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W-8000 München 22(DE)**(54) **Silver halide color reversal image forming method.**

(57) A silver halide color reversal image forming method is disclosed. The image forming method uses a silver halide color photographic material. The photographic material comprises a support, a silver halide emulsion layer containing a cyan coupler, a silver halide emulsion layer containing a magenta coupler and a silver halide emulsion layer containing a yellow coupler. The method comprises the steps of imagewise exposing to light the photographic material, subjecting the material to a black and white development process, subjecting the material to a reversal process, subjecting the material to a color development process, and subjecting the material to a desilvering process. In the present invention, the black and white development process is completed for a time of not longer than 80 seconds after the photographic material is imagewise exposed to light. The yellow coupler is a specific compound represented by the formula [I]. The layer containing the specific yellow coupler is the uppermost silver halide emulsion layer containing a coupler. The photographic material further comprises at least three protective layers provided on the layer containing the yellow coupler. The lower protective layer contains a scavenger of an oxidation product of a developing agent in an amount of not less than 0.1 mg/m². The middle protective layer contains non-photosensitive silver halide grains in an amount of not less than 0.001 mg/m². The upper protective layer is a colloidal layer. The non-photosensitive silver halide grains preferably contain silver chloride in an amount of not less than 70 % by mole.

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FIELD OF THE INVENTION

The present invention relates to a silver halide color reversal image forming method, and particularly relates to a silver halide color reversal image forming method which forms a clear image of high color reproducibility by a rapid developing process, and is reduced in density unevenness caused by the rapid developing process.

BACKGROUND OF THE INVENTION

Color reproducibility of the obtained color image for the original photograph largely depends upon properties of silver halide color photographic materials. Therefore, studies on silver halide color photographic materials have been made in various viewpoints to obtain excellent color reproducibility. For example, in the case of reproducing lemon yellow or light green, the resulting color is often tinged with orange or brown-like green. The present inventor has studied on silver halide color photographic materials improved in the yellow or yellowish color.

How wide range of color is reproduced in the obtained color image depends upon absorption properties of the used yellow, magenta and cyan dyes. When absorption profile of the used dye is broad or undesired side absorption is present, the resulting color suffers turbidity. For example, as for the yellow couplers, improvement was made to obtain a coupler having a sharper absorption profile and a shorter wavelength.

An improved yellow coupler is a compound represented by the following formula [I], which is described in Japanese Patent Provisional Publications No. 63(1988)-123047, No. 63(1988)-231451, No. 63(1988)-241547, No. 1(1989)-213648 and No. 1(1989)-250944.

A sharp yellow dye image free from turbidity can be obtained by using the yellow coupler represented by the following formula [I]. The color reproducibility of lemon yellow or light green can also be remarkably improved by the yellow coupler.

By the way, an easy and rapid developing process has recently been demanded. Therefore, various methods for conducting rapid development have been made. For example, some procedures in the developing process are unified and the number of processing baths is decreased; a developing temperature is raised or agitation is made with vigor to accelerate the reaction; the thickness of an emulsion layer or the amount of the used silver in the photographic material is reduced to accelerate permeation of processing liquids; or silver halide grains or couplers having a high reaction speed are used.

However, these methods for the rapid development sometimes have unfavorable influences on quality of an image given by a photographic material. For example, density unevenness or stain is easily brought about.

The present inventor has found that employment of the yellow coupler represented by the formula [I] can improve color reproducibility but simultaneously brings about marked unevenness of density or stain in the case of rapid developing process, that is, in the case of conducting black and white development for a time of not longer than 80 seconds.

Further, the time of the black and white development process has recently been further shortened, and the total time of the black and white development, reversal, color development and desilvering processes has also been shortened. In these cases, the unevenness of density and the stain of the image are remarkable.

For reducing this unfavorable unevenness, various trials have been made. With respect to processing machines, for example, temperature controlling, liquid cyclization, blowing direction of a processing liquid or blowing strength thereof, and shape of roller or guide have been actively improved. Otherwise, with respect to photographic materials, non-photosensitive silver halide fine grains are introduced into a protective layer to trap a development-inhibiting material.

Methods for introducing non-photosensitive silver halide fine grains into a protective layer are described, for example, in France Patent No. 912, 605, U.S. Patents No. 3,892,572, No. 3,961,963 and No. 4,607,004, and Japanese Patent Provisional Publications No. 63 (1988)-301946, No. 1(1989)-107256, No. 1-(1989)-167752 and No. 1(1989)-205163. The non-photosensitive silver halide fine grains are used to prevent release of a development-inhibiting material (particularly, halogen ion or development-inhibiting compound such as an eliminating group of DIR compound) from the photographic material into a developing liquid in the developing process so as to prevent pollution of a processing liquid.

Japanese Patent Provisional Publications No. 62(1987)-174755, No. 63(1988)-80248 and No. 63(1988)-80249 disclose that harmful influences exerted in the case of using the non-photosensitive silver halide fine grains in the protective layer for the same purpose as that in the above patents can be reduced by using a specific additive in combination. U.S. Patent No. 3,737,317 and Japanese Patent Provisional Publications

No. 62(1987)-240963, No. 63(1988)-281156, No. 63(1988)-304248 and No. 2(1990)-18550 disclose that when a colloidal silver is used in combination with the non-photosensitive silver halide fine grains in any layer of the protective layer group, release of silver ion can be restrained in addition to the above-mentioned effects, to hereby prevent storage of silver ion in the processing liquid and reduce occurrence of fogging or stain.

Further, if non-photosensitive silver chlorobromide is used in an amount of not less than 75 % by mole in the protective layer, agitation dependence in the developing process can be improved to obtain favorable photographic gradation (of., Japanese Patent Provisional Publication No. 61(1986)-39043).

SUMMARY OF THE INVENTION

The present inventor has made various experiments using the technique disclosed in the above-mentioned patents, and as a result, they have found that some effects are shown for certain unevenness, but any effect is not shown for other unevenness. Further, some troubles are brought about in the experiments.

An object of the present invention is to improve color reproducibility, particularly reproducibility of lemon yellow or light green, and to improve streaks incidental to a rapid developing process wherein black and white developing time is not longer than 80 seconds.

Another object of the invention is to reduce change of sensitivity even if a breach accelerator is included in a black and white developer, and to lower agitation dependence in the developing process.

The present inventor has found that the above-described problems are solved by the invention that is a silver halide color reversal image forming method comprises the steps of:

imagewise exposing to light a silver halide color photographic material which comprises a support, a silver halide emulsion layer containing a cyan coupler, a silver halide emulsion layer containing a magenta coupler and a silver halide emulsion layer containing a yellow coupler;

subjecting the material to a black and white development process;

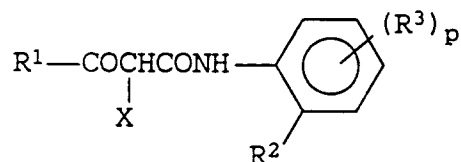
subjecting the material to a reversal process;

subjecting the material to a color development process; and

subjecting the material to a desilvering process,

wherein the black and white development process is completed for a time of not longer than 80 seconds after the photographic material is imagewise exposed to light; the yellow coupler is represented by the formula [I]; the layer containing the yellow coupler is the uppermost silver halide emulsion layer containing a coupler; the photographic material further comprises at least three protective layers provided on the layer containing the yellow coupler; the lower protective layer contains a scavenger of an oxidation product of a developing agent in an amount of not less than 0.1 mg/m²; the middle protective layer contains non-photosensitive silver halide grains in an amount of not less than 0.001 mg/m²; and the upper protective layer is a colloidal layer:

[I]



wherein R¹ is an aryl group or a tertiary alkyl group; R² is fluorine, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a dialkylamino group, an alkylthio group or an arylthio group; R³ is a substituent group of the benzene ring; X is hydrogen or a group capable of being eliminated by a coupling reaction with an oxidation product of an aromatic primary amine developing agent; p is an integer of 0 to 4; and when p is two or more, the groups represented by R³ may be different from each other.

The present invention improves a silver halide color reversal image forming method comprises the steps of image-wise exposing to light a silver halide color photographic material, subjecting the material to a black and white development process, subjecting the material to a reversal process, subjecting the material to a color development process and subjecting the material to a desilvering process.

The yellow coupler represented by the formula [I] has been known as an excellent coupler, as is described in the prior art references. However, the present inventor has found that the above-mentioned

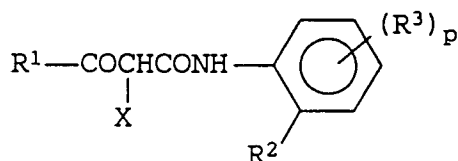
problems are caused when the yellow coupler is used in a method containing a short black and white development process.

The present inventor has surprisingly found that the problems are solved by the above-defined specific three protective layers. Accordingly, a clear image can be obtained according to the present invention, even if the the yellow coupler is used in a method containing a short black and white development process.

DETAILED DESCRIPTION OF THE INVENTION

The yellow coupler represented by the formula [I] used in the invention is described below in more detail.

[I]



In the formula [I], R^1 preferably is an aryl group of 6 - 24 carbon atoms (e.g., phenyl, p-tolyl, o-tolyl, 4-methoxyphenyl, 2-methoxyphenyl, 4-butoxyphenyl, 4-octyloxyphenyl, 4-hexadecylphenyl, 1-naphthyl), or a tertiary alkyl group of 4 - 24 carbon atoms (e.g., t-butyl, t-pentyl, t-hexyl, 1,1,3,3-tetramethylbutyl, 1-adamantyl, 1,1-dimethyl-2-chloroethyl, 2-phenoxy-2-propyl, bicyclo[2,2,2]octane-1-yl).

In the formula [I], R^2 preferably is a fluorine atom, an alkyl group of 1 - 24 carbon atoms (e.g., methyl, ethyl, isopropyl, t-butyl, cyclopentyl, n-octyl, n-hexadecyl, benzyl), an aryl group of 6 - 24 carbon atoms (e.g., phenyl, p-tolyl, o-tolyl, 4-methoxyphenyl), an alkoxy group of 1 - 24 carbon atoms (e.g., methoxy, ethoxy, butoxy, n-octyloxy, n-tetradecyloxy, benzyloxy, methoxyethoxy), an aryloxy group of 6 - 24 carbon atoms (e.g., phenoxy, p-tolyloxy, o-tolyloxy, p-methoxyphenoxy, p-dimethylaminophenoxy, m-pentadecylphenoxy), a dialkylamino group of 2 - 24 carbon atoms (e.g., dimethylamino, diethylamino, pyrrolidino, piperazino, morpholino), an alkylthio group of 1 - 24 carbon atoms (e.g., methylthio, butylthio, n-octylthio, n-hexadecylthio) or an arylthio group of 6 - 24 carbon atoms (e.g., phenylthio, 4-methoxyphenylthio, 4-t-butylphenylthio, 4-dodecylphenylthio).

In the formula [I], R^3 preferably is a halogen atom, (fluorine atom, chlorine atom, bromine atom, iodine atom), an alkyl group of 1 - 24 carbon atoms (e.g., methyl, t-butyl, n-dodecyl), an aryl group of 6 - 24 carbon atoms (e.g., phenyl, p-tolyl, p-dodecyloxyphenyl), an alkoxy group of 1 - 24 carbon atoms (e.g., methoxy, n-butoxy, n-octyloxy, n-tetradecyloxy, benzyloxy, methoxyethoxy), an aryloxy group of 6 - 24 carbon atoms (e.g., phenoxy, p-t-butylphenoxy, 4-butoxyphenoxy), an alkoxycarbonyl group of 2 - 24 carbon atoms, [e.g., ethoxycarbonyl, dodecyloxycarbonyl, 1-(dodecyloxycarbonyl)ethoxycarbonyl], an aryloxycarbonyl group of 7 - 24 carbon atoms (e.g., phenoxycarbonyl, 4-t-octylphenoxycarbonyl, 2,4-di-t-penylphenoxycarbonyl), a carbonamide group of 1 - 24 carbon atoms [e.g., acetamide, pivaloylamino, benzamide, 2-ethylhexanamide, tetradecanamide, 1-(2,4-di-t-pentylphenoxy)butanamide, 3-(2,4-di-t-pentylphenoxy)butanamide, 3-dodecylsulfonyl-2-methylpropanamide], a sulfonamide group of 1 - 24 carbon atoms (e.g., N-methylcarbamoyl, N-tetradecylcarbamoyl, N,N-dihexylcarbamoyl, N-octadecyl-N-methylcarbamoyl, N-phenylcarbamoyl), an alkylsulfonyl group of 1 - 24 carbon atoms (e.g., methylsulfonyl, benzylsulfonyl, hexadecylsulfonyl), an arylsulfonyl group of 6 - 24 carbon atoms (e.g., phenylsulfonyl, p-tolylsulfonyl, p-dodecylsulfonyl, p-methoxysulfonyl), an ureido group of 1 - 24 carbon atoms (e.g., 3-methylureido, 3-phenylureido, 3,3-dimethylureido, 3-tetradecylureido), a sulfamoylamino group of 0 - 24 carbon group (e.g., N-dimethylsulfamoylamino), an alkoxycarbonylamino group of 2 - 24 carbon atoms (e.g., methoxycarbonylamino, isobutoxycarbonylamino, dodecylozycarbonylamino), a nitro group, a heterocyclic group of 1 - 24 carbon atoms (e.g., 4-pyridyl, 2-thienyl, phtalimide, octadecylsuccinimide), a cyano group, an acyl group of 1 - 24 carbon atoms (e.g., acetyl, benzoyl, dodecanoyl), an acyloxy group of 1 - 24 carbon atoms (e.g., acetoxyl, benzoyloxy, dodecanoyloxy), an alkylsulfonyloxy group of 1 - 24 carbon atoms (e.g., methylsulfonyloxy, hexadecylsulfonyloxy), or an arylsulfonyloxy group of 1 - 24 carbon atoms (e.g., p-toluensulfonyloxy, p-dodecylphenylsulfonyloxy).

