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⑤④ **COLOR IMAGE FORMING PROCESS.**

⑤⑦ A color image-forming process which comprises processing an imagewise exposed color paper containing an anionic surfactant having a fluorine-substituted aliphatic group as a hydrophobic group and an  $-SO_3M$  or  $-OSO_3M$  group (wherein M represents hydrogen or cation) as a hydrophilic group with a substantially benzyl alcohol-free color developer. In the case of processing the above-described color paper containing the fluorine-substituted anionic surfactant, color images with high coloration density can be obtained in a short time even when the paper is processed with a color

developer which substantially does not contain a development promoter causing environmental pollution.

## SPECIFICATION

## COLOR IMAGE-FORMING PROCESS

## [TECHNICAL FIELD]

This invention relates to a color image-forming process using silver halide color light-sensitive materials and, particularly, to a color image-forming process with shortened processing time and using substantially no benzyl alcohol.

## [BACKGROUND ART]

For forming color photographic images, yellow, magenta, and cyan 3-color photographic couplers are incorporated in light-sensitive layers and after light-exposure, the layers are processed by a color developer containing a color developing agent. In this course, colored dyes are formed by the coupling reaction of the oxidation product of an aromatic primary amine and the couplers and in this case, it is necessary to give high color density as possible in a limited development time.

High color density is usually achieved by using couplers having a high coupling speed as possible, a silver halide emulsion which is liable to be developed and gives a large amount of developed silver per unit coated amount thereof, or a color developer showing high developing speed.

For hastening the development of silver halide emulsion, it is easily considered to increase the content of silver chloride in the silver halide but the increase of the content of silver chloride gives faults that the sensitivity is reduced and fog is liable to occur. Also, for increasing the developed silver amount, it may be considered to increase the content of silver chloride as described above or intensify a chemical sensitization but this case also has a fault that fog is liable to occur. It is also a means for hastening development to reduce the grain size of silver halide emulsion but this has a fatal fault that a sensitivity is reduced. A method of using a silver chloride emulsion is described, for example, in Unexamined Published Japanese Patent Application Nos. 95345/83, 232342/84, and 19140/85 but there is a problem that the control of gradation is difficult.

On the other hand, various counterplans have hitherto been made on color developer for hastening the development. Among them, various kinds of additives have been investigated for accelerating coloring by hastening the permeation of a color developing agent into color coupler-dispersed oil drops, and, in particular, a method of hastening color development by adding benzyl alcohol to color developer has a large coloring accelerating effect and hence has now been widely used for processing color photographic

light-sensitive materials, in particular, color photographic papers.

However, in the case of using benzyl alcohol, diethylene glycol, triethylene glycol, alkanolamine, etc., becomes necessary as solvent since benzyl alcohol is low in water-solubility. However, the aforesaid compounds including benzyl alcohol give high BOD and COD, which are pollution loading values, and hence it is preferred for reducing pollution load to omit benzyl alcohol.

Furthermore, even when the aforesaid solvent is used, it takes a long time to dissolve benzyl alcohol and hence for reducing the work for the preparation of solution, it is better not to use benzyl alcohol.

Also, when benzyl alcohol is carried in a bleach bath or blix bath, which is a post bath, it causes to form a leuco dye of cyan dye, which results in the reduction of color density. Furthermore, the washing out speed of developer components from light-sensitive materials is delayed, which sometimes give bad influences on the image storage stability of processed light-sensitive material. Accordingly, by the aforesaid reasons, it is preferred not to use benzyl alcohol.

In color development, it is general that the processing time is from 3 minutes to 4 minutes but recently, with the shortage of the time for delivery of finished

products and the reduction of laboratory work, it has been desired to shorten the processing time.

However, when benzyl alcohol, which is a coloring accelerating agent, is removed and the processing time is shortened, the color density is, as a matter of course, reduced remarkably.

For solving this problem, various color development accelerating agents are proposed (e.g., the compounds described in U.S. Patents 2,950,970, 2,515,147, 2,496,903, 2,304,925, 4,038,075, 4,119,462, British Patents 1,430,998, 1,455,413, Unexamined Published Japanese Patent Application Nos. 15831/78, 62450/80, 62451/80, 62452/80, 62453/80, Japanese Patent Publication Nos. 12422/76, and 49728/80) but the use of these compounds does not give sufficient color density.

Also, even when a method of incorporating 3-pyrazolidones is proposed (e.g., the methods described in Unexamined Published Japanese Patent Application Nos. 26338/85, 158444/85, and 158446/85), there are disadvantages that the sensitivity is reduced and fog forms the light-sensitive materials are stored for a long time in unexposed state.

Furthermore, a method of incorporating color developing agents is proposed (e.g., the methods described in U.S. Patents 3,719,492, 3,342,559, 3,342,597, Unexamined Published Japanese Patent Application Nos. 6235/81,

16133/81, 97531/82, 83565/82, etc.), but in this case, there occur disadvantages that the color development is delayed and fog forms, and hence such a method is not proper.

Also, various processes for processing reflection-type silver halide color photographic light-sensitive materials using a color developer containing no benzyl alcohol or containing a greatly reduced amount of benzyl alcohol are proposed and are described, for example, in Unexamined Published Japanese Patent Application Nos. 20037/82, 48755/84, 174836/84, 177553/84, 26339/85, 172042/85, 31334/83, Japanese Patent Publication No. 29461/74, etc.

For the color photographic light-sensitive materials which are processed by the aforesaid color development process, anionic or nonionic surface active agents such as saponin; sulfosuccinic acid; alkylbenzenesulfonic acids such as dodecylbenzenesulfonic acid, etc.; alkylnaphthalenesulfonic acid; sorbitansesquioleic acid esters; sorbitanmonolauric acid esters; alkylene oxide derivatives, etc., are used.

However, the use of such conventional surface active agent is insufficient for attaining the purpose of obtaining color photographs with the high maximum color density ( $D_{max}$ ) and the low minimum color density ( $D_{min}$ ), and with less change in sensitivity and gradation by processing a color light-sensitive material with a color developer containing

substantially no benzyl alcohol in a very short period of time as within 2 minutes and 30 seconds.

Therefore, a first object of this invention is to provide a color image-forming process giving high color density in short period of time even by using a color developer containing substantially no benzyl alcohol...

A second object of this invention is to provide a color image-forming process giving less formation of fog and showing quick development.

A third object of this invention is to provide a color image-forming process giving less change in sensitivity and gradation.

#### [DISCLOSURE OF THE INVENTION]

As the result of making various investigations for attaining the aforesaid objects, the inventors have discovered that in the case of processing a color photographic paper containing the specific fluorinated carbon-containing anionic surface active agent described hereinbelow in the silver halide emulsion layer thereof or a layer adjacent thereto, a high color density is obtained in short period of time even when a color developer containing substantially no benzyl alcohol is used and the present invention has been attained.

That is, the invention is a color image-forming process, which comprises processing, after exposure, a silver

halide color photographic light-sensitive material comprising a reflective support having provided thereon at least one silver halide emulsion layer and containing an anionic surface active agent having a fluorine-substituted aliphatic group having 4 to 18 carbon atoms as a hydrophobic group and  $-\text{SO}_3\text{M}$  or  $-\text{OSO}_3\text{M}$  (wherein M represents a hydrogen atom or a cation) as a hydrophilic group in the molecule thereof in the emulsion layer or a layer adjacent thereto with a color developer containing substantially no benzyl alcohol in a time of up to 2 minutes and 30 seconds.

In this invention, the term "containing substantially no benzyl alcohol" means that the concentration of benzyl alcohol in a developer is up to 0.5 ml.

Preferred examples of the aforesaid anionic surface active agent in this invention can be shown by the following general formula;



wherein Rf represents a fluorine-substituted alkyl group having 4 to 18 carbon atoms or an alkenyl group, X represents  $-\text{SO}_3\text{M}$  or  $-\text{OSO}_3\text{M}$  (wherein M represents a hydrogen atom or a cation), and B represents a di-valent or tri-valent organic residue such as a di-valent or tri-valent aliphatic hydrocarbon group (e.g., an alkylene group or an alkylene

group in which the methylene is partially substituted by  
 oxa), an arylene group (e.g., phenylene, 1,4-naphthylene, 2-  
 hydroxy-1,4-naphthylene, etc.), and a di-valent heterocyclic  
 group (e.g., a di-valent benzimidazole group, 1-alkyleneben-  
 5 zimidazol-2-yl, etc.), said B also represents a poly-valent

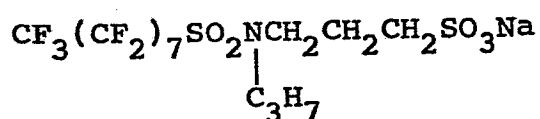
group (e.g.,  $(\text{SO}_2-\overset{\text{R}}{\underset{|}{\text{N}}}-\text{R}_1-\text{O}-\text{CO})_2\text{R}_2-$ ,  $-\text{COOR}_1-$ ,  $-\text{R}_1\text{O}-\text{CO}-\text{R}_1-$ ,  
 $-\text{CONH}-\text{R}_1-$ , or  $-\text{SO}_2\text{NR}-\text{R}_1-$ ) formed by a combination of the di-  
 valent or tri-valent organic residue and a di-valent linkage  
 group (e.g.,  $-\text{CO}-\text{O}-$ ,  $-\text{O}-\text{CO}-$ ,  $-\text{NR}-\text{CO}-$ ,  $-\text{CO}-\text{NR}-$ ,  $-\text{SO}_2\text{NR}-$ ,  
 10 wherein R is a hydrogen atom or an alkyl group having 1 to  
 18 carbon atoms).

In the above formula,  $\text{R}_1$  represents the aforesaid  
 di-valent aliphatic hydrocarbon group, arylene group, or di-  
 valent heterocyclic group and  $\text{R}_2$  represents a tri-valent  
 15 aliphatic hydrocarbon group.

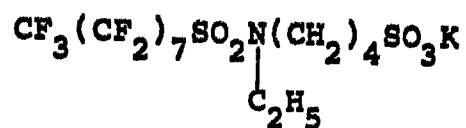
Also, n represents an integer of 1 and 2 and m  
 represents 0 or 1.

Then, some specific examples of the aforesaid  
 anionic surface active agents particularly useful in this  
 20 invention are shown below.

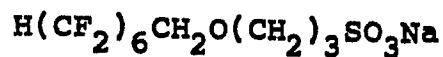
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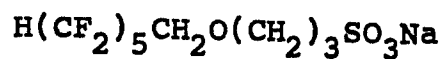
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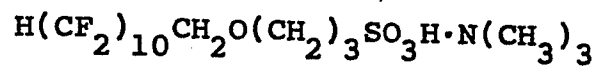
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(A - 4)

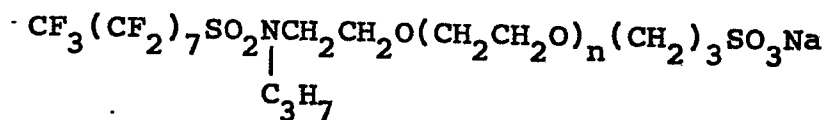


(A - 5)



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(A - 6)



n = 1

(A - 7)

"

n = 3

(A - 8)

"

n = 5

(A - 9)

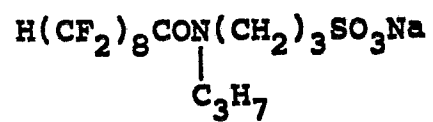
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n = 10

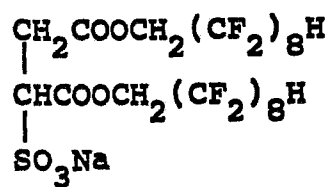
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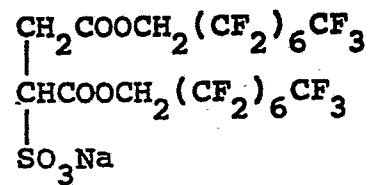
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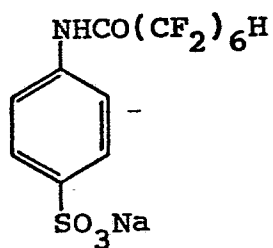
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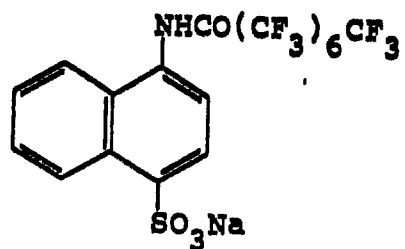
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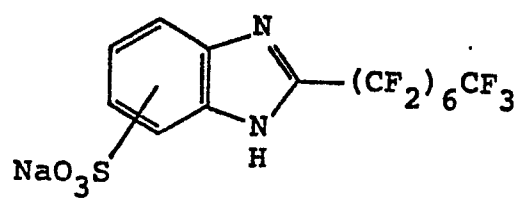
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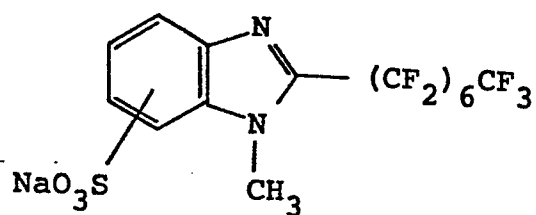
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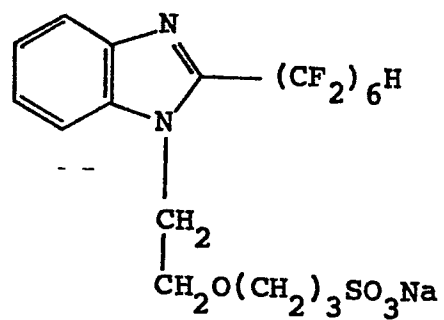
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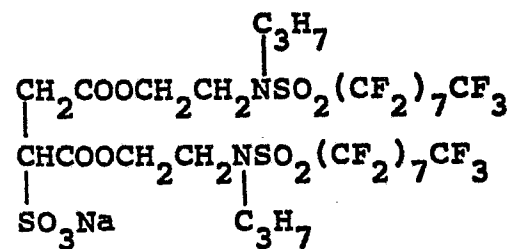
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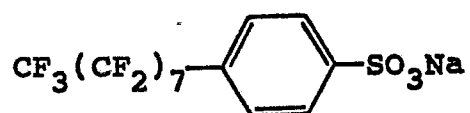
(A - 18)



