

* Replenishing amount per m^2 of light-sensitive material

** Tribath counter-current system, in which replenishment was made to the final one of the three baths.

The compositions of the processing baths used in the above steps are as follows:

Color developer

Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5g
Potassium sulfite	3.0g
Sodium bromide	1.3g
Potassium iodide	1.2mg
Hydroxylamine sulfate	2.5g
Sodium chloride	0.6g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)-aniline sulfate	4.5g
Diethylenetriaminepentaacetic acid	3.0g
Potassium hydroxide	1.2g

Water to make 1000 ml

Adjust pH to 10.06 with use of potassium hydroxide or 20% sulfuric acid.

Color developer replenisher

Potassium carbonate	35 g
Potassium hydrogencarbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.4g
Hydroxylamine sulfate	3.1g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)-aniline sulfate	5.8g
Potassium hydroxide	2 g
Diethylenetriaminepentaacetic acid	3.0g

Water to make 1000 ml

Adjust pH to 10.12 with use of potassium hydroxide or 20% sulfuric acid.

The bleaching solution, fixing solution, stabilizing solution and the respective replenishers used in above are the same as those used in the processing condition-B of Example 1.

In parallel with the processing made under the above processing condition-C, another processing was conducted in the same manner as in the processing condition-B of Example 1 except that an overflow from the bleaching bath of the above processing condition-C was used as a replenisher to the bleaching bath for processing the exposed Samples 1 to 13 of Example 1; that is, they are as follows:

Processing condition-C (for color negative film)

(Color developer bath) - (Bleaching bath) - (fixer bath) - (stabilizer bath)

Processing condition-B (for color paper)

(Color developer bath) - (Bleaching bath) - (fixer bath) - (stabilizer bath)

Each processing bath has its own replenisher added thereto. All overflows from the bleaching baths in the above processes were employed as the replenisher to the bleaching bath in the process B to thus carry out running processing.

Namely, to carry out the running processing, pipe arrangement was made so as to cause all the overflow from the color negative film bleaching bath to flow in the color paper bleaching bath as a replenisher therefor. The running processing continuously took place until the bleaching solution inflow amounts to double the capacity of the color paper bleaching bath. As for the relation in the processing quantity between color paper and color negative film, the running processing was made in a proportion of 24 8.2cmX11.7cm-sized sheets of color paper per roll of 135-size color negative film for 24 exposures.

Samples 1 to 13 that were processed under the above conditions were evaluated in the same manner as in Example 1. The results are shown in Table 5.

Table 5

Sample No.	Sharpness(%)	Gloss	Coating uniformity	Short-term image preservability	
				Stain	Image density
1 (Comp.)	45	A	A	+0.024	+0.05
2 (Comp.)	53	C	A	+0.006	+0.04
3 (Comp.)	55	A	C	+0.022	+0.03
4 (Inv.)	57	A	A	+0.005	+0.03
5 (Inv.)	56	A	A	+0.004	+0.02
6 (Inv.)	56	A	A	+0.003	+0.01
7 (Inv.)	57	A	A	+0.004	+0.01
8 (Inv.)	60	A	A	+0.003	+0.03
9 (Inv.)	63	A	A	+0.003	+0.03
10 (Inv.)	54	B	A	+0.004	+0.03
11 (Inv.)	56	A	B	+0.004	+0.03
12 (Inv.)	56	A	B	+0.007	+0.02
13 (Inv.)	58	A	A	+0.003	+0.04

As is apparent from Table 5, the samples 4 to 13 for the invention are excellent in all the photographic characteristics.