In the formula [I], p preferably is an integer of 1 or 2.

In the formula [I], X preferably is a group capable of being eliminated (referred to as eliminating group) by a coupling reaction with an oxidant of an aromatic primary amine developer. Concrete examples thereof

include a halogen atom (fluorine, chlorine, bromine, iodine), a heterocyclic group of 1 - 24 carbon group whose nitrogen atom is bonded to a coupling active position, an aryloxy group of 6 - 24 carbon atoms, an arylthio group of 6 - 24 carbon atoms (e.g., phenylthio, p-t-butylphenylthio, p-chlorophenylthio, p-carboxyphenylthio), an acyloxy group of 1 - 24 carbon atoms (e.g., acetoxy, benzoyloxy, dodecanoyloxy), an alkylsulfonyloxy group of 1 - 24 carbon atoms (e.g., methylsulfonyloxy, butylsulfonyloxy, dodecylsulfonyloxy), an arylsulfonyloxy group of 6 - 24 carbon atoms (e.g., benzensulfonyloxy, p-chlorophenylsulfonyloxy) and an heterocyclic oxy group of 1 - 24 carbon atoms (e.g., pyridyloxy, 1-phenyl-1,2,3,4-tetrazole-5-yloxy). Of these, more preferred are a heterocyclic group whose nitrogen atom is bonded to a coupling active position and an aryloxy group.

When X is a heterocyclic group whose nitrogen atom is bonded to a coupling active position, X is a substituted or unsubstituted, single or fused heterocyclic ring of 5 - 7 members which may contain a hetero atom selected from oxygen, sulfur, nitrogen, phosphorus, selenium and tellurium in addition to the nitrogen atom. Examples of the heterocyclic rings include succinimide, maleinimide, phthalimide, diglycolimide, pyrrol, pyrazole, imidazole, 1,2,4-triazole, tetrazole, indole, benzopyrazole, benzimidazole, benztriazole, imidazolidine-2,4-dione, oxazolidine-2,4-dione, thiazolidine-2,4-dione, imidazolidine-2-one, oxazoline-2-one, thiazoline-2-one, benzimidazoline-2-one, benzoxazoline-2-one, benzothiazoline-2-one, 2-pyrroline-5-one, 2-imidazoline-5-one, indoline-2,3-dione, 2,6-dioxypurine, paravanic acid, 1,2,4-triazolidine-3,5-dione, 2-pyridone, 2-pyrimidone, 6-pyridazole and 2-pyrazone. These heterocyclic rings may be substituted. Examples of the substituents include hydroxyl group, carboxyl group, sulfo group, amino group (e.g., amino, N-methylamino, N,N-dimethylamino, N,N-diethylamino, anilino, pyrrolidino, piperidino, morpholino) and substituents described above as examples of R³.

When X is an aryloxy group, X is an aryloxy group having 6 - 24 carbon atoms. When X is a heterocyclic group, X may be substituted with a group selected from the above-mentioned substituents. Preferred substituents are carboxyl group, sulfo group, cyano group, nitro group, alkoxycarbonyl group, halogen atom, carbonamide group, sulfonamide group, carbamoyl group, sulfamoyl group, alkyl group, alkylsulfonyl group, arylsulfonyl group and acyl group.

Examples of the above-described substituents R¹, R² and R³ and X which are particularly preferably used in the invention will be described below.

In the formula [I], R¹ is particularly preferably a 2-or 4-alkoxyaryl group (e.g., 4-methoxyphenyl, 4-butoxyphenyl, 2-methoxyphenyl) or a t-butyl group, and most preferred is a t-butyl group.

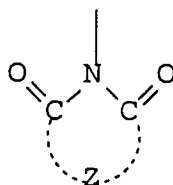
In the formula [I], R² is particularly preferably a methyl group, an ethyl group, an alkoxy group, an aryloxy group or a dialkylamino group, and most preferred is a methyl group, an ethyl group, an alkoxy group, an aryloxy group or a dimethylamino group.

In the formula [I], R³ is particularly preferably an alkoxy group, a carbonamide group or a sulfonamide group.

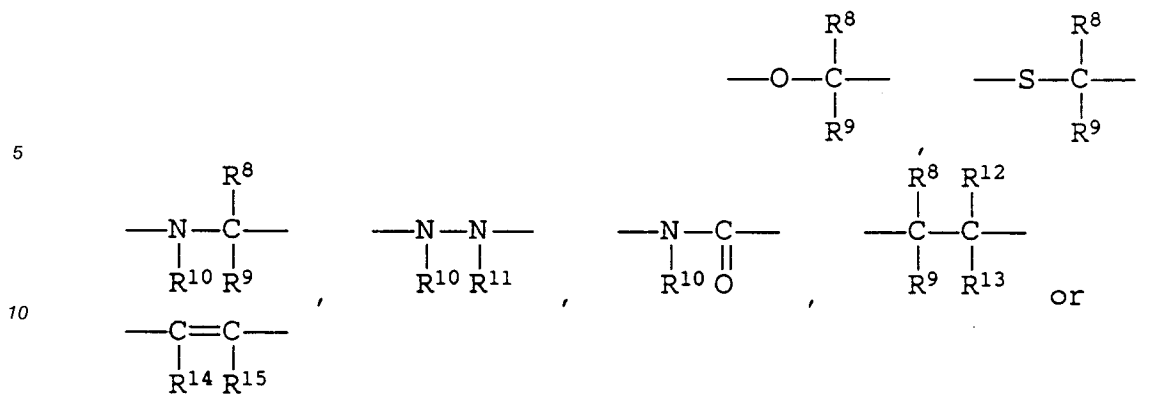
In the formula [I], X is particularly preferably a heterocyclic ring whose nitrogen atom is bonded to a coupling active position, or an aryloxy group.

When X is the aforementioned heterocyclic ring, X is represented by the formula [III].

[III]



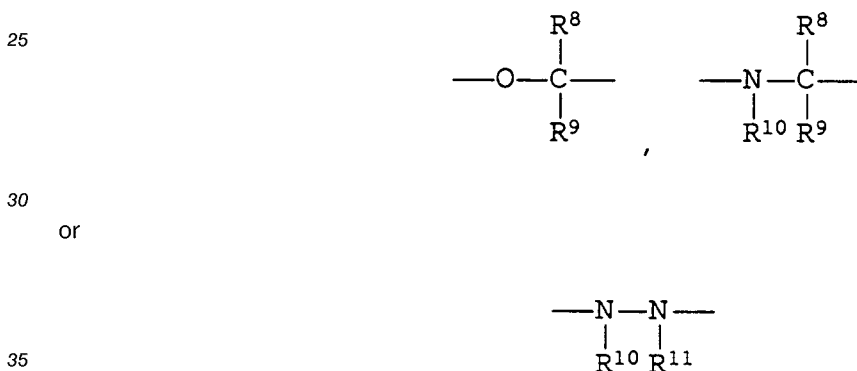
In the formula [III], Z is



15 Herein, each of R^8 , R^9 , R^{12} and R^{13} is a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an alkylsulfonyl group, an arylsulfonyl group or an amino group; each of R^{14} and R^{15} is a hydrogen atom, an alkyl group or an aryl group; and R^{14} and R^{15} may be bonded to each other to form a benzene ring.

20 R^8 and R^9 , R^9 and R^{10} , R^{10} and R^{11} , or R^8 and R^{12} may be bonded to each other to form a ring (e.g., cyclobutane, cyclohexane, cycloheptane, cyclohexene, pyrrolidine, piperidine).

Of the heterocyclic rings having the formula [III], particularly preferred is a heterocyclic ring of the formula [III] wherein Z is

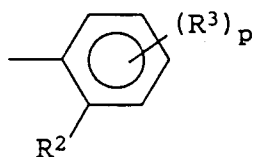


The total number of carbon atoms in the heterocyclic ring having the formula [III] is 2 to 24, preferably 4 to 20, more preferably 5 to 16. Examples of the heterocyclic rings having the formula [III] include succinimido, maleinimido, phthalimido, 1-methyl-imidazolidine-2,4-dione-3-yl, 1-benzylimidazolidine-2,4-dione-3-yl, 5,5-dimethylazolidine-2,4-dione-3-yl, 5-methyl-5-propyloxazolidine-2,4-dione-3-yl, 5,5-dimethylthiazolidine-2,4-dione-3-yl, 5,5-dimethylimidazolidine-2,4-dione-3-yl, a 3-methylimidazolidinetrione-1-yl, 1,2,4-triazolidine-3,5-dione-4-yl, 1-methyl-2-phenyl-1,2,4-triazolidine-3,5-dione-4-yl, 1-benzyl-2-phenyl-1,2,4-triazolidine-3,5-dione-4-yl, a 5-hexyloxy-1-methylimidazolidine-2,4-dione-3-yl, 1-benzyl-5-ethoxyimidazolidine-2,4-dione-3-yl and 1-benzyl-5-dodecyloxyimidazolidine-2,4-dione-3-yl.

Of the above-mentioned heterocyclic rings, most preferred is an imidazolidine-2,4-dione-3-yl (e.g., a 1-benzylimidazolidine-2,4-dione-3-yl).

When X is an aryloxy group, most preferred examples thereof are 4-carboxyphenoxy, 4-methylsulfonylphenoxy, 4-(4-benzoyloxyphenylsulfonyl)phenoxy, 4-(4-hydroxyphenylsulfonyl)phenoxy, 2-chloro-4-(3-chloro-4-hydroxyphenylsulfonyl)phenoxy, 4-methoxycarbonylphenoxy, 2-chloro-4-methoxycarbonylphenoxy, 2-acetamide-4-methoxycarbonylphenoxy, 4-isopropoxycarbonylphenoxy, 4-cyanophenoxy, 2-[N-(2-hydroxyethyl)carbomoyl]phenoxy, 4-nitrophenoxy, 2,5-dichlorophenoxy, 2,3,5-trichlorophenoxy, 4-methoxycarbonyl-2-methoxyphenyl and 4-(3-carboxypropanamide)phenoxy.

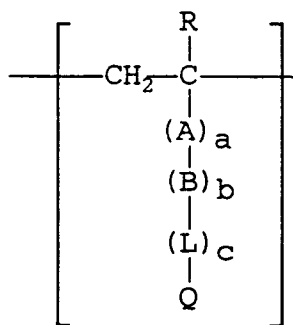
The coupler having the formula [I] may form dimer or polymer by bonding to each other through a divalent or more valence group at R^1 , X or the following formula.



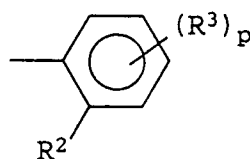
In this case, the number of carbon atoms is not restricted to the range described in each of the aforementioned substituents.

When the coupler represented by the formula [I] forms a polymer, typical examples thereof are homopolymers or copolymers of addition polymer ethylene-type unsaturated compounds (yellow color developing monomers) having an yellow dye forming coupler residue. In this case, the polymer generally contains a repeating unit of the formula [IV], and in the polymer may be contained one or more kinds of the yellow color developing repeating units having the formula [IV]. Further, the polymer may be a copolymer containing one or more kinds or color non-developing ethylene-type monomers as copolymerizable component.