(A - 19)



(A - 20)



(A - 21)

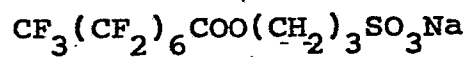


(A - 22)

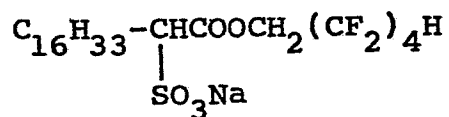


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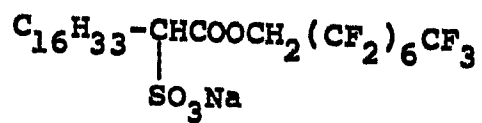
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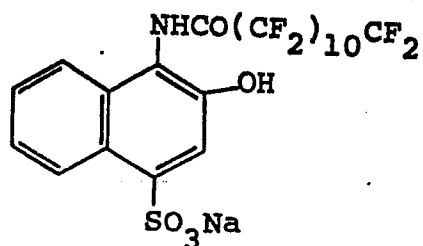
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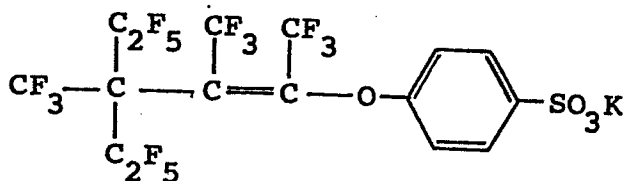
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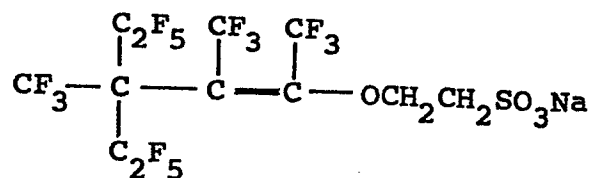
(A - 26)



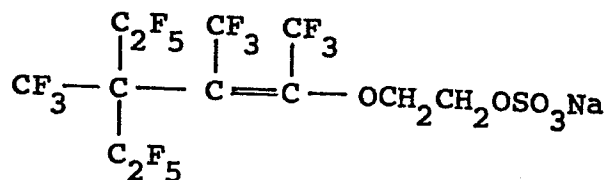
(A - 27)



(A - 28)



5 (A - 29)



These compounds which are used in this invention can be synthesized by the methods described, for example, in U.S. Patents 2,559,715, 2,567,011, 2,732,398, 2,764,602, 2,806,866, 2,809,998, 2,915,376, 2,915,528, 2,934,450, 5 2,937,098, 2,957,031, 3,472,894, 3,555,089, Japanese Patent Publication No. 37304/70, Unexamined Published Japanese Patent Application No. 9613/72, J. Chem. Soc., page 2789(1950), ibid., pages 2574 and 2640(1957), and J. Amer. Chem. Soc., Vol. 79, page 2549(1957).

10 A part of these fluorinated carbon-containing anionic surface active agents for use in this invention is commercially available as the trade name of Megafac F (e.g., F-109, F-110, F-115) from Dainippon Ink and Chemicals, Inc., or as the trade names of Monflor (e.g., Monflor 31) from 15 Imperial Chemical Industry Co.

The fluorinated carbon-containing anionic surface active agent for use in this invention can be added to one or both of an oil-soluble photographic additive (e.g., coupler, etc.) solution and an aqueous colloid solution in the 20 range such that solubility permits.

In this invention, oil drops containing coupler can contain, a DIR colorless compound-forming couplers, an ultraviolet ray absorbent, a discoloration inhibitor, a color stain preventing agent, a stain preventing agent, an 25 antioxidant, etc.

The fluorine-substituted anionic surface active agent for use in this invention can be used singly or together with other surface active agent. It is sometimes more preferred to use the anionic surface active agent together with certain kind of surface active agent than the case of using the anionic surface active agent singly.

The fluorine-substituted anionic surface active agent for use in this invention can be used together with a so-called fluorine-unsubstituted anionic surface active agent and/or a nonionic surface active agent.

As the aforesaid fluorine-unsubstituted anionic surface active agent, the use of a compound having a hydrophobic group of 8 to 30 carbon atoms (hydrophobic group without being unsubstituted by fluorine) and  $-\text{SO}_3\text{M}$  or  $-\text{OSO}_3\text{M}$  (M has the same significance as defined above about formula [I]) in one molecule thereof is preferred. These compounds are described in Ryohei Oda and Kazuhiro Teramura, Kaimen Kasseizai no Gosei to Ooyo (published by Maki Shoten) and A.W. Perry, Surface Active Agent, Interscience Publications Inc., New York.

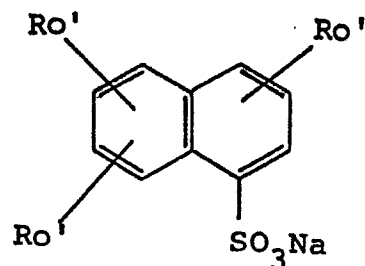
As the aforesaid nonionic surface active agent, the use of nonionic surface active agents described in Unexamined Published Japanese Patent Application No. 30933/73 and polyhydric alcohol fatty acid ester-series surface active agents is preferred. A polyhydric alcohol fatty acid ester-

series surface active agent having at least 2, preferably at least 3 hydroxy groups and also 6 to 25 carbon atoms of the fatty acid is preferred. Practically, the sorbitan fatty acid ester-series nonionic surface active agents described in U.S. Patent 3,676,141 are advantageously used in this invention.

Specific examples of the above-described fluorine-unsubstituted anionic surface active agent are illustrated below.

- 10 (A - 1)  $C_{12}H_{25}OSO_3Na$   
 (A - 2)  $C_{14}H_{29}OSO_3Na$   
 (A - 3) Turkey Red Oil  
 (A - 4)  $C_{12}H_{25}CONHCH_2CH_2OSO_3Na$   
 (A - 5)  $C_{12}H_{25}SO_3Na$   
 15 (A - 6)  $C_{14}H_{29}SO_3Na$
- (A - 7)  $C_8H_{17}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SO}_3Na$
- (A - 8) 
$$\begin{array}{c} \text{NaO}_3\text{S}-\text{CH}-\text{COOC}_8\text{H}_{17} \\ | \\ \text{CH}_2-\text{COOC}_8\text{H}_{17} \end{array}$$
- (A - 9)  $C_{12}H_{25}-\text{C}_6\text{H}_4-\text{SO}_3Na$
- (A - 10)  $C_{13}H_{27}CONH-\text{C}_6\text{H}_4-\text{SO}_3Na$

(A - 11)



In the above formula, Ro' represents  $-\text{CH} \begin{matrix} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{matrix}$ .

In this invention, it is particularly preferred to use at least one fluorine-substituted surface active agent for use in this invention together with at least one fluorine-unsubstituted anionic surface active agent having a hydrophobic group of 8 to 30 carbon atoms and  $-\text{SO}_3\text{M}$  or  $-\text{OSO}_3\text{M}$  (M has the same significance as defined above about formula [I]) in one molecule thereof and/or at least one sorbitan fatty acid ester-series nonionic surface active agent.

In this invention, it is necessary that couplers are fused by heating or dissolved in organic solvent to form a liquid thereof before the emulsification thereof. In this case, however, the coupler which can be directly emulsified by fusing it is limited to a compound having melting point of up to about  $90^\circ\text{C}$ .

As an organic solvent (so-called oil) which is used for finely dispersing a coupler in an aqueous medium, an organic solvent which is substantially insoluble in water

and has a boiling point of at least 190°C at atmospheric pressure is useful. Such an organic solvent can be selected from carboxylic acid esters, phosphoric acid esters, carboxylic acid amides, ethers, and substituted hydrocarbons.

5 Specific examples thereof are di-n-butyl phthalic acid ester, diisooctyl phthalic acid ester, dimethoxyethyl phthalic acid esters, di-n-butyl adipic acid ester, diisooctylazelaic acid ester, tri-n-butyl phthalic acid ester, butyl lauric acid ester, di-n-sebacic acid ester, tricresyl  
10 phosphoric acid ester, tri-n-butylphosphoric acid ester, triisooctyl phosphoric acid ester, N,N-diethylcaprylic amide, N,N-dimethylpalmitic amide, n-butyl-m-pentadecyl phenyl ether, ethyl-2,4-tert-butyl phenyl ether, chlorinated paraffin, etc.

15 In this invention, it is sometimes advantageous to use a low-boiling solvent (having boiling point of up to 130°C at room pressure) or a water-soluble high-boiling solvent together with the aforesaid solvent for dissolving couplers. For example, there are propylene carbonate, ethyl  
20 acetate, butyl acetate, ethyl propionic acid ester, sec-butyl alcohol, tetrahydrofuran, cyclohexanone, dimethylformamide, diethyl sulfoxide, methylcellosolve, etc.

As an emulsification apparatus which is used for the practice of this invention, an apparatus giving large  
25 shearing force to processing liquid or an apparatus giving

high-intensity ultrasonic energy thereto is suitable. In particular, a colloid mill, a homogenizer, a capillary type emulsification apparatus, or an emulsification apparatus having a liquid siren, an electromagnetostatin type ultrasonic generator, or Poleman horn gives good results.

As the photographic layer containing the fluorine-substituted anionic surface active agent for use in this invention, a silver halide emulsion layer and/or an adjacent layer thereto is preferred, and a silver halide emulsion layer is particularly preferred.

The amount of the fluorine-substituted anionic surface active agent for use in this invention depends upon the kind of couplers, the kind of other additives, the kind and amount of dispersing solvent, as the case may be, the kind and amount of other surface active agent(s), etc., but is generally from 0.2 to 50% by weight of a dispersion (i.e., a solution formed by dispersing a coupler and other oil-soluble photographic additive(s) in a dispersing medium).

As substances which can exist together with couplers, there are oil-soluble photographic additives such as discoloration inhibitor, ultraviolet ray absorbents, DIR couplers, antioxidant, etc.

The "reflective support" for use in this invention is a support having high reflectivity for clearly viewing color images formed in silver halide emulsion layer(s) and

such a reflective support includes a support coated with a hydrophobic resin having dispersed therein a light-reflecting substance such as titanium oxide, zinc oxide, calcium carbonate, calcium sulfate, etc., or a support composed of a hydrophobic resin having dispersed therein the light-reflective substance. For example, there are baryta papers, polyethylene-coated paper, polypropylene-series synthetic papers, and transparent supports such as glass plates, polyester films, e.g., polyethylene terephthalate films, cellulose triacetate films, cellulose nitrate films, etc., polyamide films, polycarbonate films, polystyrene films, etc., having provided thereon a reflective layer or having a reflective substance. The support can be properly selected from these supports according to the purposes.

Then, processing steps (image-forming step) of this invention are explained.

In the color development processing step in this invention, the processing time is as short as up to 2 minutes and 30 seconds. A preferred processing time is from 30 seconds to 2 minutes. In this case, the processing time means a period from the time at which a light-sensitive material is brought into contact with a color developer to the time of the light-sensitive material coming into contact with a next bath and includes the time for transporting the light-sensitive material from the color development bath to

the next bath.

A color developer for use in the development process of this invention is preferably an alkaline aqueous solution containing an aromatic primary amine-series color developing agent as the main component. As the color developing agent, p-phenylenediamine-series compounds are preferably used and typical examples thereof include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methoxyethylaniline and the sulfates, hydrochlorides, phosphates, or p-toluenesulfonates thereof, tetraphenylborates, p-(t-octyl)benzenesulfonates, etc. Of these compounds, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline and the salts thereof are particularly preferred.

Aminophenolic derivatives include o-aminophenol, p-aminophenol, 4-amino-2-methylphenol, 2-amino-3-methylphenol, 2-oxy-3-amino-1,4-dimethylbenzene, etc.

Other color developing agents described in L.F.A. Mason, Photographic Processing Chemistry, pages 226-229, Focal Press, U.S. Patents 2,193,015, 2,592,364, Unexamined Published Japanese Patent Application No. 64933/73, etc., can be also used. If necessary, two or more kinds of color developing agents may be used as a combination thereof.

The processing temperature of the color developer in

this invention is preferably from 30°C to 50°C, and more preferably from 33°C to 45°C.