Claims

1. A color dye image forming method comprising the steps of

imagewise exposing a silver halide color photographic light-sensitive material to light,
developing said light-sensitive material with a color developer,
fixing said developed light-sensitive material with a fixing solution, and
stabilizing said fixed light-sensitive material with a stabilizing solution,
wherein said light-sensitive material comprises

a paper support for photographic paper having polyolefin layers each provided on both side of said support, and a photographic layer including at least one silver halide emulsion layer provided on a surface of said support, and

a polyolefin layer provided on the surface of said support on which said photographic layer to be provided contains titanium oxide particles in an amount of not less than 14 % by weight of said polyolefin and has a roughness in terms of arithmetical mean deviation of the profile SRa calculated by the following equation of not more than 0.1 μm, and said photographic layer contains gelatin in an amount of not more than 7.5 g/m^2;

$$SRa = \frac{1}{SA} \int_0^{Lx} \int_0^{Ly} | f (x,y) | dx, dy$$

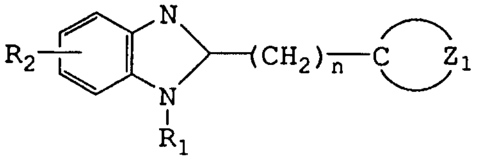
wherein Lx is the length of measured area in the direction of X axis; Ly is the length of measured area in the direction of Y axis, S_A is the measured area, S_A = Lx × Ly,
S_A = 25mm^2 and Lx = Ly = 5mm.

2. The method of claim 1, wherein said value of SR_A is within the range of from 0.05 µm to 0.09 µm.

3. The method of claim 1, wherein content of said titanium oxide particles in said polyolefin layer is within the range of from 15 % to 18 % by weight of the polyolefin.

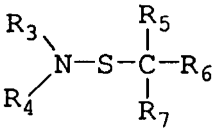
4. The method of claim 1, wherein said amount of gelatin contained in said photographic layer is within the range of from 6.5 g/m^2 to 7.2 g/m^2.

5. The method of claim 1, wherein at least one layer included in said photographic layer contains a compound represented by Formula I, II. III, IV, V or VI;



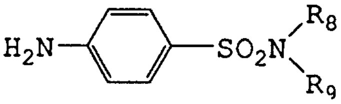
(I)

wherein R_1 is a hydrogen atom, an alkyl group or an aryl group; R_2 is a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a nitro group, a carboxyl group, a sulfo group, a sulfamoyl group, a hydroxyl group, an alkoxy group or a thiazolyl group; and Z_1 is a group of atoms necessary to form a thiazoline ring,



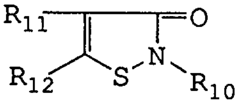
(II)

wherein R_3 and R_4 are each an alkyl group, an aryl group, a -COR group or a $-SO_2N(R')(R'')$ group, where R, R' and R'' are each an alkyl group or an aryl group, R_3 and R_4 may form a ring together with the nitrogen atom; and R_5, R_6, and R_7 are each a halogen atom or an alkyl group,



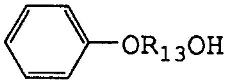
(III)

wherein R_8 and R_9 are each a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group,



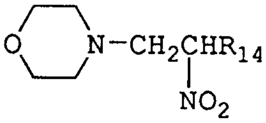
(IV)

wherein R_{10}, is a hydrogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, a heterocyclic group, an alkylcarbamoyl group, an arylcarbamoyl group, an alkylsulfamoyl group, or an arylsulfamoyl group; and R_{11}, and R_{12} are each a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, a cyano group, an alkylthio group, an arylthio group, an alkylsufonyl group, an alkylsufonyloxy group or a heterocyclic group, R_{11} and R_{12} together may form a ring,



(V)

wherein R_{13} is a alkylene group or an arylene group,



(VI)

wherein R_{14} is an alkyl group having 1 to 5 carbon atoms.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 31 0702

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 307 868 (KONICA) * page 31, line 44 - line 49 * * page 33, line 54 - line 58 * ---	1-5	G03C1/775 G03C1/37
Y	EP-A-0 368 356 (FUJI) * page 79, line 41 - page 81, line 52 * ---	1-5	
Y	EP-A-0 289 273 (KONICA) * page 38, line 44 - line 47; claim 1 * ---	1-5	
Y	US-A-4 923 790 (KATO ET AL.) * column 37, line 3 - line 6; claim 1 * ---	1-5	
Y	PATENT ABSTRACTS OF JAPAN vol. 8, no. 257 (P-316)(1694) 24 November 1984 & JP-A-59 128 537 (FUJI) 24 July 1984 * abstract * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 JANUARY 1993	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document