[IV]



In the formula, R is a hydrogen atom, an alkyl group of 1 - 4 carbon atoms or a chlorine atom; A is -CONH-, -COO- or a substituted or unsubstituted phenylene group; B is a substituted or unsubstituted alkylene group, a phenylene group or an aralkylene group; and L is -CONH-, -NHCONH-, -NHCOO-, -NHCO-, -OCONH-, -NH-, -COO-, -OCO-, -CO-, -O-, -S-, SO₂-, -NHSO₂- or -SO₂NH-. Each of a, b and c is 0 or 1. Q is an yellow coupler residue obtained by elimination of a hydrogen atom from R¹, X or



of the compound having the formula [I].

As the polymer, preferred is a copolymer of an yellow color developing monomer represented by a coupler unit of the formula [IV] and the following color non-developing ethylene-type monomer.

As examples of the color non-developing ethylene-type monomers which do not undergo a coupling reaction with an oxidate of the aromatic primary amine developer, there can be mentioned acrylic acid, α -chloroacrylic acid, α -alkylacrylic acid (e.g., methacrylic acids), amide or ester derived from these acrylic acids (e.g., acrylamide, methacrylamide, n-butylacrylamide, t-butylacrylamide, diacetone acrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, iso-butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and β -hydroxy methacrylate), vinyl ester (e.g., vinyl acetate, vinyl propionate and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compound, (e.g., styrene and its derivative such as vinyl toluene, divinyl benzene, vinyl acetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ether (e.g., vinyl ethyl ether), maleic ester, N-vinyl-2-pyrrolidone, N-vinylpyridine, 2-

vinylpyridine, and 4-vinylpyridine.

Particularly preferred are acrylic esters, methacrylic esters and maleic esters. The color non-developing ethylene-type monomers can be employed in combination of two or more kinds. For example, a combination of methyl acrylate and butyl acrylate, that of butyl acrylate and styrene, that of butyl methacrylate and methacrylic acid, that of methyl acrylate and diacetone acrylamide can be employed.

As well known in the art of polymer couplers, the ethylene-type unsaturated monomer which is to be copolymerized with a vinyl monomer corresponding to the aforementioned formula [IV] can be appropriately selected so that the physical and/or chemical properties of the resulting copolymer (e.g., solubility, compatibility with photographic colloidal composition such as gelatin, flexibility and heat stability) are favorably influenced.

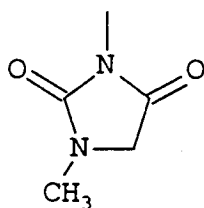
The yellow polymer coupler employable in the invention can be prepared by dissolving in an organic solvent a hydrophilic polymer coupler obtained by polymerization of vinyl monomers which can provide a coupler unit of the aforementioned formula [IV], and then emulsifying and dispersing the resulting solution of the hydrophilic polymer coupler in an aqueous solution of gelatin in the form of latex. Otherwise, the yellow polymer coupler can be also prepared by a direct emulsifying polymerization method.

For emulsifying and dispersing the hydrophilic polymer coupler in an aqueous solution of gelatin in the form of latex, a method described in U.S. Patent No. 3,451,820 can be employed. As for the emulsifying polymerization, methods described in U.S. Patents No. 4,080,211 and No. 3,370,952 can be employed.

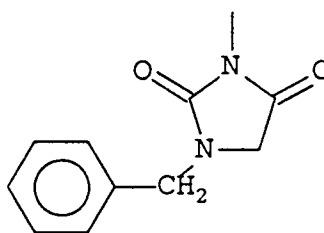
Concrete examples of R^3 and X in the yellow dye forming coupler represented by the formula [I] are given below, but the invention is by no means restricted to those examples.

Concrete examples of X are shown below.

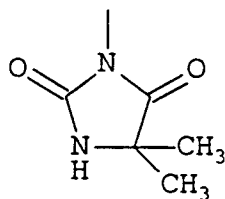
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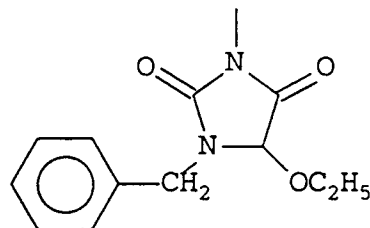
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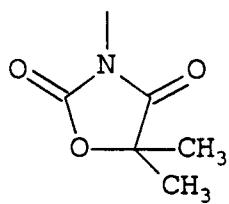
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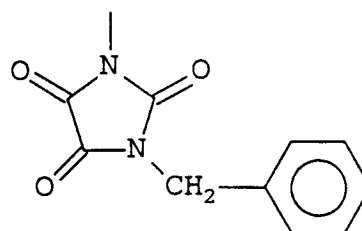
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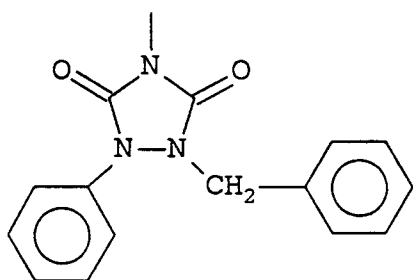
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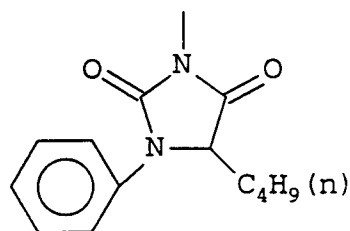
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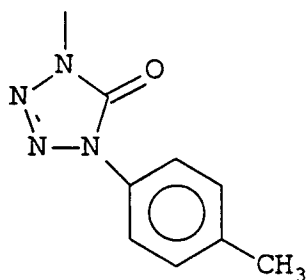
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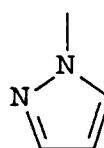
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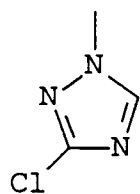
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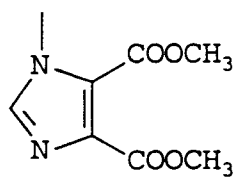
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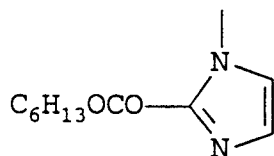
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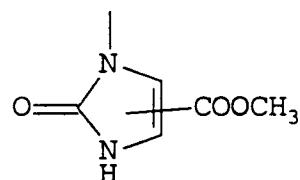
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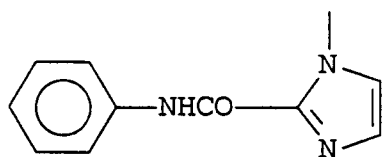
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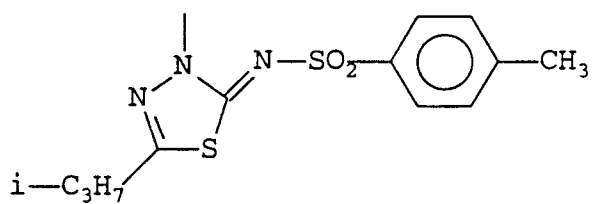
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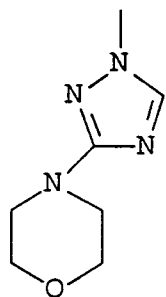
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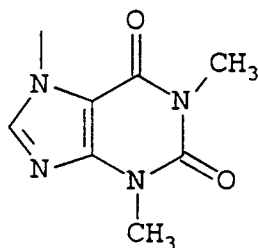
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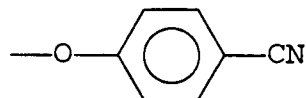
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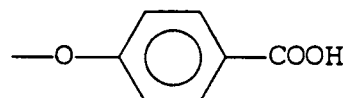
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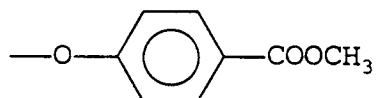
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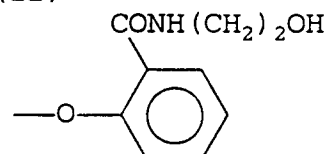
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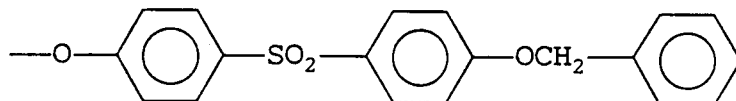
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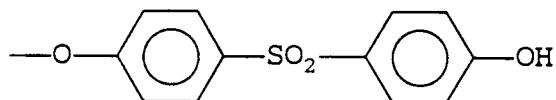
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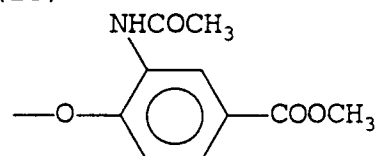
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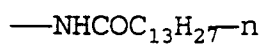


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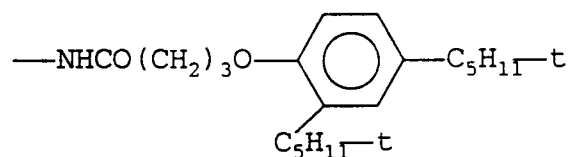


Concrete examples of R³ are shown below.

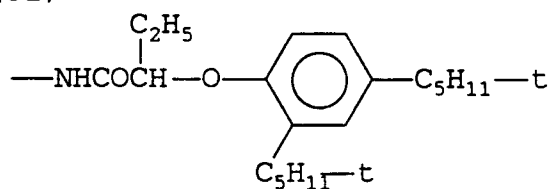
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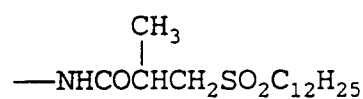
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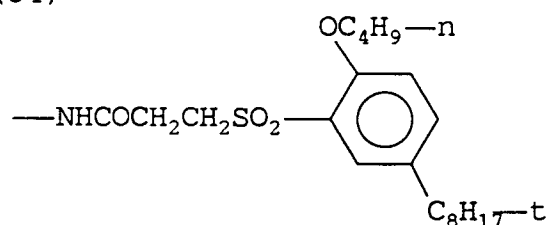
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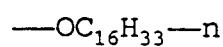
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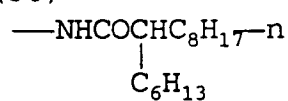
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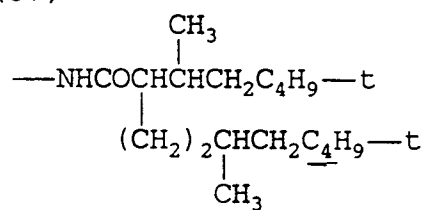
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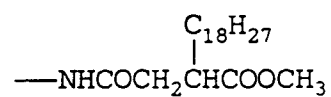
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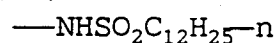
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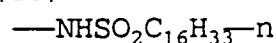
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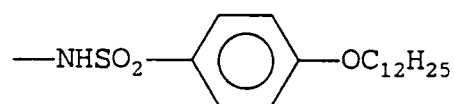
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(40)



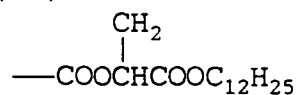
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(42)



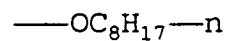
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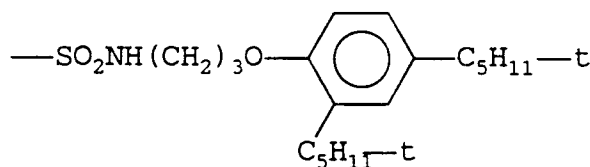
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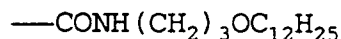
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(46)



(47)

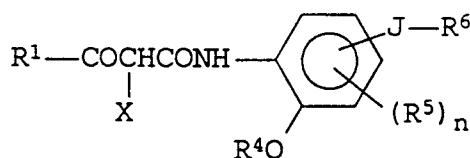


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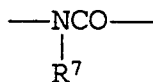


Of the yellow couplers represented by the formula [I], preferred are compounds having the formula [II].

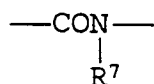
[II]



In the formula [II], R⁴ is an alkyl group, a cycloalkyl group, an acyl group or an aryl group; and R⁵ is a group capable of being substituted to form a benzene ring. n is 0 or 1. R⁶ is an organic group containing one linking group having a carbonyl or sulfonyl unit, and J is



or



wherein R⁷ is a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group. R¹ and X have the same meanings as those of the formula [I].