Also, as development accelerators, various compounds substantially excluding benzyl alcohol may be used. Examples thereof are various kinds of pyrimidium compounds and other cationic compounds described in U.S. Patent 2,648,604, Japanese Patent Publication No. 9503/69, and U.S. Patent 3,171,247, cationic dyes such as phenosafranine, neutral salts such as thallium nitrate and potassium nitrate, polyethylene glycol and the derivatives thereof described in Japanese Patent Publication No. 9304/69, U.S. Patents 2,533,990, 2,531,832, 2,950,970, and 2,577,127, nonionic compounds such as polythioethers, etc., thioether-series compounds described in U.S. Patent 3,201,242, and other compounds described in Unexamined Published Japanese Patent Application Nos. 156934/73 and 220344/85.

Also, in the short time development process as in this invention, not only the means for accelerating development but also a technique for preventing the formation of development fog becomes important. As an antifoggant in this invention, an alkali metal halide such as potassium bromide, sodium bromide or potassium iodide, and also an organic antifoggant are preferred. As organic antifoggants, there are, for example, nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-

nitroisindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolylbenzimidazole, 2-thiazolylmethylbenzimidazole or hydroxyazaindrizine, mercapto-substituted heterocyclic compounds such as 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzimidazole or 2-mercaptobenzothiazole, and further mercapto-substituted aromatic compounds such as thiosalicylic acid. Of these compounds, halides are particularly preferred. The antifoggant may be accumulated in the color developer by dissolving out from color light-sensitive materials during processing.

Furthermore, the color developer in this invention may contain a pH buffer such as carbonates, borates, or phosphates of an alkali metal; a preservative such as hydroxylamine, triethanolamine, compounds described in West German Patent Application (OLS) No. 2,622,950, sulfites, and bisulfites; an organic solvent such as diethylene glycol; a dye-forming coupler; a competing coupler; a nucleating agent such as sodiumboron hydride; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a tackifier; an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, nitrilotriacetic acid, cyclohexanediaminetetraacetic acid, iminodiacetic acid, N-hydroxymethylethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, or triethylenetetraminehexaacetic acid; an organic phosphonic acid such as 1-hydroxyethylidene-1,1'-diphosphonic acid or those de-

scribed in Research Disclosure, No. 18170 (May, 1979); an aminophosphonic acid such as aminotris(methylenephosphonic acid), ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, etc., and a chelating agent such as phosphonocarboxylic acids, etc., described in Unexamined Published Japanese Patent Application Nos. 102726/77, 42730/78, 121127/79, 4024/80, 4025/80, 126241/80, 65955/80, 65956/80, and Research Disclosure, No. 18170 (May, 1979).

Also, if necessary, the color development bath is composed of two or more baths and a replenisher for color developer is supplied from the first bath or the last bath for practicing the shortage of the development time and reduction of the amount of the replenisher.

A silver halide color light-sensitive material is usually bleached after color development. The bleach process may be performed simultaneously with fix process (blix) or separately with fix process. As a bleaching agent, for example, compounds of multivalent metals such as iron(III), cobalt(III), chromium(VI), copper(II), etc., peracids, quinones, nitroso compounds, etc., are used. Examples thereof include ferricyanides, dichromates, organic complex salts of iron(III) or cobalt(III), aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, 1,3-diamino-2-propanoltetraacetic acid, etc., complex salts

of organic acid such as citric acid, tartaric acid, malic acid, etc., persulfates, manganates, nitrosophenol, etc. Of these substances, potassium ferricyanide, sodium ethylenediaminetetraacetato ferrate, ammonium ethylenediaminetetraacetato ferrate, ammonium triethylenetetraminepentaacetato ferrate, and persulfates are particularly useful. Ethylenediaminetetraacetic acid iron(III) complex salt is useful in an independent bleach solution and in a monobath blix solution.

Also, the bleach solution or blix solution may, if necessary, contain various kinds of accessorators. For example, bromine ion, iodine ion, as well as thiourea-series compounds as shown in U.S. Patent 3,706,561, Japanese Patent Publication Nos. 8506/70, 26586/74, Unexamined Published Japanese Patent Application Nos. 32735/78, 36233/78, and 37016/78, thiol-series compounds shown in Unexamined Published Japanese Patent Application Nos. 124424/78, 95631/78, 57831/78, 32736/78, 65732/78, 52534/79, and U.S. Patent 3,893,858, heterocyclic compounds described in Unexamined Published Japanese Patent Application Nos. 59644/74, 140129/75, 28426/78, 141623/78, 104232/78, 35727/79, etc., thioether-series compounds described in Unexamined Published Japanese Patent Application Nos. 20832/77, 25064/80, 26506/80, etc., quaternary amines described in Unexamined Published Japanese Patent Application No. 84440/73, and

thiocarbamoyls described in Unexamined Published Japanese Patent Application No. 42349/74 may be used.

As a fixing agent, there are thiosulfates, thiocyanates, thioether-series compounds, thioureas, a large amount of iodide, etc., but thiosulfates are generally used. As a preservative for the blix solution or the fix solution, sulfites, bisulfites, or carbonyl-bisulfite adducts are preferred.

After blix process or fix process, wash process is usually performed. For the wash step, various known compounds may be used for preventing precipitation or saving water. Examples of these compounds are a water softener for preventing precipitation, such as inorganic phosphoric acids, aminopolycarboxylic acid, organic phosphoric acids, etc., antibacterial agents or antifungal agents for preventing the generation of various bacteria, algae, and molds, a hardening agent represented by magnesium salts or aluminum salts, a surface active agent for reducing drying load and preventing the occurrence of uneven drying, etc. Furthermore, the compounds described in L.E. West, Photographic Science and Engineering, Vol. 9, No. 6 (1965), etc., may be added to wash water. In particular, the addition of chelating agents and antifungal agents is effective.

Also, by employing a multistage (e.g., 2 to 5 stages) countercurrent system for the wash step, the amount

of water can be saved.

Also, after or in place of a wash step, a multistage countercurrent stabilization process as described in Unexamined Published Japanese Patent Application No. 8543/82 may be used. In this process, 2 to 9 countercurrent tanks are necessary. The stabilization solution may contain various compounds for stabilizing images. For example, there are buffers for adjusting the pH of photographic layers (e.g., borates, metaborates, borax, phosphates, carbonates, potassium hydroxide, sodium hydroxide, aqueous ammonia, monocarboxylic acid, dicarboxylic acid, polycarboxylic acid, etc.) or formalin. Furthermore, if necessary, water softeners (e.g., inorganic phosphoric acids, aminopolycarboxylic acids, organic phosphoric acids, aminopolyphosphonic acids, phosphonocarboxylic acids, etc.), germicides (e.g., Proxel, isothiazolone, 4-thiazolylbenzimidazole, halogenated phenol-benzotriazole, etc.), surface active agents, brightening agents, hardening agents, etc., may be added thereto.

Also, as a layer pH controlling agent after processing, various ammonium salts such as ammonium chloride, ammonium nitrate, ammonium sulfate, ammonium phosphate, ammonium sulfite, ammonium thiosulfate, etc., can be added thereto.

It is preferred that couplers incorporated into light-sensitive materials are rendered non-diffusible by

having a ballast group or being polymerized. Furthermore, 2-equivalent color couplers the coupling active position of which is substituted by a releasing group is more effective for reducing the amount of silver coated than the case of using 4-equivalent color couplers having a hydrogen atom at the coupling active position thereof. Couplers providing colored dyes having a proper diffusibility, colorless compound-forming couplers, DIR couplers releasing a development inhibitor with the coupling reaction or couplers releasing a development accelerator with the coupling reaction thereof can be used.

Typical examples of the yellow couplers which can be used in this invention are oil-protect type acylacetamide-series couplers. Specific examples thereof are described in U.S. Patents 2,407,210, 2,875,057, 3,265,506, etc.

In this invention, 2-equivalent yellow couplers are preferably used and typical examples thereof are oxygen atom-releasing type yellow couplers described in U.S. Patents 3,408,194, 3,447,928, 3,933,501, 4,022,620, etc., or nitrogen atom-releasing type yellow couplers described in Japanese Patent Publication No. 10739/83, U.S. Patents 4,401,752 and 4,326,024, RD 18053 (April, 1979), British Patent 1,425,020, West German Patent Application (OLS) Nos. 2,219,917, 2,261,361, 2,329,587, 2,433,812, etc. Of these couplers,  $\alpha$ -pivaloylacetanilide-series couplers are excel-

lent in fastness, in particular light fastness of the colored dyes formed, while  $\alpha$ -benzoylacetanilide-series couplers give high color density.

As magenta couplers which can be used in this invention, there are oil-protect type indazolone-series or cyanoacetyl-series couplers, preferably 5-pyrazolone-series couplers and pyrazoloazole-series couplers such as pyrazolotriazoles, etc. The 5-pyrazolone-series couplers the 3-position of which is substituted by an arylamino group or an acylamino group are preferred in the viewpoints of the hue and color density of colored dyes and typical examples thereof are described in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896, 3,936,015, etc. Preferred releasing groups for the 2-equivalent 5-pyrazolone-series couplers include nitrogen atom-releasing groups described in U.S. Patent 4,310,619 and arylthio groups described in U.S. Patent 4,351,897. Also, 5-pyrazolone-series couplers having a ballast group described in European Patent 73,636 give high color density.

Pyrazoloazole-series magenta couplers include pyrazolobenzimidazoles described in U.S. Patent 3,369,879, preferably pyrazolo[5,1-c][1,2,4]triazoles described in U.S. Patent 3,725,067, pyrazolotetrazoles described in Research Disclosure, No. 24220 (June, 1984), and pyrazolopyrazoles described in Research Disclosure, No. 24230 (June, 1984).

From the viewpoints of less yellow side absorption of colored dyes and high light fastness of colored dyes, imidazo-[1,2-b]pyrazoles described in European Patent 119,741 are preferred and pyrazolo[1,5-b][1,2,4]triazole described in  
5 European Patent 119,860 is particularly preferred.

Cyan couplers for use in this invention include oil-protect type naphthoic and phenolic couplers.

As typical naphthoic cyan couplers, there are naphthoic couplers described in U.S. Patent 2,474,293 and,  
10 preferably oxygen atom-releasing type 2-equivalent naphthoic couplers described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, and 4,296,200. Also, specific examples of the phenolic couplers are described in U.S. Patents 2,369,929, 2,801,171, 2,772,162, 2,895,826, etc. Cyan couplers having  
15 high fastness to moisture and heat are preferably used in this invention, and typical examples there are the phenolic cyan couplers having an alkyl group of at least two carbon atoms at the meta-position of the phenol nucleus described in U.S. Patent 3,772,002, 2,5-diacylamino-substituted pheno-  
20 lic couplers described in U.S. Patents 2,772,162, 3,758,308, 4,126,396, 4,334,011, and 4,327,173, West German Patent Application (OLS) No. 3,329,729, Unexamined Published Japanese Patent Application No. 166956/84, etc., and pheno-  
25 lic couplers having a phenylureido group at the 2-position thereof and an acylamino group at the 5-position thereof

described in U.S. Patents 3,446,622, 4,333,999, 4,451,559, 4,427,769, etc.

5 In this invention, the graininess of the color images formed can be improved by using a coupler giving colored dye having a proper diffusibility together with the aforesaid coupler(s). About such couplers giving diffusible dyes, specific examples of the magenta couplers are described in U.S. Patent 4,366,237 and British Patent 2,125,570 and specific examples of the yellow, magenta and 10 cyan couplers are described in European Patent 96,570 and West German Patent Application (OLS) No. 3,234,533.

The dye-forming couplers and the specific couplers described above may form a dimer or higher polymer. Typical examples of the polymerized dye-forming couplers are de- 15 scribed in U.S. Patents 3,451,820 and 4,080,211. Also, specific examples of the polymerized magenta couplers are described in British Patent 2,102,173 and U.S. Patent 4,367,282.

20 The couplers for use in this invention can be used for one light-sensitive layer as a mixture of two or more for meeting the properties required for the light-sensitive materials or the same kind of coupler may be incorporated in two or more light-sensitive layer.

25 A standard amount of a color coupler is in the range of from 0.001 mol to 1 mol per mol of the light-sensitive

silver halide, with from 0.01 mol to 0.5 mol of a yellow coupler, from 0.003 mol to 0.3 mol of a magenta coupler, and from 0.002 mol to 0.3 mol of a cyan coupler, per mol of the light-sensitive silver halide being preferred.

5           The light-sensitive materials for use in this invention may further contain hydroquinone derivatives, aminophenol derivatives, amines, gallic acid derivatives, catechol derivatives, ascorbic acid derivatives, colorless compound-forming couplers, sulfoamidophenol derivatives,  
10       etc., as color fog preventing agents or color stain preventing agents.

          Also, the light-sensitive materials for use in this invention can further contain known discoloration inhibitors. Typical examples of organic discoloration inhibitors  
15       are hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols, hindered phenols comprising bisphenols, gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines and the ether or ester derivatives of the aforesaid compounds formed by silylating or  
20       alkylating the phenolic hydroxy group of these compounds. Also metal complexes represented by (bissalicylaldoxymato)-nickel complex and (bis-N,N-dialkyldithiocarbamato)nickel complex, etc. can also be used.

          For preventing the deterioration of yellow dye  
25       images by heat, moisture, and light, the compound having

both moieties of hindered amine and hindered phenol in one molecule as described in U.S. Patent 4,268,593 gives good results. Also, for preventing the deterioration of magenta dye image, particularly by light, spiroindans described in  
5 Unexamined Published Japanese Patent Application No. 159644/81 and chromans substituted by hydroquinone diether or hydroquinone monoether described in Unexamined Published Japanese Patent Application No. 89835/80 give preferred results.