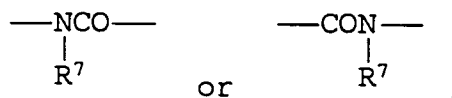
As the alkyl group or the cycloalkyl group indicated by R⁴ in the formula [II], the same groups as those for R¹ can be mentioned. As the aryl group indicated by R⁴ in the formula [II], there can be mentioned, for example, a phenyl group. These alkyl, cycloalkyl and aryl groups indicated by R⁴ may have the same substituents as those for R¹. As the acyl group, there can be mentioned, for example, an acetyl group, a propionyl group, a butyl group, a hexanoyl group and a benzoyl group. As R⁴, preferred are an alkyl group and an aryl group, and more preferred is an alkyl group.

Examples of the groups indicated by R⁴ in the formula [II] which can be substituted to form a benzene ring include a halogen atom (e.g., chlorine atom), an alkyl group (e.g., ethyl group, i-propyl group, t-butyl group), an alkoxy group (e.g., methoxy group), an aryloxy group (e.g., phenyloxy group), an acyloxy group (e.g., methylcarbanyloxy group, benzoyloxy group), an acylamino group (e.g., acetamide group, phenylcarbonylamino group), a carbamoyl group (e.g., N-methylcarbamoyl group, N-phenylcarbamoyl group), an alkylsulfonamide group (e.g., ethylsulfonylamino group), an arylsulfonamido group (e.g., phenylsulfonylamino group), a sulfamoyl group (e.g., N-propylsulfamoyl group, N-phenylsulfamoyl group), and an imide group (e.g., succinimide group, glutarimide group). n is 0 or 1.

In the formula [II], R⁶ is an organic group containing one linking group having carbonyl or sulfonyl unit. Examples of the group having carbonyl unit include an ester group, an amido group, a carbamoyl group, an

ureido group and an urethane group, and examples of the group having sulfonyl unit include a sulfone group, a sulfonamide group, a sulfamoyl group and an aminosulfonamido group. J is

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wherein R^7 is a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group.

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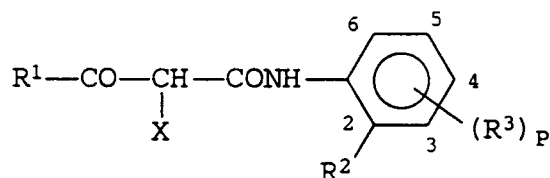
Examples of the alkyl group indicated by R^7 include a methyl group, an ethyl group, an isopropyl group, a t-butyl group and a dodecyl group. Examples of the aryl group indicated by R^7 include a phenyl group and a naphthyl group. These alkyl, aryl and heterocyclic groups indicated by R^7 may have a substituent.

R^1 and X are the same as those in the formula [I].

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A concrete example of the yellow dye forming coupler having the formula [I] is given below. This concrete example is described in Table 1 and Table 2 wherein R^1 , R^2 , $(\text{R}^3)_p$ and X in the formula [I] are concretely shown.

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Table 1

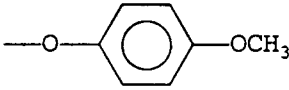
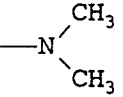
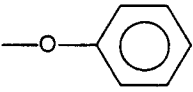
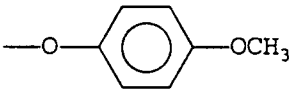
No.	R ¹	R ²	(R ³) _p	X
Y-1	t-C ₄ H ₉ -	-OCH ₃	(32) [5]	(4)
Y-2	t-C ₄ H ₉ -	-OCH ₃	(32) [5]	(5)
Y-3	t-C ₄ H ₉ -	-CH ₃	(31) [5]	(2)
Y-4	t-C ₄ H ₉ -		(32) [5]	(5)
Y-5	t-C ₄ H ₉ -		(32) [5]	(4)
Y-6	t-C ₄ H ₉ -	-OCH ₃	(33) [5]	(8)
Y-7	t-C ₄ H ₉ -	-OC ₂ H ₅	(33) [5]	(7)
Y-8	t-C ₄ H ₉ -	-OCH ₃	(31) [5]	(23)
Y-9	t-C ₄ H ₉ -		(40) [5]	(19)
Y-10	t-C ₄ H ₉ -	-OC ₈ H ₁₇ -n	(45) [4]	(5)
Y-11	t-C ₄ H ₉ -	-OC ₈ H ₁₇ -n	(45) [5]	(5)
Y-12	t-C ₄ H ₉ -	-OCH ₃	(42) [5]	(4)
Y-13	t-C ₄ H ₉ -		(30) [5]	(10)
Y-14	t-C ₄ H ₉ -	-OC ₁₄ H ₂₉ -n	-	(15)
Y-15	t-C ₄ H ₉ -	-OCH ₂ CH ₂ OCH ₃	(34) [5]	(8)

Table 2

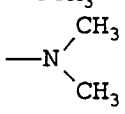
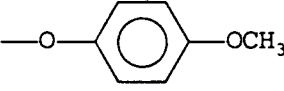
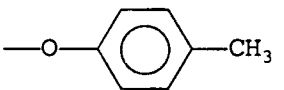
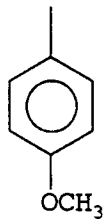
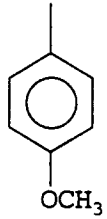
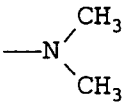
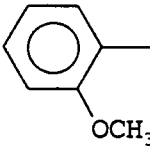
No.	R ¹	R ²	(R ³) _p	X
Y-16	t-C ₄ H ₉ -	-CH ₃	(43) [5]	(9)
Y-17	t-C ₄ H ₉ -	-C ₂ H ₅	(47) [5]	(8)
Y-18	t-C ₄ H ₉ -	-CH ₃	(46) [5]	(2)
Y-19	t-C ₄ H ₉ -	-OC ₈ H ₁₇ -n	(45) [4]	(5)
Y-20	t-C ₄ H ₉ -	-OCH ₃	(31) [5]	(19)
Y-21	t-C ₄ H ₉ -		(36) [4]	(18)
Y-22	t-C ₄ H ₉ -		(41) [5]	(11)
Y-23	t-C ₄ H ₉ -		(37) [5]	(3)
Y-24	t-C ₄ H ₉ -	-OC ₂ H ₅	(37) [5]	(1)
Y-25	t-C ₄ H ₉ -	-CH ₃	(38) [5]	(2)
Y-26	t-C ₄ H ₉ -	-O ₂ H ₅	(38) [5]	(2)
Y-27	t-C ₄ H ₉ -	-CH ₃	(33) [5]	(2)

Table 2 (continued)

No.	R ¹	R ²	(R ³) _p	X
Y-28		-OCH ₃	(42) [5]	(4)
Y-29			(40) [5]	(4)
Y-30		-CH ₃	(43) [5]	(2)

In the above tables, the numerals within () indicate numerals attached to the aforementioned concrete examples of X and R³, respectively, and the numerals within [] indicate substituting positions on the anilide group, respectively.

The yellow coupler may be used alone or in the form of a mixture of two or more kinds. Further, it may be used in combination with other known yellow dye forming coupler.

The yellow coupler can be used in any layer of the photographic material, but the coupler is preferably used in the light-sensitive silver halide emulsion layer or its adjoining layer, and most preferably used in the light-sensitive silver halide emulsion layer.

The yellow coupler can be synthesized by conventionally known synthesis methods, and a concrete example of the methods is described in Japanese Patent Provisional Publication No. 63(1988)-123047.

The amount of the coupler used in the photographic material of the invention is in the range of 1×10^{-5} mole to 10^{-5} mole, preferably 1×10^{-4} mole to 5×10^{-3} mole, more preferably 2×10^{-4} mole to 10^{-3} mole, per 1 m².

The non-photosensitive silver halide grains contained in the protective layer(s) of the invention may be any of silver chloride, silver chlorobromide, silver chloriodobromide, silver bromide and silver iodobromide. Of these, silver chloride and silver chlorobromide are preferred. Further, silver chlorobromide or silver chloride, containing silver chloride in an amount of not less than about 70 % by mole, is particularly preferred, from the viewpoint of effectively preventing processing-unevenness in the rapid processing.

The shape of the silver halide grain may be any of cubic, tetradecahedron, octahedron, globular, tabular and indefinite-shape. Particularly, grains of regular shape such as cubic, tetradecahedron and octahedron or tabular grains having aspect ratio of not less than 5 are preferred. The emulsion containing the silver halide grains may be either a monodispersed emulsion or a polydispersed emulsion. The emulsion preferably is a monodispersed emulsion having a grain size distribution of not more than 20 %. The grain size distribution mentioned herein is measured according to a method described in James, "Theory of Photographic Process", 4th edit., 3rd chap., p. 102.

The non-photosensitive silver halide grains are silver halide grains having extremely low sensitivity or those homogeneously developed regardless of light amount of exposure. The expression "grains having an

extremely low sensitivity" mentioned herein means that the silver halide grains have light sensitivity of only less than 1/10 as compared with the photosensitive silver halide grains of lowest sensitivity contained in the image forming layer of the photographic material.

The silver halide having extremely low sensitivity to light can be prepared utilizing the following three kinds of methods. The first method is a method to prepare the silver halide without chemical sensitization after grain-formation. The second method is a method of subjecting inside of silver halide grains to fogging treatment. Such grains can be prepared, for example, by conducting grain formation in two or more stages wherein fogging-treatment is carried out by allowing a reducing agent to strongly act on the core grain surfaces and then shell formation is performed. The third method is a method of allowing a heavy metal salt to act in the stage of grain formation. As the heavy metal salt, water-soluble rhodium salts are most preferably employed. Examples of the water-soluble rhodium salts employable in the invention include rhodium chloride, rhodium trichloride and rhodium ammonium chloride. Further, complex salts can be also employed. The amount of the rhodium salt used in the invention is preferably not less than 1×10^{-6} mole, more preferably in the range of 5×10^{-5} mole to 1×10^{-3} mole, per 1 mole of silver. These three kinds of the methods can be used singly or in combination of two or three kinds.

The grains which are homogeneously developed regardless of light amount and exposure light amount can be prepared by strongly reducing the grain surfaces. For example, such grains can be prepared by heating the grains under the conditions of high pH or low pAg, adding a reducing agent or a gold salt to the grains, or applying uniform exposure light to the grains. As the reducing agent, stannous chloride, hydrazine compounds, ethanol amine or thiourea dioxide can be used.

In the invention, sensitizing dyes can be adsorbed on the surfaces of the silver halide grains, or various compounds can be also adsorbed thereon as additives to stabilize performance of the grains. Useful sensitizing dyes are described in, for example, German Patent No. 929,080, and U.S. Patents No. 2,493,748, No. 2,503,776, No. 2,519,001, No. 2,912,329, No. 3,656,959, No. 3,672,897, No. 3,694,217, No. 4,025,349 and No. 4,046,576. As the additives, there can be used compounds known as stabilizers such as azoles (e.g., benzothiazolium salts, nitroindazoles, triazoles, benzotriazoles, benzimidazoles), heterocyclic mercapto compounds (e.g., mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiazoles, mercaptotetrazoles, mercaptopyrimidines), the above-mentioned heterocyclic mercapto compounds having carboxyl group or sulfone group, thioketo compounds (e.g., oxazolinethione), azaindenes (e.g., tetrazaindenes, particularly 4-hydroxy substituted (1,3,3a,7)tetrazaindenes), benzenethiosulfonic acids, and benzenesulfonic acids.

The amount of the silver halide contained in the protective layer(s) is preferably in the range of 0.001 g/m² to 0.5 g/m², more preferably in the range of 0.01 g/m² to 0.2 g/m², in terms of silver.

The size of the silver halide grain is preferably in the range of 0.02 to 0.5 μm more preferably in the range of 0.05 to 0.3 μm .

The total thickness of the protective layers is preferably not more than 6 μm , more preferably not more than 3 μm most preferably in the range of 2.5 to 1.5 μm , in dry basis. The thickness in dry basis of the middle protective layer containing the above-mentioned silver halide grains is preferably not more than 30 %, more preferably not more than 15 %, of the total thickness of all of the protective layers. The thickness of the lower protective layer containing the oxidant scavenger of a developing agent positioned below the middle protective layer containing the silver halide grains is preferably not less than 20 %, more preferably not less than 40 %, of the total thickness of all of the protective layers.

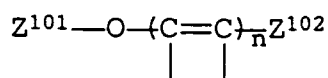
In the invention, the protective layer means an image-non-forming layer which is located on the side outer than the farthest light-sensitive image-forming layer from the support. When three or more image-non-forming layers are provided on the silver halide emulsion layers containing a coupler, whole of those image-non-forming layers are referred to as protective layers. The typical structure of the protective layers according to the invention merely consists of the three layers. These three layers are referred to as a lower layer, a middle layer and an upper layer, respectively, from the side of the support. The middle layer contains the silver halide grains. The lower layer contains the scavenger of an oxidation product of a developing agent. The upper layer is a protective colloidal layer. Each of the protective layers may be of either a single-layer structure or a plural-layer structure. Between those layers may be further provided an intermediate layer made of a protective colloid. Accordingly, a photographic material having four or more protective layers is also included within the scope of the present invention provided that three layers among the four or more protective layers have the definitions of the present invention. In the case that four or more protective layers are provided in the photographic material, the middle protective layer of the present invention is one of the protective layers except the uppermost and lowermost layers. The lower protective layer is arranged below the middle layer (between the middle layer and the silver halide emulsion layer containing a yellow coupler). The upper protective layer is arranged on or above the middle layer.

The lower protective layer preferably contains an UV absorbent in addition to the scavenger of an oxidation product of a developing agent. The middle protective layer can contain a UV absorbent and an oxidant scavenger in addition to the silver halide grains. The upper protective layer can contain a matting agent to prevent adhesion, a surface active agent (e.g., fluorine-containing surface active agent) to prevent electrostatically charging, a polymer (e.g., modified POVAL) to improve rigidity.

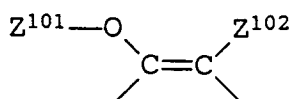
The scavenger of an oxidation product of a developing agent (referred to as "ND compound" hereinafter) used in the invention include (A) an electron donor (ED) capable of donating at least one electron to an oxidation product of a color developing agent (T^+) and (B) a colorless coupler which undergoes coupling reaction with T^+ to form a colorless compound.

Preferred ED compounds have a partial structure represented by the following formula.

[XI]



In this formula, n is an integer of from 1 to 4, preferably an integer of 1 or 2; and each of Z^{101} and Z^{102} independently is -OH, -NH₂, -NHR¹⁰¹, -NR¹⁰²R¹⁰³ or -NHSO₂R¹⁰⁴. R¹⁰¹ is an alkyl group. Each of R¹⁰² and R¹⁰³ is an alkyl group, or a combination of R¹⁰² and R¹⁰³ is an atom group to form in cooperation a heterocyclic ring containing nitrogen. R¹⁰⁴ is an alkyl group or an aryl group. When n is 1,



may be a partial structure of a benzene ring or a naphthalene ring.

The alkyl group indicated by R¹⁰¹, R¹⁰², R¹⁰³ or R¹⁰⁴ may be substituted, and examples of the substituents include a halogen atom and alkoxy group. The alkyl group may be of either straight chain or branched form, and preferably has 1 to 5 carbon atoms. The aryl group indicated by R¹⁰⁴ may have a substituent, and examples of the aryl group include phenyl, alkoxy-substituted phenyl and alkyl-substituted phenyl. Examples of the heterocyclic ring containing nitrogen which is formed by cooperation of R¹⁰² and R¹⁰³ include a morpholino group, a piperidino group and a piperazino group.

Preferred ED represented by the formula [XI] are hydroquinone type compounds, catechol type compounds, o-aminophenol type compounds and p-aminophenyl type compounds.

The hydroquinone type compounds employable as the ED compound in the invention desirably show low diffusion properties when added to the light-sensitive layer. Such hydroquinone compounds are widely used as stain inhibitors or color antifoggants in normal color photosensitive materials or diffusion transfer color photosensitive materials.

Straight-chain dialkyl-substituted hydroquinones described in U.S. Patents No. 2,728,659, No. 2,732,300 and No. 3,243,294 and branched dialkyl-substituted hydroquinones described in U.S. Patents No. 2,732,300, No. 3,243,294 and No. 3,700,453 and Japanese Patent Provisional Publications No. 52(1977)-4819 and No. 54(1979)-29637 are preferred hydroquinones because they have low electric potential and high activity as scavengers of T^+ .

Straight-chain monoalkylhydroquinones described in U.S. Patents 2,728,659 and No. 3,960,570, branched monoalkylhydroquinones described in U.S. Patent No. 3,700,453 and Japanese Patent Provisional Publications No. 49(1974)-106329 and No. 50(1975)-156433, and hydroquinones described in Japanese Patent Provisional Publication No. 56(1981)-109344 and U.S. Patents No. 4,345,616 and No. 4,277,553 can be also used as ED in the invention.

Concrete examples of the dialkylhydroquinones employable in the invention are described below.

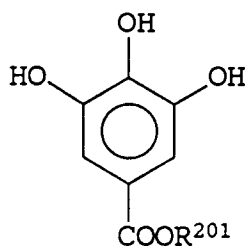
- Q-1 2,5-di-n-octylhydroquinone
- Q-2 2,5-di-n-dodecylhydroquinone
- Q-3 2,6-di-n-octylhydroquinone
- Q-4 2,5-di-t-pentadecylhydroquinone
- Q-5 2,5-di-sec-dodecylhydroquinone
- Q-6 2,5-di-t-dodecylhydroquinone
- Q-7 2,5-di-sec-octylhydroquinone

Q-8 2,5-di-t-octylhydroquinone

Q-9 2,6-di-t-octylhydroquinone

ED preferably used in the invention is represented by the following formula [XII] or [XIII].

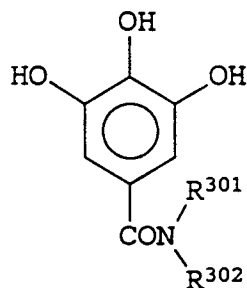
[XII]



In the above formula, R²⁰¹ is a straight-chain or branched-chain alkyl group having 1 - 18 carbon atoms. Examples of alkyl esters of gallic acids represented by the formula [XII] are as follows.

- A1 methyl gallate
- A2 ethyl gallate
- A3 n-propyl gallate
- A4 isopropyl gallate
- A5 n-butyl gallate
- A6 isoamyl gallate
- A7 d-amyl gallate
- A8 n-hexyl gallate
- A9 n-heptyl gallate
- A10 n-octyl gallate
- A11 n-nonyl gallate
- A12 n-decyl gallate
- A13 n-hendecyl gallate
- A14 n-dodecyl gallate
- A15 n-tetradecyl gallate
- A16 n-hexadecyl gallate
- A17 n-octadecyl gallate

[XIII]



In the above formula, each of R³⁰¹ and R³⁰² is a hydrogen atom, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, or a substituted or unsubstituted-hetero ring. R³⁰¹ and R³⁰² together may form a ring. When R³⁰¹ is a hydrogen atom, R³⁰² does not take a hydrogen atom.

As the aliphatic group indicated by R³⁰¹ or R³⁰² in the formula [XIII], there can be mentioned a straight-chain or branched alkyl group, a straight-chain or branched alkenyl group, a cycloalkyl group, and a straight-chain or branched alkynyl group.

The straight-chain or branched alkyl group has 1 - 30 carbon atoms, preferably 1 - 20 carbon atoms. Examples of such alkyl group include methyl, ethyl, propyl, n-butyl, sec-butyl, t-butyl, n-hexyl, 2-ethylhexyl, n-octyl, t-octyl, n-dodecyl, n-hexadecyl, n-octadecyl, isostearyl and eicocyl.

The straight-chain or branched alkenyl group has 2 - 30 carbon atoms, preferably 3 - 20 carbon atoms. Examples of such alkenyl group include aryl, butynyl, prenyl, octenyl, dodecenyl and oleyl.

The cycloalkyl group has 3 to 12 members, preferably 5 to 7 members. Examples of such cycloalkyl group include cyclopropyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclododecyl.

5 The straight-chain or branched alkynyl group has 3 - 30 carbon atoms, preferably 3 - 22 carbon atoms. Examples of such alkynyl group include propargyl and butynyl.

Examples of the aromatic group indicated by R^{301} or R^{302} include phenyl and naphthyl.

Examples of the hetero ring indicated by R^{301} or R^{302} include thiazolyl, oxazolyl, imidazolyl, furyl, thienyl, tetrahydrofuryl, piperidyl, thiadiazolyl, oxadiazolyl, benzothiazolyl, benzoxazolyl and benzimidazolyl.

10 When R^{301} and R^{302} together form a ring, the ring has 3 to 12 members, preferably 5 to 12 members. Examples of such ring include ethylene, tetramethylene, pentamethylene, hexamethylene and dodecamethylene.

Each of the above-mentioned groups may have a substituent, and examples of the substituents include an alkoxy group, an aryloxy group, a hydroxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, a
15 halogen atom, a carboxyl group, a sulfo group, a cyano group, an alkyl group, an alkenyl group, an aryl group, an alkylamino group, an arylamino group, a carbamoyl group, an alkylcarbamoyl group, an arylcarbamoyl group, an acyl group, a sulfonyl group, an acyloxy group and an acylamino group.

Concrete examples of the compounds represented by the formula [XIII] are shown below.