10 For improving the storage stability, in particular, the light fastness of cyan images, it is preferred to use a benzotriazole-series ultraviolet ray absorbent with the cyan coupler(s). The ultraviolet ray absorbent may be coemulsified with the cyan coupler(s).

15 The ultraviolet ray absorbent is desirably used in an amount sufficient for imparting light stability to cyan dye images but since if the amount is too much, the unexposed portions (background portions) of the color photographic light-sensitive material are sometimes yellowed, the  
20 amount thereof is usually selected in the range of from  $1 \times 10^{-4}$  mol/m<sup>2</sup> to  $2 \times 10^{-3}$  mol/m<sup>2</sup>, particularly from  $5 \times 10^{-4}$  mol/m<sup>2</sup> to  $1.5 \times 10^{-3}$  mol/m<sup>2</sup>.

In the light-sensitive layer structure of an ordinary color photographic paper, the ultraviolet ray absorbent(s) are incorporated in either one of both layers  
25

adjacent to or, preferably, in both layers adjacent to a red-sensitive emulsion layer containing cyan coupler. When the ultraviolet ray absorbent(s) are incorporated in the interlayer between a green-sensitive layer and a red-sensitive layer, they may be emulsified together with a color stain preventing agent. When the ultraviolet ray absorbent(s) are incorporated in a protective layer, another protective layer may be formed on the protective layer as the outermost layer. The outermost protective layer may contain a matting agent having a proper particle size.

The light-sensitive materials which are processed in this invention can contain ultraviolet ray absorbents in the hydrophilic colloid layers.

The light-sensitive materials which are processed in this invention may further contain water-soluble dyes in the hydrophilic colloid layers as filter dyes or for the purpose of irradiation or halation prevention.

The light-sensitive materials which are processed in this invention may further contain whitening agents such as stilbene-series, triazine-series, oxazole-series, or coumarin-series whitening agents in the photographic emulsion layers or other hydrophilic colloid layers. The whitening agent may be water-soluble or a water-insoluble whitening agent may be used in the form of the dispersion.

The light-sensitive materials for use in this inven-

tion, as described above, can be applied to a multilayer multicolor photographic material having at least two emulsion layers each having different spectral sensitivity on a support. A multilayer natural color photographic material usually has at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer, and at least one blue-sensitive emulsion layer on a support. The disposition order of the layers can be optionally selected according to the purposes. Also, each of the aforesaid emulsion layers may be composed of two or more emulsion layers each having different sensitivity or a light-insensitive layer may exist between two or more emulsion layers each having the same sensitivity.

The light-sensitive material for use in this invention preferably has auxiliary layers such as protective layer(s), interlayers, a filter layer, an antihalation layer, a back layer, etc., in addition to the silver halide emulsion layers.

As a binder or protective colloid which can be used for the emulsion layers and interlayers of the light-sensitive materials for use in this invention, gelatin is advantageously used but other hydrophilic colloids can be used.

Examples of the binders or protective colloids are proteins such as gelatin derivatives, graft polymers of

gelatin and other polymers, albumin, casein, etc.; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfuric acid ester, etc.; saccharose derivatives such as sodium alginate, starch derivatives, etc.; and synthetic hydrophilic polymeric substances such as homopolymers or copolymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole, polyvinylpyrazole, etc.

As gelatin lime-processed gelatin as well as acid-processed gelatin and enzyme-processed gelatin as described in Bull. Soc. Sci. Phot. Japan, No. 16, p. 30(1966) can be used. Furthermore, the hydrolyzed product or enzyme-decomposed product of gelatin can be used.

The light-sensitive materials in this invention may further contain various stabilizers, stain preventing agents, developing agents or the precursors thereof, development accelerators or the precursors thereof, lubricants, mordants, matting agents, antistatic agents, plasticizers, or other additives useful for the photographic light-sensitive materials in addition to the above-described additives. Typical examples of such additive are described in Research Disclosure, 17643 (December, 1978) and ibid., 18716 (November, 1979).

In this invention, silver chlorobromide, silver

chloride, silver chloriodobromide, silver bromide, silver iodobromide, etc., are used as a silver halide, but silver bromide, silver chlorobromide and silver chloride each containing substantially no silver iodide are preferred, and  
5 silver chloribromide containing 20 to 98 mol% of silver bromide is more preferred. Also, for the purpose of processing a far short time, the use of silver chloride or silver chlorobromide containing at least 90 mol%, in particular, at least 95% silver chloride is preferred.

10 The silver halide grains for use in this invention may have different phase between the inside and the surface layer thereof, may be a multiphase structure having a junction structure, or may be composed of a uniform phase throughout the whole grain. Also, the silver halide grains  
15 may be composed of a mixture thereof.

The average grain size (shown by the diameter of the grains when the grain is spherical or similar to spherical, and shown by the average value based on the projected area using, in the case of cubic grains, the edge length as the  
20 grain size) of the silver halide grains for use in this invention is preferably in the range of from  $0.1 \mu$  to  $2 \mu$ , particularly preferably from  $0.15 \mu$  to  $1 \mu$ . The grain size distribution may be narrow or broad but the use of so-called monodispersed silver halide emulsion, wherein the value  
25 (coefficient of variation) obtained by dividing the standard

deviation in the grain size distribution curve of the silver halide emulsion by the average grain size of the silver halide grains in the emulsion is within 20%, particularly preferably within 15%, is preferred. Also, for satisfying the desired gradation for the light-sensitive material, in the emulsion layers each having substantially the same color sensitivity, two or more kinds of monodispersed silver halide emulsions (preferably having the above-described coefficient of variation) each having different grain size can be used as a mixture thereof for one emulsion layer or can be used as separate emulsion layers. Furthermore, two or more kinds of polydispersed silver halide emulsion layers or a combination of the monodispersed silver halide emulsion and a polydispersed silver halide emulsion can be used as a mixture thereof for one emulsion layer or can be used as separate emulsion layers.

The silver halide grains for use in this invention may have a regular crystal form such as cube, octahedron, dodecahedron, tetradecahedron, etc., an irregular crystal form such as sphere, etc.. or a composite form of these crystal forms. However, silver halide grains having a regular crystal form such as cube and tetradecahedron are preferred. Also, the silver halide grains may be tabular grains and in this case, an emulsion wherein tabular grains of at least 5, in particular at least 8 in the ratio of

length/thickness account for at least 50% of the total projected area of the grains can be used in this invention. An emulsion containing a mixture of various silver halide grains having different crystal form may be also used. The  
5 emulsion may be of a surface latent image type of forming latent images mainly on the surface thereof or of an internal latent image type of forming latent images mainly in the inside of the grains although the former type is preferred.

10 The photographic emulsions which are used for the light-sensitive materials processed according to this invention can be prepared by the methods described in P. Glafkides, Chimie et Physique Photographique, published by Paul Montel, (1967); G.F. Duffin, Photographic Emulsion  
15 Chemistry, published by Focal Press, (1966); and V.L. Zelikman et al., Making and Coating Photographic Emulsion, published by Focal Press, (1964), etc. That is, the emulsion can be prepared by an acid method, a neutral method, an ammonia method, etc., and as a method of reacting a soluble  
20 silver salt and a soluble halide, a single jet method, a double jet method, a combination thereof, etc., may be employed. A method (so-called reverse mixing method) of forming grains in the existence of excess silver ions can also be used. As one system of the double jet method, a  
25 method of keeping pAg constant in a liquid phase of forming

a silver halide, so-called controlled double jet method, can also be used. According to the method, a silver halide emulsion containing grains having a regular crystal form and approximately uniform grain sizes can be obtained.

Furthermore, an emulsion prepared by a so-called conversion method including a step of converting a silver halide already formed before finishing the formation of the silver halide grains into a silver halide having small solubility product or an emulsion to which the similar halogen conversion was applied after finishing the formation of the silver halide grains can also be used in this invention.

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

The silver halide emulsions are, after the formation of the silver halide grains, usually physically ripened, desalted, and chemically ripened before coating.

A known silver halide solvent (e.g., ammonia, potassium rhodanate, or thioethers and thione compounds described in U.S. Patent 3,271,157, Unexamined Published Japanese Patent Application Nos. 12360/76, 83408/78, 144319/78, 100717/79, 155828/79, etc.) can be used for the precipitation, physical ripening, and chemical ripening.

For removing soluble silver salts from emulsions after physical ripening, a noodle washing method, a flocculation sedimentation method, an ultrafiltration method, etc. can be employed.

5           The silver halide emulsions which are used for the light-sensitive materials to be processed in this invention can be chemically sensitized by a sulfur sensitization method using active gelatin or a sulfur-containing compound capable of reacting with silver (e.g., thiosulfates, thio-  
10   ureas, mercapto compounds, or rhodanines); a reduction sensitization method using a reducing substance (e.g., stannous salts, amines, hydrazine derivatives, formamidinesulfinic acid, or silane compounds); a noble metal sensitization method using a metal compound (e.g., gold complex salts and  
15   complex salts of metal belonging to group VIII of the Periodic Table, such as Pt, Ir, Pd, Rh, Fe, etc.), a combination thereof, etc.

Of the aforesaid chemical sensitizations, independent use of the sulfur sensitization is more preferred.

20           Each of the blue-sensitive, green-sensitive and red-sensitive emulsions for the color light-sensitive material for use in this invention is spectrally sensitized by a methine dye, etc., such that the emulsion has each color sensitivity. The dyes for use include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine  
25   cyanine dyes, complex merocyanine



dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes. Particularly useful dyes are dyes belonging to cyanine dyes, merocyanine dyes, and complex merocyanine dyes.

5           For these dyes can be applied nuclei usually utilized for cyanine dyes as basic heterocyclic nuclei. That is, pyrroline nuclei, oxazoline nuclei, thiazoline nuclei, pyrrole nuclei, oxazole nuclei, thiazole nuclei, selenazole nuclei, imidazole nuclei, tetrazole nuclei,  
10           pyridine nuclei, etc.; the nuclei formed by fusing an alicyclic hydrocarbon ring to the aforesaid nuclei, and the nuclei formed by fusing an aromatic hydrocarbon ring to the aforesaid nuclei, such as indolenine nuclei, benzindolenine nuclei, indole nuclei, benzoxazole nuclei, naphthoxazole  
15           nuclei, benzothiazole nuclei, naphthothiazole nuclei, benzo-selenazole nuclei, benzimidazole nuclei, quinoline nuclei, etc., can be applied for the dyes described above. These nuclei may be substituted on carbon atoms.

          For merocyanine dyes or complex merocyanine dyes may  
20           be applied 5-membered or 6-membered heterocyclic nuclei such as pyrazolin-5-one nuclei, thiohydantoin nuclei, 2-thiooxazolidine-2,4-dione nuclei, thiazolidine-2,4-dione nuclei, rhdanine nuclei, thiobarbituric acid nuclei, etc., as a nucleus having a ketomethylene structure.

25           These sensitizing dyes may be used singly or as a

combination thereof. A combination of sensitizing dyes is frequently used for the purpose of supersensitization. Typical examples of the combinations are described in U.S. Patents 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, and 4,026,707, British Patents 1,344,281 and 1,507,803, Japanese Patent Publication Nos. 4936/68 and 12375/78, and Unexamined Published Japanese Patent Application Nos. 110618/77, 109925/77.

The emulsion may contain a dye having no spectrally sensitizing activity by itself or a substance which does not substantially absorb visible light and shows supersensitizing activity together with the sensitizing dye(s).

[BEST MODE FOR CARRYING OUT THE INVENTION]

Then, the invention is explained in detail by the examples but the invention is not limited thereto.

EXAMPLE 1.

To 24.0 g of yellow coupler (Y - 1) were added 35 ml of ethyl acetate and 12 ml of dibutyl phthalate as a solvent to dissolve the coupler, the solution was added to 160 ml of an aqueous 12% gelatin solution containing 10 ml of an aqueous solution of 10% Comparison Compound R - 1 (sodium dibutylenesulfonate) as a dispersing agent, and the mixture was emulsified by means of a high-speed stirrer.

A whole amount of the emulsified dispersion was added to a silver chlorobromide emulsion (containing 70 g/kg of Ag) containing 80% of Br, the mixture was coated on a paper support, both surfaces of which had been laminated with polyethylene, such that the coated amount of silver became  $0.31 \text{ g/m}^2$ , and then a gelatin layer was formed on the emulsion layer to provide Comparison Sample (A).

Then, Samples (B) to (R) were prepared as follows.

Sample (B)

10 Same sample as Sample (A) except that 1.0 g of Compound A - 1 of this invention was used in place of R - 1 as a dispersing agent.

Sample (C)

15 Same sample as Sample (A) except that 1.0 g of Compound A - 9 of this invention was used in place of R - 1 as a dispersing agent.

Sample (D)

20 Same sample as Sample (A) except that 1.0 g of Compound A - 11 of this invention was used in place of R - 1 as a dispersing agent.

Sample (E)

Same sample as Sample (A) except that 1.0 g of Compound A - 20 of this invention was used in place of R - 1 as a dispersing agent.