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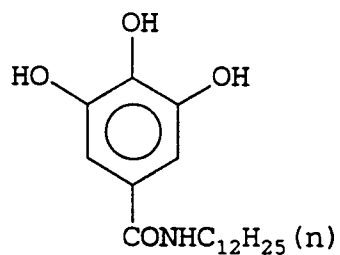
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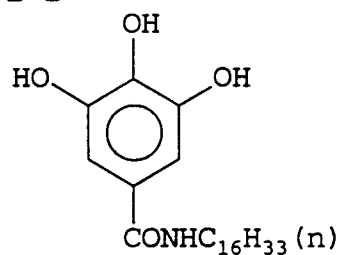
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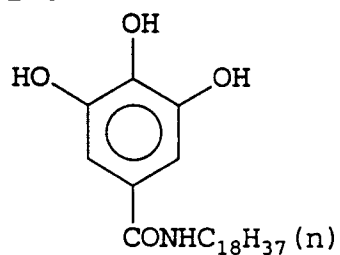
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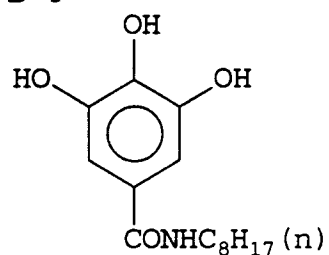
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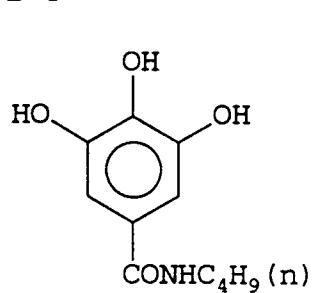
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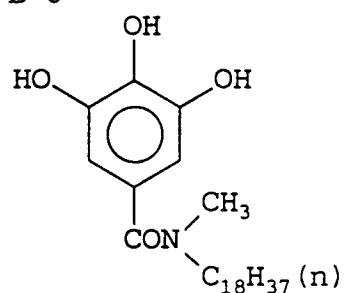
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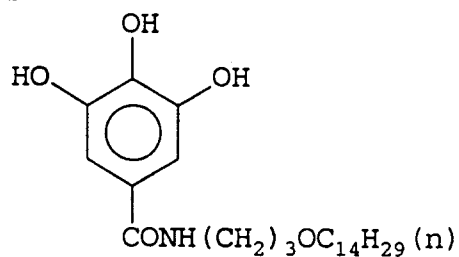
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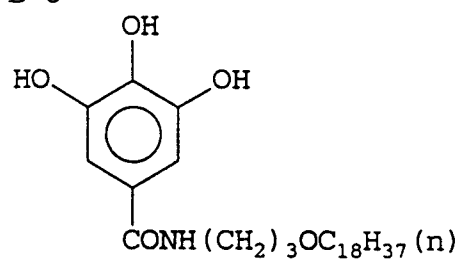
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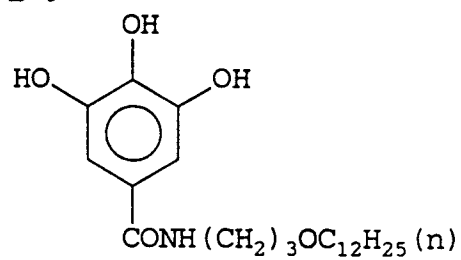
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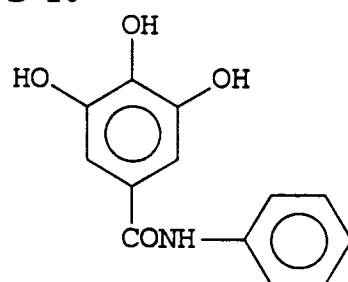
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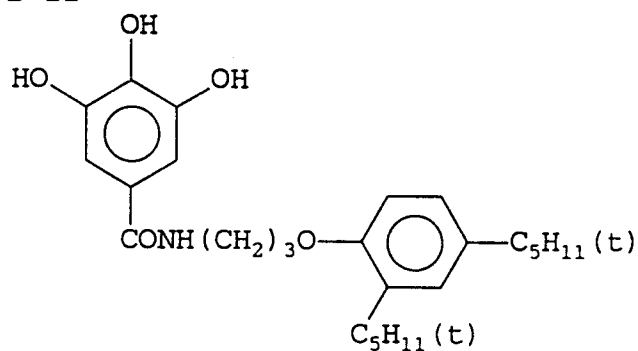
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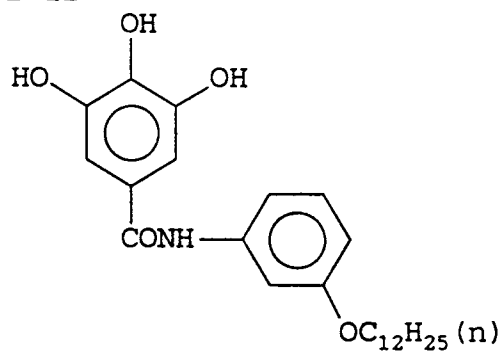
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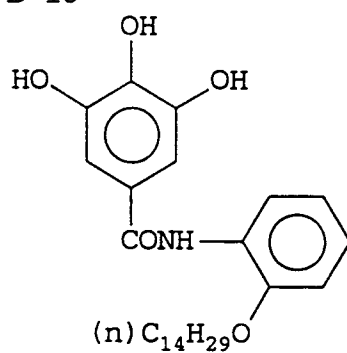
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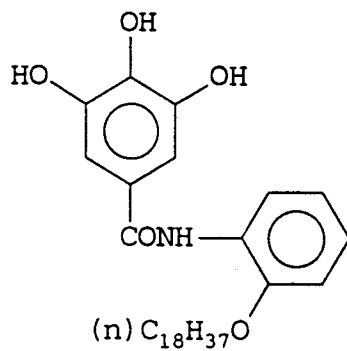
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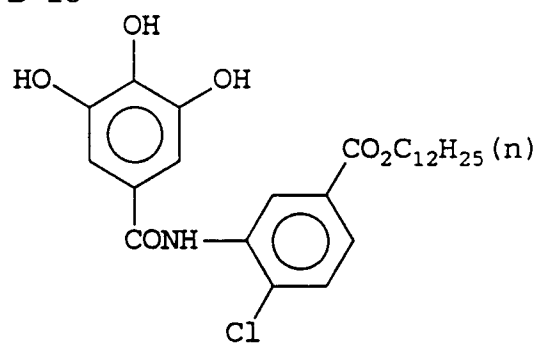
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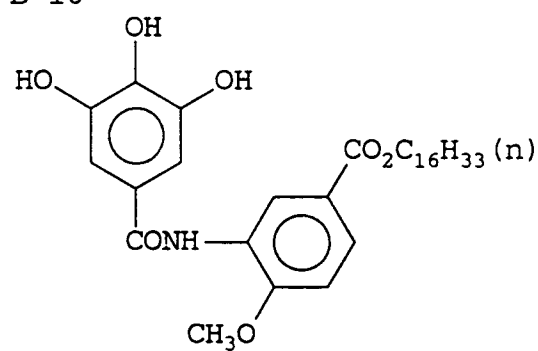
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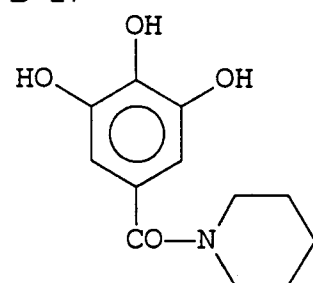
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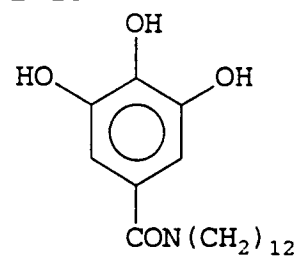
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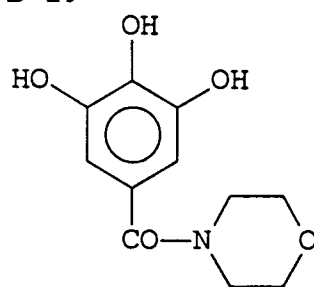
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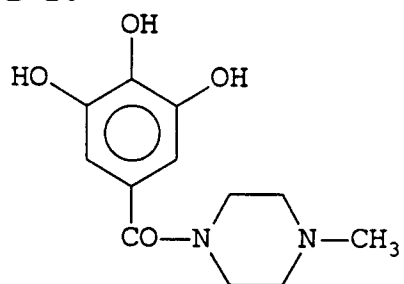
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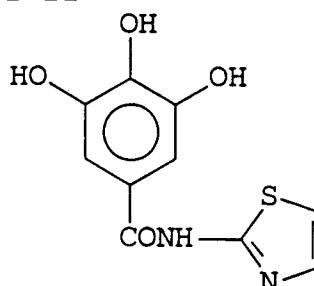
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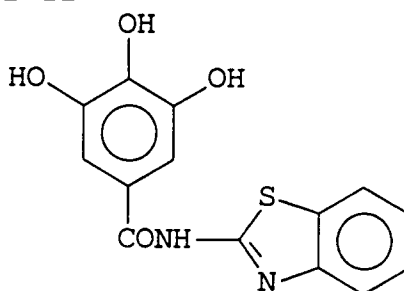
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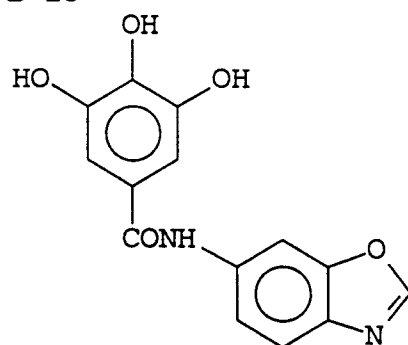
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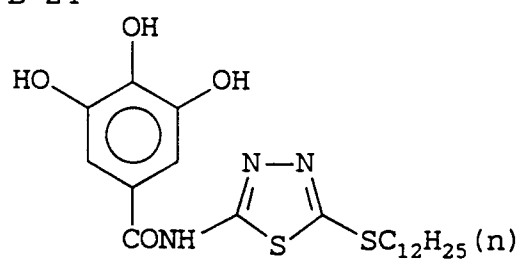
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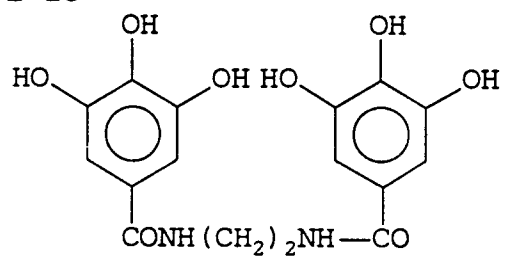
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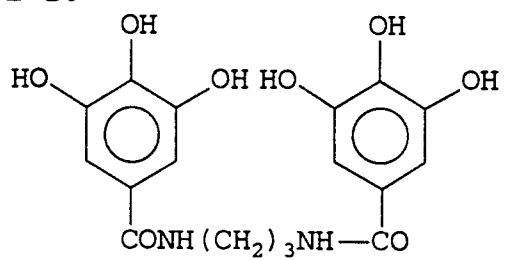
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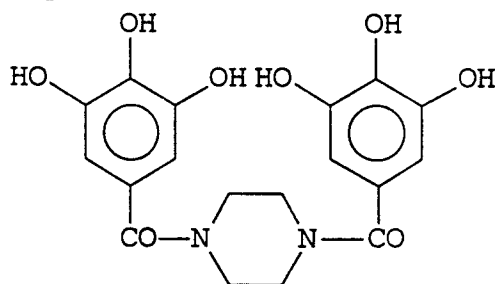
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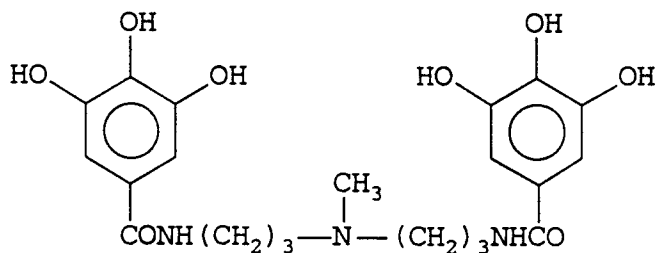
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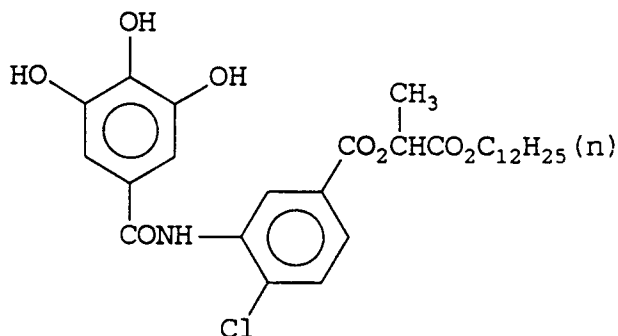
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B-28

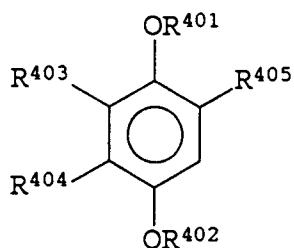


B-29



As the ED compounds particularly preferably used in the invention, there can be also mentioned compounds having the following formula [XIV].

[XIV]



In the above formula, each of R^{401} and R^{402} is a hydrogen atom or a group capable of being hydrolyzed by alkali, and they may be the same as or different from each other. Each of R^{403} , R^{404} and R^{405} is a hydrogen atom, a sulfo group, a carboxyl group, a sulfoalkyl group, a carboxyalkyl group or an alkyl group. At least one of R^{403} , R^{404} and R^{405} is a group selected from a sulfo group, a carboxyl group, a sulfoalkyl group and a carboxyalkyl group, and at least one of them is an alkyl group.

In the above formula [XIV], when R^{401} or R^{402} is a group capable of being hydrolyzed by alkali,

examples of such group include an acetyl group, a trichloroacetyl group, an ethoxycarbonyl group and a benzoyl group. When R^{403} , R^{404} or R^{405} is a sulfoalkyl group, an example of the group is a 1,1-dimethyl-2-sulfoethyl group. When R^{403} , R^{404} or R^{405} is a carboxyalkyl group, an example of the group is a 5-carboxypentyl group. When R^{403} , R^{404} or R^{405} is an alkyl group, examples of the group include a methyl group, an ethyl group, a t-octyl group, a n-octyl group, a sec-dodecyl group, a n-pentadecyl group and a sec-octadecyl group.

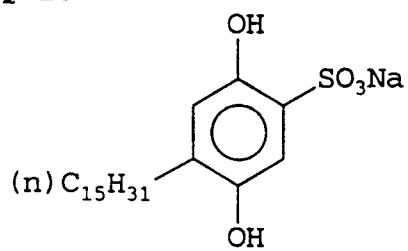
In the formula [XIV], each of R^{401} and R^{402} is preferably a hydrogen atom, and each of R^{403} , R^{404} and R^{405} is preferably an sulfo group or an alkyl group. Further, it is more preferred that R^{405} is a sulfo group or a carboxyl group, and one of R^{403} and R^{404} is an alkyl group and the other is a hydrogen atom.

Furthermore, it is most preferred that R^{403} is a hydrogen atom, R^{404} is an alkyl group, and R^{405} is a sulfo group.

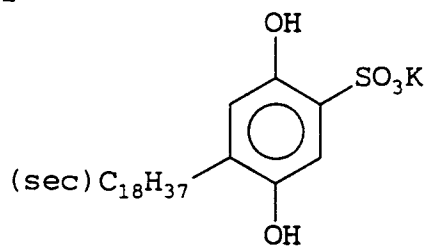
The compound of the formula [XIV] can be synthesized by processes described in U.K. Patent No. 891,158 and U.S. Patent No. 2,701,197 and other processes according to those processes.

Concrete examples of the compounds having the formula [XIV] employable in the invention are given below, but the invention is by no means restricted to the examples.