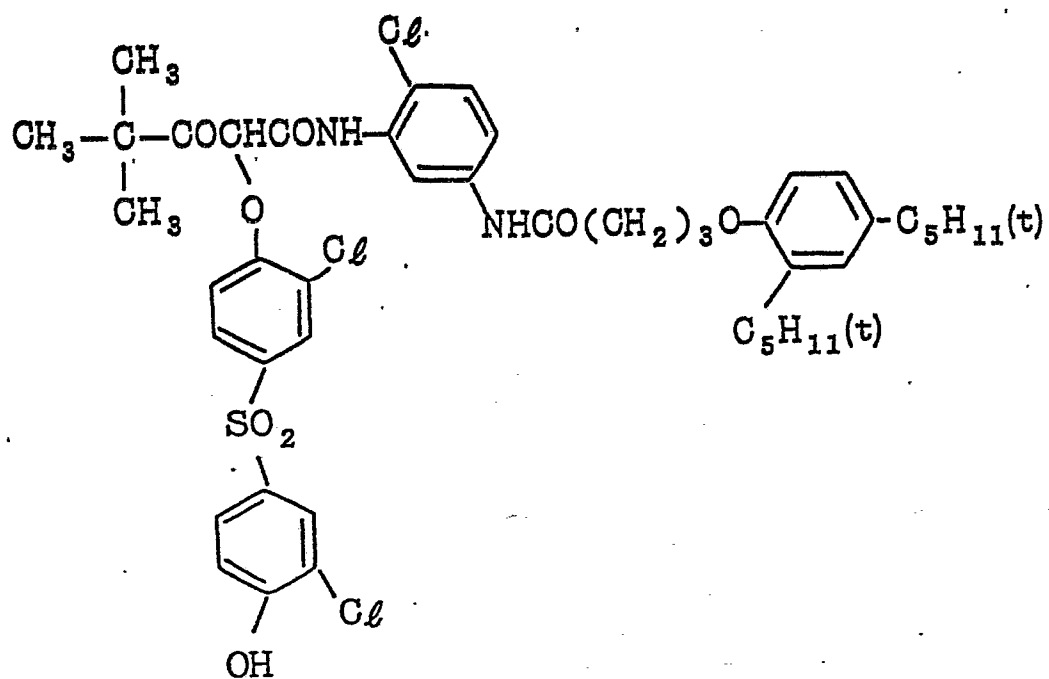
Sample (F)

Same sample as Sample (A) except that 1.0 g of Compound A - 26 of this invention was used in place of R - 1 as a dispersing agent.

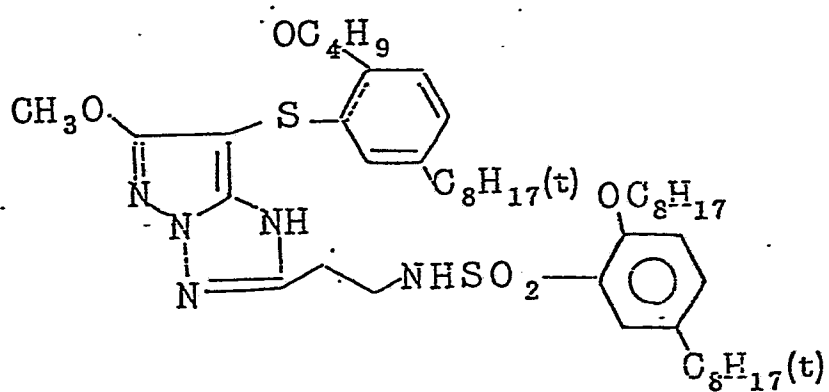
5 Furthermore, Samples (G) to (L) and Samples (M) to (R) were, respectively, prepared by using magenta coupler (M - 1) and cyan coupler (C - 1), respectively, in place of the yellow coupler (Y - 1) in Samples (A) to (F).

10 In addition, in the case of using the magenta coupler, the coated amount of the coupler was  $0.37 \text{ g/m}^2$ , the coated amount of the silver chlorobromide emulsion containing 75 mol% of Br was  $0.20 \text{ g/m}^2$  as silver and in the case of using the cyan coupler, the coated amount of the coupler was  $0.33 \text{ g/m}^2$  and the coated amount of the silver chlorobromide  
15 emulsion containing 70 mol% Br was  $0.28 \text{ g/m}^2$  as silver.

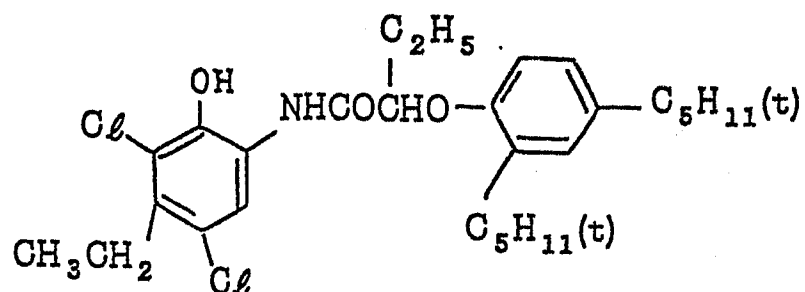
Y - 1



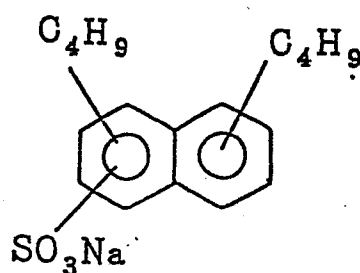
M - 1



C - 1



Comparison Compound R-1



5            These samples were subjected to stepwise exposure  
 for sensitometry and then processed by Process A or Process  
 B using Color Developer (A) or (B) as described below,  
 respectively. Process A differs from Process B by the  
 difference in content between Color Developers (A) and (B)  
 10 and other contents are same in both processes.

| (Processing Step) | (Temperature) | (Time)   |
|-------------------|---------------|----------|
| Development       | 38°C          | 2.0 min. |
| Blix              | 33°C          | 1.5 min. |
| Wash              | 28 to 35°C    | 3.0 min. |

5 (Composition of Developer)

Color Developer (A):

|    |                                                                                     |          |
|----|-------------------------------------------------------------------------------------|----------|
|    | Diethylenetriaminepentaacetic acid<br>5Na Salt                                      | 2.0 g    |
|    | Benzyl Alcohol                                                                      | 15 ml    |
|    | Diethylene Glycol                                                                   | 10 ml    |
| 10 | Na <sub>2</sub> SO <sub>3</sub>                                                     | 2.0 g    |
|    | KBr                                                                                 | 0.5 g    |
|    | Hydroxylamine Sulfate                                                               | 3.0 g    |
|    | 4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]-p-phenylenediamine·Sulfate | 5.0 g    |
|    | Na <sub>2</sub> CO <sub>3</sub> (monohydrate)                                       | 30.0 g   |
| 15 | Brightening Agent (stilbene-series)                                                 | 1.0 g    |
|    | Water to make                                                                       | 1,000 ml |
|    | (pH 10.1)                                                                           |          |

Color Developer (B):

|    |                                                |       |
|----|------------------------------------------------|-------|
|    | Diethylenetriaminepentaacetic acid<br>5Na Salt | 2.0 g |
|    | Na <sub>2</sub> SO <sub>3</sub>                | 2.0 g |
| 20 | KBr                                            | 0.5 g |
|    | Hydroxylamine Sulfate                          | 3.0 g |

4-Amino-3-methyl-N-ethyl-N-[ $\beta$ -(methanesulfonamido)ethyl]-p-phenylenediamine·Sulfate 5.0 g  
Na<sub>2</sub>CO<sub>3</sub> (monohydrate) 30.0 g  
5 Brightening Agent (stilbene-series) 1.0 g  
Water to make 1,000 ml  
(pH 10.1)

(Blix Solution Composition)

10 Ammonium Thiosulfate (54 wt.%) 150 ml  
Na<sub>2</sub>SO<sub>3</sub> 15 g  
NH<sub>4</sub>[Fe(III)(EDTA)] 55 g  
EDTA·2Na 4 g  
Water to make 1,000 ml  
(pH 6.9)

15 The evaluation of the photographic properties was performed on two items of maximum density (D<sub>max</sub>) and minimum density (D<sub>min</sub>). The results are shown in Table 1.

Table 1

| Sample         | Coupler | Dispersing Agent | Photographic Property |      |           |      |
|----------------|---------|------------------|-----------------------|------|-----------|------|
|                |         |                  | Process A             |      | Process B |      |
|                |         |                  | Dmin                  | Dmax | Dmin      | Dmax |
| (A) Comparison |         | R-1              | 0.08                  | 2.10 | 0.08      | 1.97 |
| (B) ↑          | Y-1     | A-1              | 0.09                  | 2.17 | 0.08      | 2.14 |
| (C)            |         | A-9              | 0.08                  | 2.20 | 0.08      | 2.16 |
| (D) (Note 1)   |         | A-11             | 0.09                  | 2.21 | 0.08      | 2.19 |
| (E) ↓          |         | A-20             | 0.08                  | 2.19 | 0.08      | 2.15 |
| (F)            |         | A-26             | 0.08                  | 2.19 | 0.08      | 2.15 |
| (G) Comparison |         | R-1              | 0.09                  | 2.66 | 0.09      | 2.48 |
| (H) ↑          | M-1     | A-1              | 0.09                  | 2.70 | 0.09      | 2.64 |
| (I)            |         | A-9              | 0.09                  | 2.71 | 0.08      | 2.67 |
| (J) (Note 1)   |         | A-11             | 0.10                  | 2.67 | 0.09      | 2.62 |
| (K) ↓          |         | A-20             | 0.10                  | 2.68 | 0.09      | 2.65 |
| (L)            |         | A-26             | 0.10                  | 2.67 | 0.09      | 2.66 |
| (M) Comparison |         | R-1              | 0.11                  | 2.77 | 0.10      | 2.58 |
| (N) ↑          | C-1     | A-1              | 0.10                  | 2.79 | 0.09      | 2.71 |
| (O)            |         | A-9              | 0.10                  | 2.78 | 0.09      | 2.70 |
| (P) (Note 1)   |         | A-11             | 0.11                  | 2.77 | 0.09      | 2.69 |
| (Q) ↓          |         | A-20             | 0.11                  | 2.78 | 0.09      | 2.77 |
| (R)            |         | A-26             | 0.10                  | 2.78 | 0.09      | 2.71 |

(Note 1): Samples (B)-(F), (H)-(L) and (N)-(R) processed by Process B are samples in this invention.

From the results in Table 1, it can be seen that in any cases of using yellow coupler, magenta coupler, and cyan coupler, respectively, the samples in this invention show higher maximum density than those of comparison samples and show almost the same coloring property as in Process A, even in Process B not using benzyl alcohol.

EXAMPLE 2.

Comparison multilayer color photographic paper (A) having the layer construction shown in Table 2 below on a paper support both surface of which had been laminated by polyethylene was prepared.

In addition, the coating solutions for the layers were prepared as follows.

Preparation of Coating Solution for Layer 1

To 19.1 g of yellow coupler (a) and 4.4 g of color image stabilizer (b) were added 27.2 ml of ethyl acetate and 7.9 ml of solvent (c) to dissolve the aforesaid components, the solution was added to 185 ml of an aqueous 10% gelatin solution containing 12 ml of a 10% solution of sodium dibutylnaphthalenesulfonate (R - 1) as a dispersing agent, and the mixture was emulsified by a continuous stirrer to provide an emulsified dispersion.

On the other hand, a blue-sensitive sensitizing dye shown below was added to a silver chlorobromide emulsion (containing 80 mol% silver bromide and 70 g/kg of silver) in

an amount of  $7.0 \times 10^{-4}$  mol per mol of silver chlorobromide to provide 90 g of a blue-sensitive emulsion.

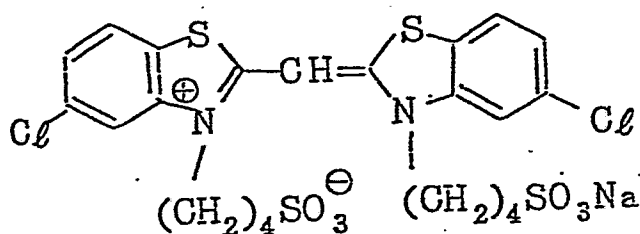
The emulsified dispersion was mixed with the emulsion and the concentration of gelatin was adjusted as shown in Table 2 to provide the coating solution for Layer 1.

The coating solutions for Layer 2 to Layer 7 were also prepared by the same manner as for the coating solution for Layer 1.

In addition, as a gelatin hardening agent for each layer, 1-oxy-3,5-dichloro-s-triazine sodium salt was used.

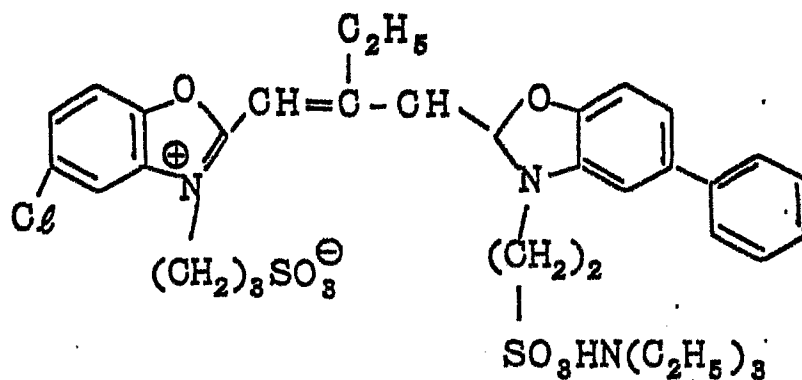
Also, for each emulsion layer, the following spectral sensitizer was used.

Blue-Sensitive Emulsion Layer:



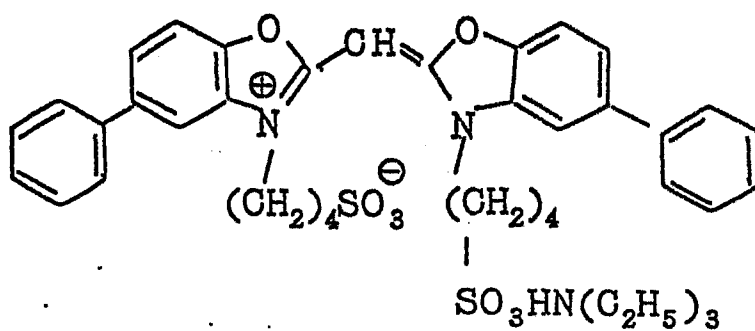
( $7.0 \times 10^{-4}$  mol per mol of silver halide)

## Green-Sensitive Emulsion Layer:



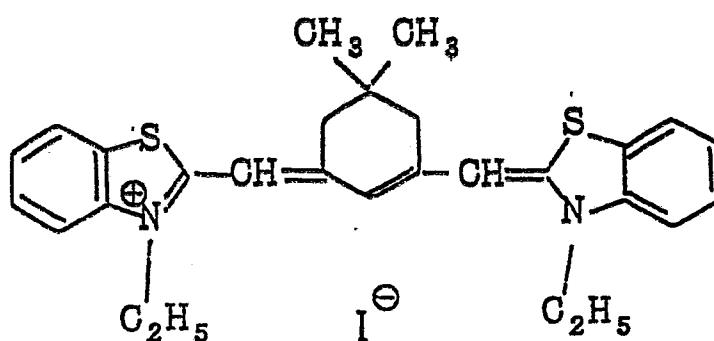
$(4.0 \times 10^{-4}$  mol per mol of silver halide)

and



$(7.0 \times 10^{-5}$  mol per mol of silver halide)

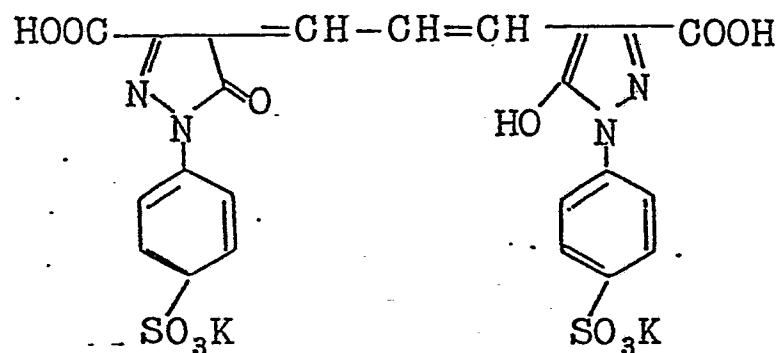
Red-Sensitive Emulsion Layer:



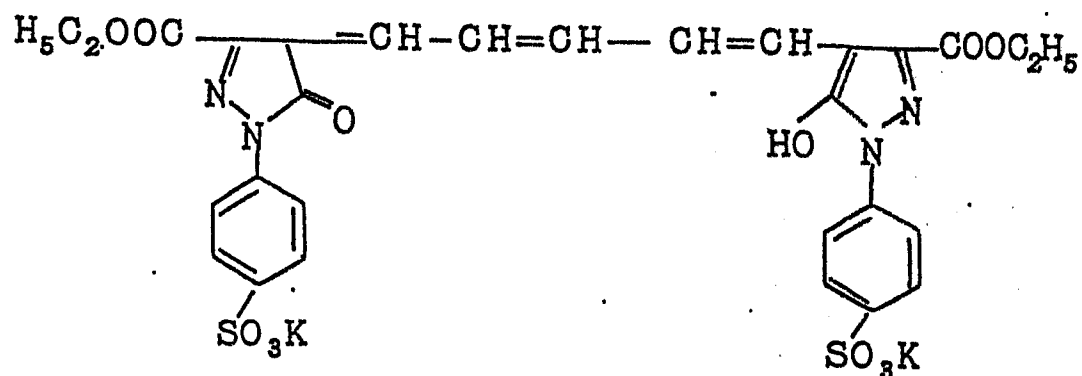
( $1.0 \times 10^{-4}$  mol per mol of silver halide)

Also, for each emulsion layer was used the following  
5 dye as an irradiation preventing dye:

Green-Sensitive Emulsion Layer:

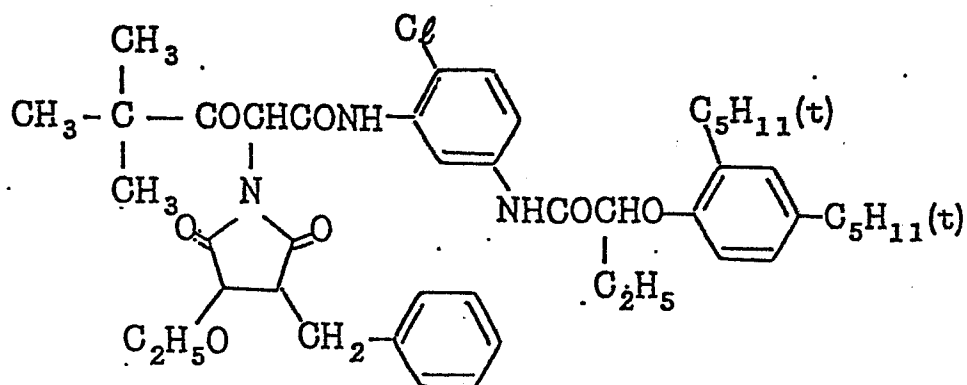


## Red-Sensitive Emulsion Layer:

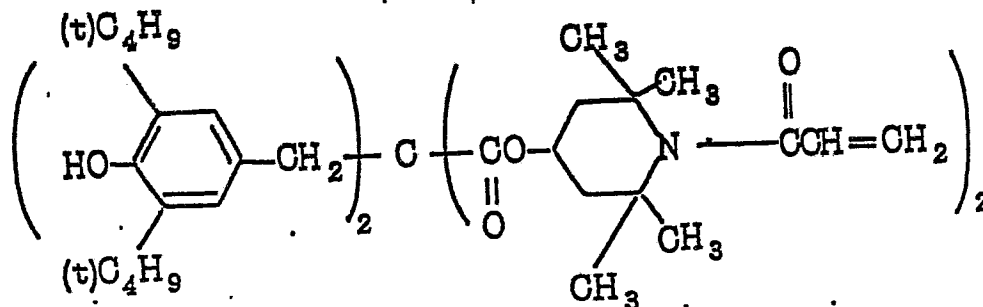


The structural formulae of the compounds such as couplers, etc., used in the example were as follows.

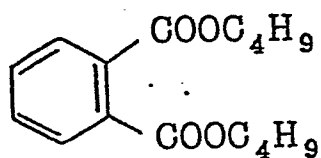
## 5 Yellow Coupler (a)



## Color Image Stabilizer (b)

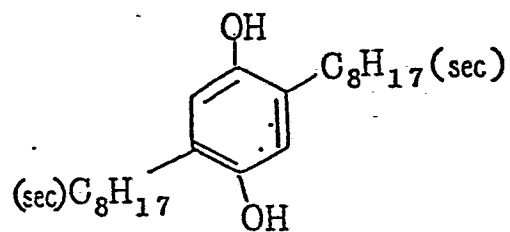


## Solvent (c)

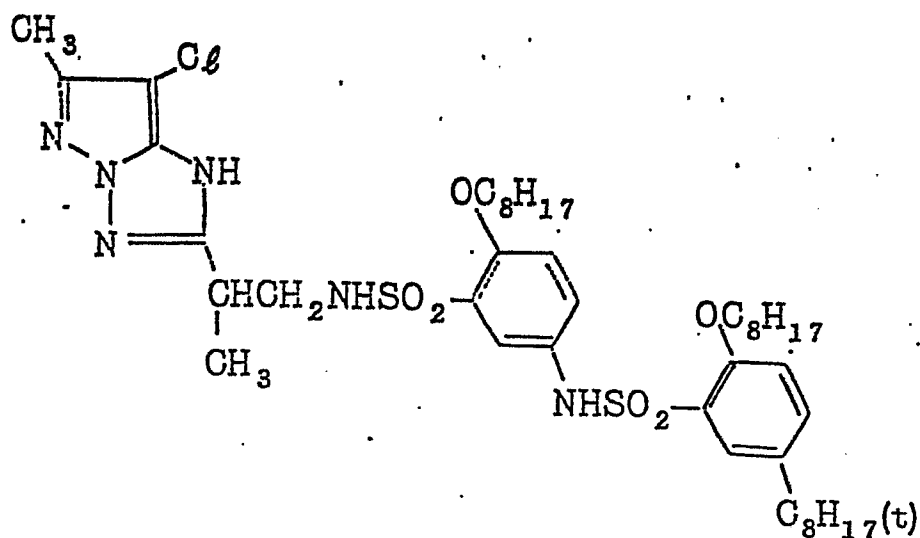


5

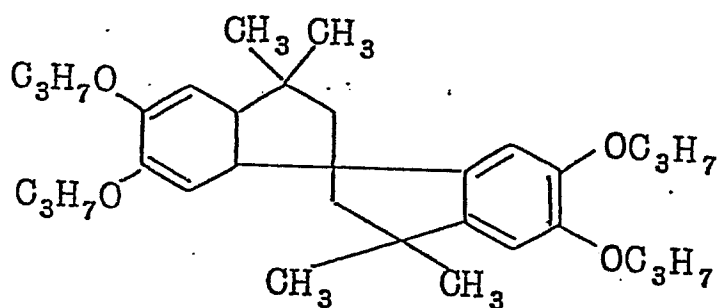
## Color Stain Preventing Agent (d)



## Magenta Coupler (e)

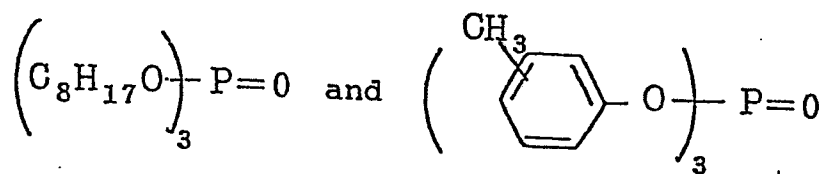


## Color Image Stabilizer (f)



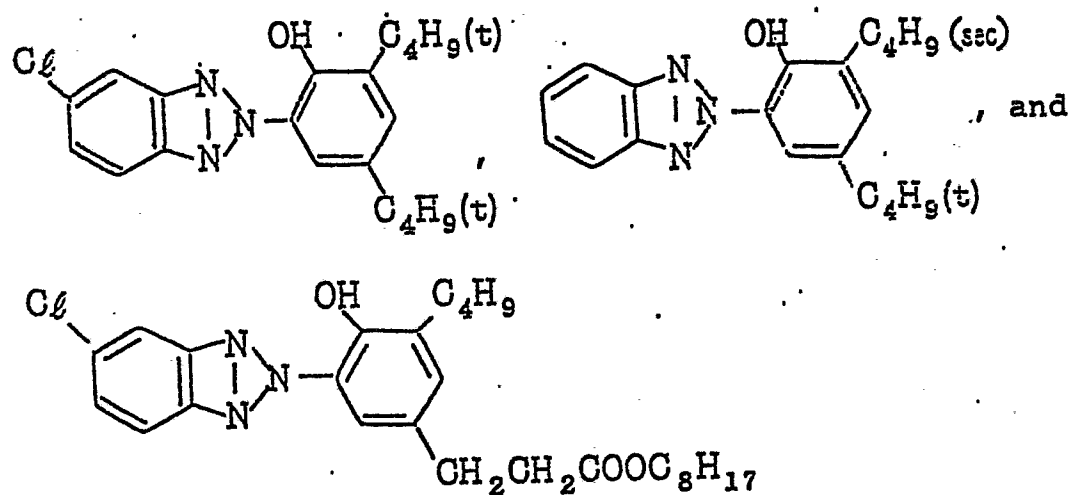
5

## Solvent (g)



2:1 Mixture (weight ratio)

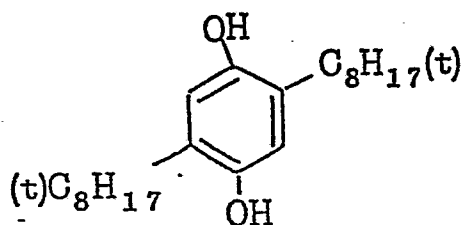
## Ultraviolet Ray Absorbent (h)



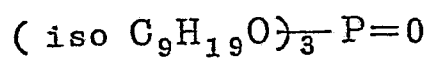
1:5:3 Mixture (mol ratio)