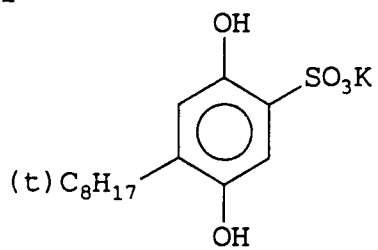
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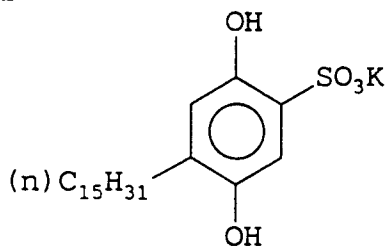
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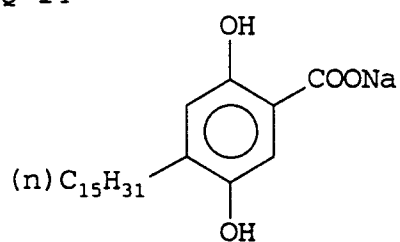
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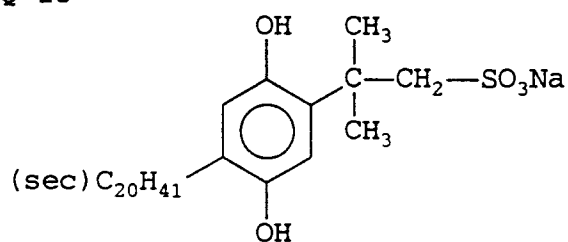
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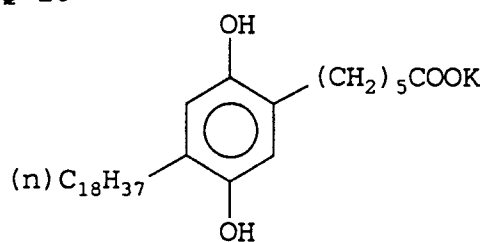
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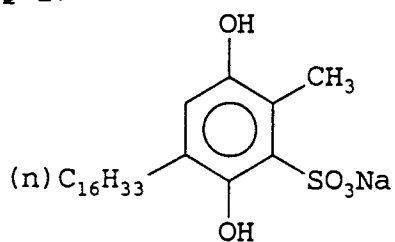
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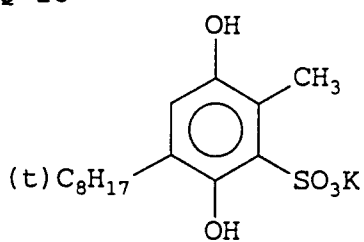
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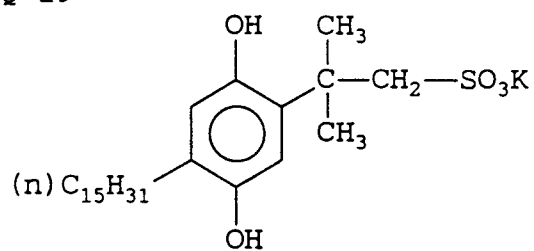
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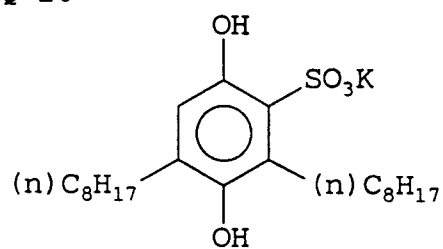
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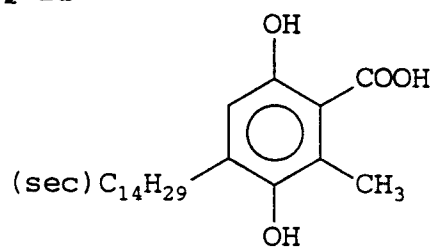
Q-19



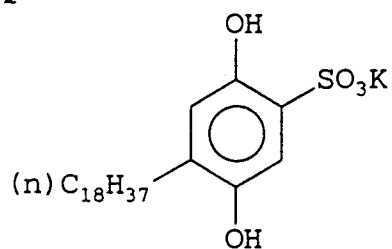
Q-20



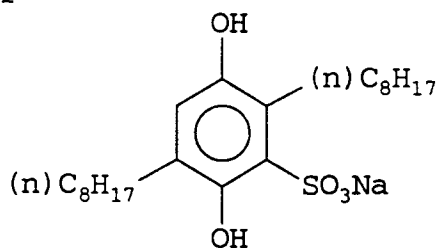
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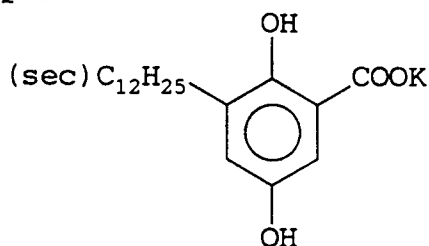
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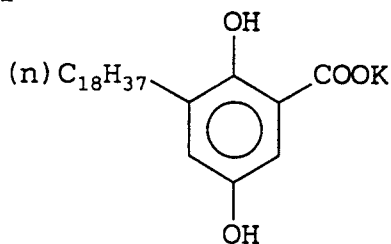
Q-23



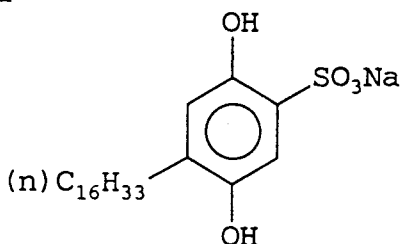
Q-24



Q-25



Q-26



A colorless coupler used as the ND compound in the invention is a coupler which undergoes a coupling reaction with an oxidant of a color developing agent but finally produces no chromatic dye in any layer of the photographic material owing to various reasons, for example, (1) the coupler still remains in the form of a leuco type; (2) a chromatic dye is once formed but decomposed in the developing process or the post bath to become colorless; and (3) a produced chromatic dye is eluded into the processing liquid because the dye is water-soluble.

Those colorless couplers are disclosed in the following literature. U.K. Patent No. 914,145 describes couplers in which a hydrogen atom of active methylene such as pyrazolone, benzoylactic acid ester, benzoylactic acid anilide and acetoacetic acid anilide is substituted with a substituted alkyl group or a substituted allyl group. U.S. Patent No. 1,284,649 describes couplers in which the fourth position of pyrazolone is substituted with a methyl group, an ethyl group or a cyanoethyl group. Japanese Patent Provisional Publication No. 50(1975)-83031 describes 5-pyrazolone type couplers improved in coupling activity in which the fourth position is substituted with an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, and the third position is substituted with a substituted acylamido group.

All of these couplers belong to the above-mentioned couplers of type (1).

Non-cyclic ketone type colorless DIR couplers as described in Japanese Patent Publication No. 46-(1971)-22514 and cyclic ketone type colorless DIR couplers as described in Japanese Patent Publication No. 51(1976)-16141 belong to the above-mentioned couplers of type (2). Couplers described in U.S. Patent
 5 No. 2,742,832 belong to the above-mentioned couplers of type (3).

The ND compound is contained in a protective layer positioned on the side lower than the protective layer containing the non-photosensitive silver halide grains. The amount of the ND compound added to the protective layer is preferably not less than 0.01 mg/m², more preferably not less than 0.1 mg/m².

10 In the present invention, one of the protective layers preferably further contains a block copolymer of polyvinyl alcohol and a polymer having an ionic group.

The ratio (A/B) of polyvinyl alcohol (A) and a polymer having an ionic group (B) is preferably in the range of 0.2 to 50, more preferably in the range of 0.3 to 40, and most preferably in the range of 2 to 10. In the case that the ratio is 2 to 10, the copolymer is well miscible with gelatin. The molecular weight of the block copolymer is preferably in the range of 10,000 to 100,000.

15 The block copolymer is preferably prepared by a radical polymerization of a monomer having an ionic group (which is polymerized) in the presence of polyvinyl alcohol having mercapto group as the terminal group. This process for preparation is disclosed in Japanese Patent Provisional Publication No. 59(1984)-189113.

The monomer having an ionic group preferably is a vinyl monomer. The ionic group preferably has an
 20 affinity with gelatin so that the copolymer is miscible with gelatin. Examples of the ionic group include carboxyl, sulfuric acid, sulfo and phosphoric acid. Examples of the monomer include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, 2-acryloyloxyethylphosphoric acid, vinylsulfuric acid, vinylsulfonic acid, 2-acrylamidopropanesulfonic acid, p-styrenesulfonic acid, a metal salt thereof and an ammonium salt thereof. The polymer having an ionic group may be a copolymer of a monomer having
 25 an ionic group and a nonionic monomer. Examples of the nonionic monomer include an olefin (e.g., ethylene, propylene, isobutylene), a halogenated olefin (e.g., vinyl chloride), a vinyl ester (e.g., vinyl acetate), an acrylate or a methacrylate (e.g., methyl acrylate, ethyl methacrylate), an acrylamide monomer (e.g., acrylamide), a styrene monomer (e.g., styrene) and N-vinyl pyrrolidone. The ratio of the ionic group in the polymer preferably is not less than 0.5 mole %, more preferably not less than 1 mole %, and most
 30 preferably not less than 2 mole %. The ionic group is used to have an affinity with gelatin so that the copolymer is miscible with gelatin.

The amount of the block copolymer is preferably in the range of 0.2 to 80 weight %, more preferably 0.5 to 20 weight %, and most preferably 1 to 10 weight % based on the amount of gelatin used as the binder of the protective layers.

35 Examples of the block copolymer are (P-1) a block copolymer of polyvinyl alcohol and acrylic acid (17 % of polyvinyl alcohol is denatured, and molecular weight is 20,000) and (P-2) a block copolymer of polyvinyl alcohol and acrylic acid (23 % of polyvinyl alcohol is denatured, and molecular weight is 30,000).

The block copolymer is preferably contained in the upper protective layer.

40 Preferred silver halide contained in the light-sensitive emulsion layer of the photographic material used in the invention may be any of silver iodobromide, silver iodochloride, silver chloriodobromide, silver bromide, silver chlorobromide and silver chloride. Particularly preferred is silver iodobromide, silver iodochloride or silver chloriodobromide, containing silver iodide in an amount of not more than about 30 % by mole.

45 The shape of the silver halide grain in the photographic emulsion may be either in the form of a regular crystal such as cube, octahedron and tetradecahedron, or in the form of an irregular crystal such as globular shape and plate shape, or in the form of a crystal having crystal defect such as twinning plane. Further, the shape of the grain may be complex of these crystals.

50 The silver halide grains may be either fine grains whose size is not more than about 0.2 μ m or large grains whose projected area is about 10 μ m in diameter. The emulsion containing the silver halide grains may be either a polydispersed emulsion or a monodispersed emulsion.

A photographic emulsion of silver halide available for the invention can be prepared in accordance with a known method described in, for example, "Emulsion Preparation and Types", *Research disclosure*, No. 17643 (December, 1978), pp. 22-23; or *ibid.*, No. 18716 (November, 1979), pp. 648; "Chimie et Physique Photographique" by P. Glafkides, Paul Montel, 1967; "Photographic Emulsion Chemistry" by G.F. Duffin,
 55 Focal Press, 1966; or "Making and Coating Photographic Emulsion" by V.L. Zelikman et al., Focal Press, 1964.

A monodispersed emulsion described in U.S. Patents No. 3,574,628 and No. 3,655,394, and U.K. Patent 1,413,748 is also preferable.

A tabular silver halide grain having an aspect ratio of not less than 5 can be also employed in the invention. A tabular silver halide grain can be easily prepared in accordance with methods described in "Photographic Science and Engineering" by Gutoff, vol. 14(1970), pp. 248-257; U.S. Patents No. 4,434,226, No. 4,414,310, No. 4,433,048 and No. 4,439,520; and U.K. Patent No. 2,112,157.

The crystal of the grain may have either a homogeneous structure, a heterogeneous structure in which halogens located at the inside and the outside are different from each other, or a structure consisting of layers. Further, silver halides whose halogen compositions are different from each other may be connected to each other by epitaxial bond, or silver halide may be connected to a compound other than silver halide, such as silver rhodanite and lead oxide.

A mixture of grains of various crystals is also available.

Generally, a silver halide emulsion having been subjected to physical ripening, chemical ripening and spectral sensitization is used in the invention. Various additives used in these processes are described in *Research Disclosure* No. 17643 and *ibid.*, No. 18716. Pages of *Research Disclosure* wherein the additives are described are set forth in the following table.