## Color Stain Preventing Agent (i)

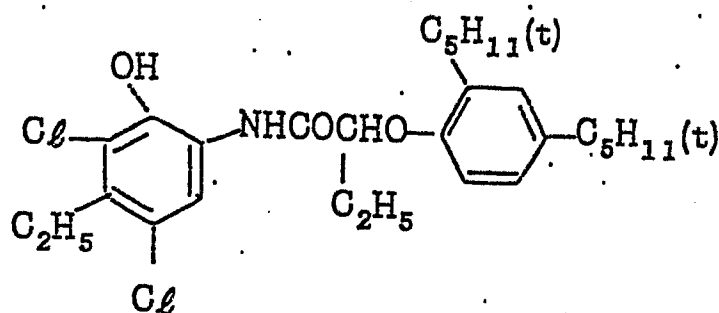
5



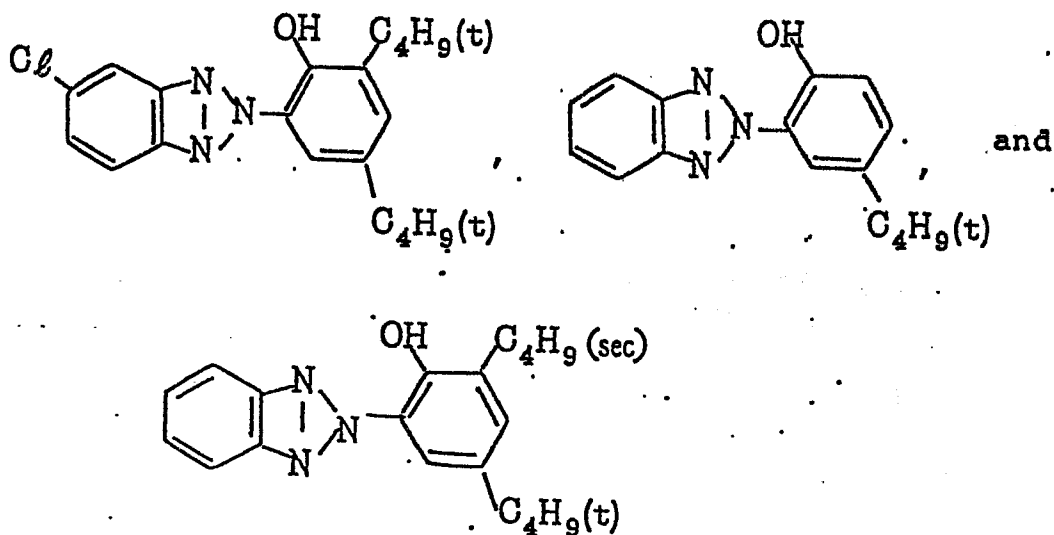
## Solvent (j)



## Cyan Coupler (k)



## Ultraviolet Ray Absorbent (1)



5

1:3:3 Mixture (mol ratio)

Solvent (m)

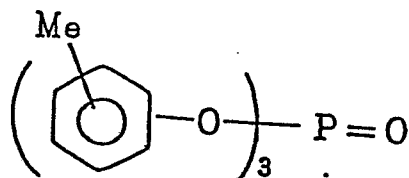


Table 2

| Layer                                         | Main Components                                                        | Amount                             |
|-----------------------------------------------|------------------------------------------------------------------------|------------------------------------|
| Layer 7<br>(Protective layer)                 | Gelatin                                                                | 1.33 g/m <sup>2</sup>              |
|                                               | Acryl-modified copolymer (modified degree of 17%) of polyvinyl alcohol | 0.17 "                             |
| Layer 6<br>(Ultraviolet Ray Absorptive Layer) | Gelatin                                                                | 0.54 "                             |
|                                               | Ultraviolet Ray Absorbent (h)                                          | 0.21 "                             |
|                                               | Solvent (j)                                                            | 0.09 cc/m <sup>2</sup>             |
| Layer 5<br>(Red-Sensitive Layer)              | Silver chlorobromide emulsion (silver bromide 70 mol%)                 | 0.23 g/m <sup>2</sup><br>as silver |
|                                               | Gelatin                                                                | 0.98 g/m <sup>2</sup>              |
|                                               | Cyan Coupler (k)                                                       | 0.30 "                             |
|                                               | Color Image Stabilizer (l)                                             | 0.17 "                             |
|                                               | Solvent (m)                                                            | 0.23 cc/m <sup>2</sup>             |
| Layer 4<br>(Ultraviolet Ray Absorptive Layer) | Gelatin                                                                | 1.60 g/m <sup>2</sup>              |
|                                               | Ultraviolet Ray Absorbent (h)                                          | 0.62 "                             |
|                                               | Color Stain Preventing Agent (i)                                       | 0.05 "                             |
|                                               | Solvent (j)                                                            | 0.26 cc/m <sup>2</sup>             |
| Layer 3<br>(Green-Sensitive Layer)            | Silver chlorobromide emulsion (silver bromide 75 mol%)                 | 0.13 g/m <sup>2</sup><br>as silver |
|                                               | Gelatin                                                                | 1.80 g/m <sup>2</sup>              |
|                                               | Magenta Coupler (e)                                                    | 0.30 "                             |
|                                               | Color Image Stabilizer (f)                                             | 0.20 "                             |
|                                               | Solvent (g)                                                            | 0.68 cc/m <sup>2</sup>             |
| Layer 2<br>(Color Stain Preventing Layer)     | Gelatin                                                                | 0.99 g/m <sup>2</sup>              |
|                                               | Color Stain Preventing Agent (d)                                       | 0.08 "                             |

Table 2 (cont.)

| <u>Layer</u>                      | <u>Main Components</u>                                                                                                                        | <u>Amount</u>                      |
|-----------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|
| Layer 1<br>(Blue-sensitive layer) | Silver chlorobromide emulsion (silver bromide 80 mol%)                                                                                        | 0.27 g/m <sup>2</sup><br>as silver |
|                                   | Gelatin                                                                                                                                       | 1.86 g/m <sup>2</sup>              |
|                                   | Yellow Coupler (a)                                                                                                                            | 0.71 "                             |
|                                   | Color Image Stabilizer (b)                                                                                                                    | 0.19 "                             |
|                                   | Solvent (c)                                                                                                                                   | 0.34 cc/m <sup>2</sup>             |
| Support                           | Polyethylene-laminated paper (containing white pigment (TiO <sub>2</sub> ) and bluish dye (ultramarine blue) in polyethylene at Layer 1 side) |                                    |

Then, light-sensitive materials (B) to (D) were prepared as follows.

5 Light-Sensitive Material B

Same light-sensitive material as Light-Sensitive Material (A) except that 1.2 g of Compound A - 1 of this invention was used in place of R - 1 in Layers 1, 3 and 5 of Light-Sensitive Material (A) as a dispersing agent.

10 Light-Sensitive Material C

Same light-sensitive material as Light-Sensitive Material (A) except that 1.2 g of Compound A - 9 of this invention was used in place of R - 1 in Layers 1, 3 and 5 of Light-Sensitive Material (A) as a dispersing agent.

15 Light-Sensitive Material D

Same light-sensitive material as Light-Sensitive Material (A) except that 1.2 g of Compound A - 26 of this

invention was used in place of R - 1 in Layers 1, 3 and 5 of Light-Sensitive Material (A) as a dispersing agent.

5 These samples were subjected to gradation exposure for sensitometry through each of blue, green, and red filters using a sensitometer (Type FWH, made by Fuji Photo Film Co, Ltd., color temperature of light source: 3,200°K). In this case, the exposure was performed such that the exposure amount became 250 CMS in an exposure time of 0.5 second.

10 Thereafter, the samples were processed by Process A or Process B using Color developer (A) or (B), respectively.

The process was composed of the steps of color development, blix, and wash and by changing the developing time to 1 minute, 2 minutes, and 3 minutes, the evaluation  
15 of the photographic properties were performed. Process A differs from Process B in the content between Color Developers A and B and other contents are same in both processes.

The evaluation of the photographic properties was performed on the four items of relative sensitivity, gradation, maximum density (Dmax), and minimum density (Dmin).  
20 The relative sensitivity was a relative value taking the sensitivity of each light-sensitive layer of each light-sensitive material color developed for 2 minutes in Process A as 100. The sensitivity was represented as a relative  
25 value of a reciprocal of an exposure amount necessary for

giving a density of the minimum density + 0.5. The gradation was represented as the difference in density between the sensitive point to a point increased by 0.5 in logarithm (logE) of exposure amount.

5 The results obtained are shown in Table 3 (A) and (B).

| (Processing Step) | (Temperature) | (Time)          |
|-------------------|---------------|-----------------|
| Development       | 38°C          | 1.0 to 3.0 min. |
| Blix              | 33°C          | 1.5 min.        |
| 10 Wash           | 28 to 35°C    | 3.0 min.        |

(Color Developer Composition)

Color Developer (A):

|    |                                                                                     |           |
|----|-------------------------------------------------------------------------------------|-----------|
|    | Diethylenetriaminepentaacetic acid<br>5Na Salt                                      | 2.0 g     |
| 15 | Benzyl Alcohol                                                                      | 15 ml     |
|    | Diethylene Glycol                                                                   | 10 ml     |
|    | Na <sub>2</sub> SO <sub>3</sub>                                                     | 2.0 g     |
|    | KBr                                                                                 | 0.5 g     |
|    | Hydroxylamine Sulfate                                                               | 3.0 g     |
| 20 | 4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]-p-phenylenediamine·Sulfate | 5.0 g     |
|    | Na <sub>2</sub> CO <sub>3</sub> (monohydrate)                                       | 30.0 g    |
| 25 | Brightening Agent (stilbene-series)                                                 | 1.0 g     |
|    | Water to make                                                                       | 1,000 ml  |
|    |                                                                                     | (pH 10.1) |

## Color Developer (B):

|    |                                                                                                     |           |
|----|-----------------------------------------------------------------------------------------------------|-----------|
|    | Diethylenetriaminepentaacetic acid<br>5Na Salt                                                      | 2.0 g     |
|    | $\text{Na}_2\text{SO}_3$                                                                            | 2.0 g     |
| 5  | KBr                                                                                                 | 0.5 g     |
|    | Hydroxylamine Sulfate                                                                               | 3.0 g     |
|    | 4-Amino-3-methyl-N-ethyl-N-[ $\beta$ -<br>(methanesulfonamido)ethyl]-p-<br>phenylenediamine Sulfate | 5.0 g     |
| 10 | $\text{Na}_2\text{CO}_3$ (monohydrate)                                                              | 30.0 g    |
|    | Brightening Agent (stilbene-<br>series)                                                             | 1.0 g     |
|    | Water to make                                                                                       | 1,000 ml  |
|    |                                                                                                     | (pH 10.1) |

## (Blix Solution Composition)

|    |                                                   |          |
|----|---------------------------------------------------|----------|
| 15 | Ammonium Thiosulfate (54 wt.%)                    | 150 ml   |
|    | $\text{Na}_2\text{SO}_3$                          | 15 g     |
|    | $\text{NH}_4[\text{Fe}(\text{III})(\text{EDTA})]$ | 55 g     |
|    | EDTA $\cdot$ 2Na                                  | 4 g      |
|    | Water to make                                     | 1,000 ml |
|    |                                                   | (pH 6.9) |

Table 3A

| Light-Sensitive<br>Material | Layer | Dispersing<br>Agent | Process A       |      |      |      |     |           |      |      |     |      |
|-----------------------------|-------|---------------------|-----------------|------|------|------|-----|-----------|------|------|-----|------|
|                             |       |                     | Developing Time |      |      |      |     |           |      |      |     |      |
|                             |       |                     | 1 minute        |      |      |      |     | 2 minutes |      |      |     |      |
|                             |       |                     | RS              | Gd   | Dmin | Dmax | RS  | Gd        | Dmin | Dmax | RS  | Gd   |
| A                           | B     | R-1                 | 53              | 0.89 | 0.10 | 1.78 | 100 | 0.92      | 0.10 | 1.84 | 106 | 1.00 |
|                             | G     |                     | 65              | 1.14 | 0.10 | 2.34 | 100 | 1.16      | 0.11 | 2.40 | 111 | 1.19 |
|                             | R     |                     | 68              | 1.24 | 0.10 | 2.50 | 100 | 1.26      | 0.11 | 2.53 | 114 | 1.28 |
| B                           | B     | A-1                 | 57              | 0.97 | 0.09 | 1.81 | 100 | 1.01      | 0.10 | 1.87 | 116 | 1.10 |
|                             | G     |                     | 71              | 1.25 | 0.10 | 2.35 | 100 | 1.28      | 0.10 | 2.44 | 130 | 1.31 |
|                             | R     |                     | 74              | 1.37 | 0.10 | 2.51 | 100 | 1.39      | 0.10 | 2.55 | 125 | 1.41 |
| C                           | B     | A-9                 | 55              | 0.93 | 0.10 | 1.81 | 100 | 0.97      | 0.10 | 1.87 | 111 | 1.05 |
|                             | G     |                     | 68              | 1.20 | 0.10 | 2.37 | 100 | 1.22      | 0.09 | 2.43 | 117 | 1.25 |
|                             | R     |                     | 71              | 1.30 | 0.10 | 2.53 | 100 | 1.32      | 0.10 | 2.56 | 119 | 1.34 |
| D                           | B     | A-26                | 60              | 1.00 | 0.10 | 2.02 | 100 | 1.02      | 0.10 | 1.89 | 117 | 1.12 |
|                             | G     |                     | 76              | 1.27 | 0.10 | 2.39 | 100 | 1.28      | 0.10 | 2.45 | 122 | 1.33 |
|                             | R     |                     | 77              | 1.38 | 0.10 | 2.55 | 100 | 1.40      | 0.10 | 2.58 | 125 | 1.43 |

RS: Relative Sensitivity  
Gd: Gradation

Table 3B

| Light-Sensitive<br>Material | Layer | Dispersing<br>Agent | Process B<br>Developing Time |      |      |           |     |      |           |      |     |      |      |      |
|-----------------------------|-------|---------------------|------------------------------|------|------|-----------|-----|------|-----------|------|-----|------|------|------|
|                             |       |                     | 1 minute                     |      |      | 2 minutes |     |      | 3 minutes |      |     |      |      |      |
|                             |       |                     | RS                           | Gd   | Dmin | Dmax      | RS  | Gd   | Dmin      | Dmax | RS  | Gd   | Dmin | Dmax |
|                             |       |                     |                              |      |      |           |     |      |           |      |     |      |      |      |
| A                           | B     |                     | 46                           | 0.78 | 0.10 | 1.57      | 72  | 0.80 | 0.10      | 1.60 | 87  | 0.90 | 0.10 | 1.70 |
|                             | G     | R-1                 | 61                           | 1.00 | 0.10 | 2.05      | 72  | 1.10 | 0.10      | 2.07 | 92  | 1.12 | 0.10 | 2.11 |
|                             | R     |                     | 59                           | 1.10 | 0.10 | 2.21      | 75  | 1.15 | 0.10      | 2.20 | 94  | 1.20 | 0.10 | 2.30 |
| B                           | B     |                     | 49                           | 0.85 | 0.08 | 1.74      | 107 | 1.06 | 0.09      | 1.79 | 85  | 1.08 | 0.09 | 1.86 |
|                             | G     | A-1                 | 66                           | 1.10 | 0.08 | 2.28      | 120 | 1.26 | 0.10      | 2.39 | 90  | 1.28 | 0.09 | 2.43 |
|                             | R     |                     | 64                           | 1.21 | 0.08 | 2.46      | 115 | 1.35 | 0.09      | 2.49 | 92  | 1.39 | 0.09 | 2.54 |
| C                           | B     |                     | 48                           | 0.90 | 0.09 | 1.73      | 103 | 1.03 | 0.09      | 1.84 | 105 | 1.05 | 0.10 | 1.87 |
|                             | G     | A-9                 | 64                           | 1.05 | 0.09 | 2.23      | 109 | 1.20 | 0.09      | 2.43 | 111 | 1.22 | 0.10 | 2.45 |
|                             | R     |                     | 62                           | 1.16 | 0.09 | 2.32      | 111 | 1.27 | 0.09      | 2.53 | 113 | 1.31 | 0.10 | 2.55 |
| D                           | B     |                     | 52                           | 0.88 | 0.09 | 1.75      | 110 | 1.08 | 0.10      | 1.86 | 113 | 1.10 | 0.10 | 1.88 |
|                             | G     | A-26                | 69                           | 1.12 | 0.09 | 2.25      | 116 | 1.30 | 0.10      | 2.45 | 118 | 1.32 | 0.10 | 2.47 |
|                             | R     |                     | 67                           | 1.23 | 0.09 | 2.78      | 117 | 1.39 | 0.10      | 2.53 | 120 | 1.41 | 0.10 | 2.57 |

RS: Relative Sensitivity

Gd: Gradation

(Note 1): Light-Sensitive Materials (B), (C) and (D) processed  
by Process B are samples in this invention.

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As shown in Table 3, it can be seen that Light-Sensitive Materials (B) to (D) for use in this invention give less difference in relative sensitivity, gradation, and maximum density between the case of processing by Process A and the case of processing by Process B as compared with Comparison Light-Sensitive Material (A) and show almost the same performance as the case of processing in Process A, even in Process B containing no benzyl alcohol.

Also, Light-Sensitive Materials (B) to (D) for use in this invention show good photographic properties by the development of 2 minutes in Process B containing no benzyl alcohol even in the case of using the high-bromine containing emulsion showing relatively slow development. Therefore, it can be seen that the development time is more shortened in the case of using a high-chlorine containing emulsion.

#### [INDUSTRIAL APPLICABILITY]

By the practice of this invention, the pollution load and work for preparing color developer can be reduced by substantially omitting benzyl alcohol and further in such a case, the effect for preventing the reduction in density by a cyan dye remaining as a leuco compound can be obtained.

Also, by using the silver halide emulsions for use in this invention, such effect that photographic properties of high Dmax, low Dmin, and less change of sensitivity and gradation

are obtained even in the case of using no benzyl alcohol is provided.

## WHAT IS CLAIMED IS

1. A color image-forming process, which comprises processing, after imagewise exposure, a silver halide color photographic light-sensitive material comprising a reflective support having provided thereon at least one silver halide emulsion layer and containing an anionic surface active agent having in the molecule a fluorine-substituted aliphatic group having 4 to 18 carbon atoms as a hydrophobic group and  $-\text{SO}_3\text{M}$  or  $-\text{OSO}_3\text{M}$  (wherein M represents a hydrogen atom or a cation) as a hydrophilic group in the emulsion layer or a layer adjacent thereto with a color developer containing substantially no benzyl alcohol in a time of up to 2 minutes and 30 seconds.

2. The color image-forming process as claimed in claim 1, wherein the anionic surface active agent is a surface active agent represented by following general formula (1)



wherein Rf represents a fluorine-substituted alkyl group having 4 to 18 carbon atoms or a fluorine-substituted alkenyl group, X represents  $-\text{SO}_3\text{M}$  or  $-\text{OSO}_3\text{M}$  (wherein M represents a hydrogen atom or a cation), B represents a di-valent or tri-valent organic residue or a poly-valent group formed by bonding of a di-valent or tri-valent organic

residue and a di-valent linkage group; n represents 1 or 2; and m represents 0 or 1.

3. The color image-forming process as claimed in claim 2, wherein the di-valent or tri-valent organic residue represented by B is a di-valent or tri-valent aliphatic hydrocarbon group, an arylene group, or a di-valent hetero-  
5 cyclic group.

4. The color image-forming process as claimed in claim 2, wherein the poly-valent group represented by B is

$$\begin{array}{c} \text{R} \\ | \\ (\text{SO}_2-\text{N}-\text{R}_1-\text{O}-\text{CO})_2\text{R}_2-, \quad -\text{COOR}_1-, \quad -\text{R}_1\text{O}-\text{CO}-\text{R}_1-, \quad -\text{CONH}-\text{R}_1-, \quad \text{or} \\ -\text{SO}_2\text{NR}-\text{R}_1- \end{array}$$
 (wherein R represents a hydrogen atom or an alkyl  
5 group having 1 to 18 carbon atoms,  $\text{R}_1$  represents a di-valent aliphatic hydrocarbon group, an arylene group, or a di-valent heterocyclic group, and  $\text{R}_2$  represents a tri-valent aliphatic hydrocarbon group).

5. The color image-forming process as claimed in claim 1, wherein the silver halide emulsion layer or the layer adjacent thereto contains a fluorine-unsubstituted anionic surface active agent and/or a nonionic surface active agent  
5 together with the anionic surface active agent.

6. The color image-forming process as claimed in claim 5, wherein the fluorine-unsubstituted anionic surface active agent is a fluorine-unsubstituted anionic surface active agent having a hydrophobic group having 8 to 30 carbon atoms

and an  $-\text{SO}_3\text{M}$  or  $-\text{OSO}_3\text{M}$  group in the molecule.

7. The color image-forming process as claimed in claim 5, wherein the nonionic surface active agent is a sorbitan fatty acid ester-series nonionic surface active agent.

8. The color image-forming process as claimed in claim 1, wherein the color developer is an alkaline aqueous solution containing an aromatic primary amine-series color developing agent as the main component.

9. A color image-forming process which comprises subjecting, after imagewise exposure, a silver halide color photographic light-sensitive material comprising a reflective support having provided thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, and at least one blue-sensitive silver halide emulsion layer to color development, bleach and fix, or blix, and wash and/or stabilization, said silver halide emulsion layer or a layer adjacent thereto containing an anionic surface active agent having in the molecule a fluorine-substituted aliphatic group having 4 to 18 carbon atoms as a hydrophobic group and  $-\text{SO}_3\text{M}$  or  $-\text{OSO}_3\text{M}$  (wherein M represents a hydrogen atom or a cation) as a hydrophilic group and said color development being performed with a color developer containing substantially no benzyl alcohol in a time of up to 2 minutes and 30 seconds.

10. The color image-forming process as claimed in claim

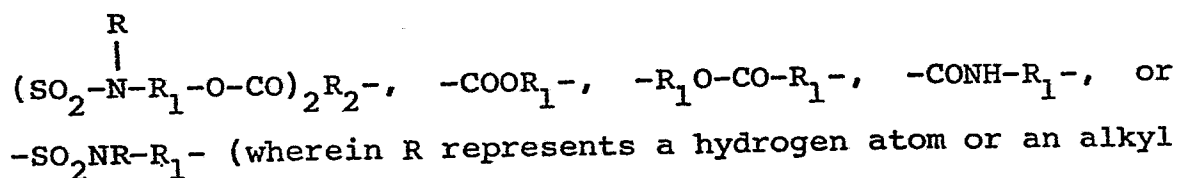
9, wherein the anionic surface active agent is a surface active agent represented by following general formula (1)



5 wherein Rf represents a fluorine-substituted alkyl group having 4 to 18 carbon atoms or a fluorine-substituted alkenyl group, X represents  $-SO_3M$  or  $-OSO_3M$  (wherein M represents a hydrogen atom or a cation), B represents a di-valent or tri-valent organic residue or a poly-valent group  
10 formed by bonding of a di-valent or tri-valent organic residue and a di-valent linkage group, n represents 1 or 2, and m represents 0 or 1.

11. The color image-forming process as claimed in claim 10, wherein the di-valent or tri-valent organic residue represented by B is a di-valent or tri-valent aliphatic hydrocarbon group, an arylene group, or a di-valent hetero-  
5 cyclic group.

12. The color image-forming process as claimed in claim 10, wherein the poly-valent group represented by B is



5 group having 1 to 18 carbon atoms,  $R_1$  represents a di-valent aliphatic hydrocarbon group, an arylene group, or a di-

valent heterocyclic group, and  $R_2$  represents a tri-valent aliphatic hydrocarbon group).

13. The color image-forming process as claimed in claim 9, wherein the silver halide emulsion layer or the layer adjacent thereto contains a fluorine-unsubstituted anionic surface active agent and/or a nonionic surface active agent together with the anionic surface active agent.

14. The color image-forming process as claimed in claim 13, wherein the fluorine-unsubstituted anionic surface active agent is a fluorine-unsubstituted anionic surface active agent having a hydrophobic group having 8 to 30 carbon atoms and an  $-SO_3M$  or  $-OSO_3M$  group in the molecule.

15. The color image-forming process as claimed in claim 13, wherein the nonionic surface active agent is a sorbitan fatty acid ester-series nonionic surface active agent.

16. The color image-forming process as claimed in claim 9, wherein the color developer is an alkaline aqueous solution containing an aromatic primary amine-series color developing agent as the main component.

17. The color image-forming process as claimed in claim 1, wherein the silver halide is of a type mainly forming latent images on the surface of the grain.

18. The color image-forming process as claimed in claim 1, wherein the color developer contains no benzyl alcohol.

19. The color image-forming process as claimed in claim

8, wherein the aromatic primary amine-series color developing agent is a p-phenylenediamine-series compound.

20. The color image-forming process as claimed in claim 19, wherein the p-phenylenediamine-series compound is 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline or 3-methyl-4-amino-N-ethyl-N-hydroxyethylaniline.

21. The color image-forming process as claimed in claim 19, wherein the p-phenylenediamine-series compound is 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline.

22. The color image-forming process as claimed in claim 1, wherein the anionic surface active agent is contained in the silver halide emulsion layer.

23. The color image-forming process as claimed in claim 1, wherein the anionic surface active agent is contained in the silver halide emulsion layer and/or a layer adjacent thereto in an amount of 0.2 to 50% by weight to a hydrophobic substance dispersed by emulsification in said layer.

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/JP87/00062

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|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                         |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                         |                                     |
| Int.C1 <sup>4</sup> G03C7/30, G03C7/26                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                         |                                     |
| <b>II. FIELDS SEARCHED</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                         |                                     |
| Minimum Documentation Searched <sup>5</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                         |                                     |
| Classification System                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Classification Symbols                                                                                                                  |                                     |
| IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | G03C7/30, G03C7/26                                                                                                                      |                                     |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in the Fields Searched <sup>6</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                         |                                     |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                         |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                         |                                     |
| Category <sup>7</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Citation of Document, <sup>16</sup> with Indication, where appropriate, of the relevant passages <sup>17</sup>                          | Relevant to Claim No. <sup>18</sup> |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | JP, A, 60-158446 (Konishiroku Photo Ind. Co., Ltd.)<br>19 August 1985 (19. 08. 85)<br>(Family: none)                                    | 1                                   |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | JP, A, 51-129229 (Fuji Photo Film Co., Ltd.)<br>10 November 1976 (10. 11. 76)<br>& DE, A1, 2619248 & GB, A, 1507961<br>& US, A, 4385110 | 1                                   |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | JP, A, 59-72442 (Konishiroku Photo Ind. Co., Ltd.)<br>24 April 1984 (24. 04. 84)<br>(Family: none)                                      | 1                                   |
| <p><sup>15</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> |                                                                                                                                         |                                     |
| <b>IV. CERTIFICATION</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                         |                                     |
| Date of the Actual Completion of the International Search <sup>2</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Date of Mailing of this International Search Report <sup>2</sup>                                                                        |                                     |
| April 27, 1987 (27. 04. 87)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | May 6, 1987 (06. 05. 87)                                                                                                                |                                     |
| International Searching Authority <sup>1</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Signature of Authorized Officer <sup>20</sup>                                                                                           |                                     |
| Japanese Patent Office                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                         |                                     |