Known photographic additives available for the invention are also described in the above two Research Disclosures. The pages are also set forth in the following table.

TABLE

Additives	R.D. No.17643	R.D. No. 18716
1. Chemical Sensitizer	p. 23	p. 648, Right
2. Sensitivity Promoter		same as above
3. Spectral Sensitizer Color Sensitizer	pp. 23-24	pp. 648, Right - 649, Left
4. Whitening Agent	p. 24	
5. Antifoggant and Stabilizer	pp. 24-25	p. 649, Right
6. Light Absorber, Filter Dye, U.V. Absorber	pp. 25-26	pp. 649, Right - 650, Left
7. Antistain Agent	p. 25, Right	p. 650, Left-Right
8. Dye Image Stabilizer	p. 25	
9. Hardening Agent	p. 26	p. 651, Left
10. Binder	p. 26	same as above
11. Plasticizer, Lubricant	p. 27	p. 650, Right
12. Coating Aid, Surface Active Agent	pp. 26-27	p. 650, Right
13. Antistatic Agent	p. 27	same as above

To prevent deterioration of photographic properties caused by formaldehyde gas, compounds which react with formaldehyde to fix it, described in U.S. Patents No. 4,411,987 and No. 4,435,503, are preferably added to the photographic material.

Various color couplers can be used for the invention. Concrete examples of the couplers are described in the patents cited in the aforementioned *Research Disclosure* No. 17643, VII C-G.

As yellow couplers, employable are those described in, for example, U.S. Patents No. 3,933,501, No. 4,022,620, No. 4,326,024, No. 4,401,752 and No. 4,248,961, Japanese Patent Publication No. 58(1983)-10739, U.K. Patents No. 1,425,020 and No. 1,476,760, U.S. Patents No. 3,973,968, No. 4,314,023 and No. 4,511,649, and European Patent No. 249,473A, in addition to the yellow coupler represented by the formula [I].

As magenta couplers, 5-pyrazolone type and pyrazoloazole type compounds are preferred, and particularly preferred are those described in U.S. Patents No. 4,310, 619 and No. 4,351,897, European Patent No. 73,636, U.S. Patents No. 3,061,432 and No. 3,725,067, *Research Disclosure* No. 24220 (June, 1984), Japanese Patent Provisional Publication No. 60(1985)-33552, *Research Disclosure* No. 24230 (June, 1984), Japanese Patent Provisional Publications No. 60(1985)-43659, No. 61(1986)-72238, No. 60(1985)-35730, No. 55(1980)-118034 and No. 60(1985)-185951, U.S. Patents No. 4,500,630, No. 4,540,654 and No. 4,556,630, and International Publication No. WO88/04795.

As cyan couplers, there can be mentioned phenol type and naphthol type couplers, and preferred examples are those described in U.S. Patents No. 4,052,212, No. 4,146,396, No. 4,228,233, No. 4,296,200, No. 2,369,929, No. 2,801,171, No. 2,772,162, No. 2,895,826, No. 3,772,002, No. 3,758,308, No. 4,334,011 and No. 4,327,173, West German Patent Publication No. 3,329,729, European Patents No. 121,365A and No. 249,453A, U.S. Patents No. 3,446,622, No. 4,333,999, No. 4,775,616, No. 4,451,559, No. 4,427,767, No. 4,690,889, No. 4,254,212 and No. 4,296,199, and Japanese Patent Provisional Publication No. 61(1986)-

42658.

Colored couplers to compensate incidental absorption of a formed dye are preferably those described in *Research Disclosure* No. 17643, VII-G, U.S. Patent No. 4,163,670, Japanese Patent Publication No. 57-(1982)-39413, U.S. Patents No. 4,004,929 and No. 4,138,258, and U.K. Patent No. 1,146,368. It is also preferred to use a coupler whose fluorescent dye released in coupling stage compensates incidental absorption of a formed dye as described in U.S. Patent No. 4,774,181, and a coupler having as an eliminating group a dye precursor which reacts with a developing agent to form a dye as described in U.S. Patent No. 4,777,120.

As a coupler which gives a color developing dye exhibiting a proper diffusion, preferred are those described in U.S. Patent No. 4,366,237, U.K. Patent No. 2,125,570, European Patent No. 96,570, and West German Patent Publication No. 3,234,533.

Typical examples of polymerized dye-forming couplers are described in U.S. Patents No. 3,451,820, No. 4,080,211, No. 4,367,282, No. 4,409,320 and No. 4,576,910, and U.K. Patent No. 2,102,173.

A coupler which releases a photographically useful residue in accordance with coupling can be also used in the invention. DIR couplers which release a development inhibitor are preferably those described in the patents cited in the aforementioned *Research Disclosure* No. 17643, VII-F, Japanese Patent Provisional Publications No. 57(1982)-151944, No. 57(1982)-154234, No. 60(1985)-184248 and No. 63(1988)-37346, and U.S. Patents No. 4,248,962 and No. 4,782,012.

Couplers which imagewise release a nucleating agent or a development accelerator in the developing process are preferably those described in U.K. Patents No. 2,097,140 and No. 2,131,188, and Japanese Patent Provisional Publications No. 59(1984)-157638 and No. 59(1984)-170840.

Examples of other couplers available for the photographic material of the invention include a competing coupler described in U.S. Patent No. 4,130,427; a polyvalent coupler described in U.S. Patents No. 4,283,472, No. 4,338,393 and No. 4,310,618; a DIR redox compound-releasing coupler, a DIR coupler-releasing coupler, a DIR coupler-releasing redox compound or a DIR redox-releasing redox compound described in Japanese Patent Provisional Publications No. 60(1985)-185950 and No. 62(1987)-24252; a coupler which releases a dye having restoration to original color after elimination described in European Patent No. 173,302A; a bleach accelerator-releasing coupler described in *Research Disclosure* No. 11449, *ibid.* No. 24241, and Japanese Patent Provisional Publication No. 61(1986)-201247; a coupler which releases ligand described in U.S. Patent No. 4,553,477; a coupler which releases a leuco dye described in Japanese Patent Provisional Publication No. 63(1988)-75747; and a coupler which releases a fluorescent dye described in U.S. Patent No. 4,774,181.

The couplers used in the invention can be introduced into the photographic material by various known dispersing methods.

Examples of high-boiling solvents employable in an O/W dispersing method are described in U.S. Patent No. 2,322,027.

Concrete examples of the high-boiling organic solvents having a boiling point of not lower than 175 °C under a normal pressure employable in the O/W dispersing method include phthalic esters (e.g., dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-*t*-amylphenyl)-phthalate, bis(2,4-di-*t*-amylphenyl)isophthalate, bis(1,1-diethylpropyl)phthalate); esters of phosphoric acids or phosphonic acids (e.g., triphenyl phosphate, tricresyl phosphate, 2-ethylhexyldiphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate, di-2-ethylhexylphenyl phosphate); benzoic esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate, 2-ethylecyl-*p*-hydroxybenzoate); amides (e.g., *N,N*-diethyldodecanamide, *N,N*-diethyl-laurylamide, *N*-tetradecylpyrrolidone); alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-*tert*-amylphenol); aliphatic carboxylic esters (e.g., bis(2-ethylhexyl)sebacate, dioctyl azelate, glycerol tributylate, isostearyl lactate, trioctyl citrate); aniline derivatives (e.g., *N,N*-dibutyl-2-butoxyl-5-*tert*-octylaniline); and hydrocarbons (e.g., paraffin, dodecyl benzene, diisopropyl naphthalene).

As an assisting solvent, there can be used organic solvents having a boiling point of not lower than about 30 °C, preferably in the range of 50 °C to about 160 °C, and typical examples thereof include ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

A process of a latex dispersing method, effects thereof and concrete examples of latex for impregnation are described in U.S. Patent No. 4,199,363, West German Patent Applications (OLS) No. 2,541,274 and No. 2,541,230.

The color photographic material of the invention preferably contains various antiseptic or antimold agents such as 1,2-benzisothiazoline-3-one, *n*-butyl, *p*-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol and 2-(4-thiazolyl)benzimidazole described in Japanese Patent Provisional Pub-

lications No. 63(1988)-257747, No. 62(1987)-272248 and No. 1(1989)-80941.

The present invention can be applied to various color reversal photographic materials.

When the present invention is applied to color reversal paper, effects of the invention are markedly shown.

5 Appropriate supports employable in the invention are described in, for example, the aforementioned *Research Disclosure* No. 17643, p. 28, and *ibid.*, No. 18716, pp. 647 (right) - 648 (left).

In the photographic material of the invention, the total film thickness of all of the hydrophilic colloidal layers on the emulsion layer side is preferably not more than 28 μm more preferably not more than 23 μm , most preferably not more than 20 μm . Further, the film swelling speed $T_{1/2}$ is preferably not more than 30
10 sec, more preferably not more than 20 sec. The terms "film thickness" mean a film thickness measured at 25 °C and a relative humidity of 55 % under moisture conditioning (2 days), and the film swelling speed $T_{1/2}$ can be measured in accordance with methods known in the art.

The film swelling speed can be measured using, for example, a swellometer described in *Photographic Science and Engineering*, vol. 19, No. 2, pp.124-129, by A. Green et al. $T_{1/2}$ is defined as a time required to
15 reach 1/2 of a saturated film thickness of a film, in the case where the saturated film thickness is 90 % of a maximum swelling film thickness given when the film is treated with a color developer at 30 °C for 3 minutes and 15 seconds.

The film swelling speed $T_{1/2}$ can be adjusted by adding a hardening agent to gelatin used as a binder or varying conditions on the elapsed time after a coating process. Further, the swelling degree is preferably
20 between 150 and 400 %. Using the maximum swelling film thickness obtained under the above-mentioned conditions, the swelling degree can be calculated from the formula: (maximum swelling film thickness - film thickness) / film thickness.

Next, processing liquids for the color reversal photographic material used in the invention and processing stages therefor will be described.

25 In the invention, black and white developing process of the color reversal photographic material is carried out for not longer than 80 seconds, preferably not longer than 60 seconds, and more preferably not longer than 40 seconds. In such rapid black and white development, effects of the invention are markedly shown.

The total time of the black and white development, reversal, color development and desilvering
30 processes (other than the time required for drying the photographic material) is preferably shortened to improve productivity. On the other hand, unevenness of the density or stain was observed in the obtained image when the total time was shortened. The effects of the present invention is remarkable with respect to these problems. The total time is preferably not longer than 6 minutes and 30 seconds, and more preferably not longer than 4 minutes and 40 seconds.

35 In the process of the color reversal photographic material of the invention, processing stages of from black and white development to color development are as follows.

- 1) black and white development - washing - reversing - color development
- 2) black and white development - washing - photo reversing - color development
- 3) black and white development - washing - color development

40 The washing stage in any of the processes 1) to 3) can be replaced with a rinsing stage described in U.S. Patent No. 4,804,616 to simplify the process and to reduce waste water.

Processing stages after the color development are described below.

- 4) color development - compensating - bleaching - fixing - washing - stabilizing
- 5) color development - washing - bleaching - fixing washing - stabilizing
- 45 6) color development - compensating - bleaching - washing - fixing - washing - stabilizing
- 7) color development - washing - bleaching - washing - fixing - washing - stabilizing
- 8) color development - bleaching - fixing - washing - stabilizing
- 9) color development - bleaching - bleach fixing - washing - stabilizing
- 10) color development - bleaching - bleach fixing - fixing - washing - stabilizing
- 50 11) color development - bleaching - washing - fixing - washing - stabilizing
- 12) color development - compensating - bleach fixing - washing - stabilizing
- 13) color development - washing - bleach fixing - washing - stabilizing
- 14) color development - bleach fixing - washing - stabilizing
- 15) color development - fixing - bleach fixing - washing - stabilizing

55 In the present invention, all of the stages after the color development are referred to as a desilvering process.

In the above processes 4) to 15), the washing stage immediately before the stabilizing stage may be omitted, or the last stabilizing stage may be omitted. Any one of the processes 1) to 3) and any one of the

processes 4) to 15) are combined to form a color reversal process.

Processing liquids used in the color reversal process of the invention are described below.

For the black and white developer, any known developing agents can be employed. Examples of the developing agents include dihydroxybenzenes (e.g., hydroquinone), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone), aminophenols (e.g., N-methyl-p-aminophenol), 1-phenyl-3-pyrazolines, ascorbic acids, and heterocyclic compounds in which 1,2,3,4-tetrahydroquinoline ring is condensed with indolene ring described in U.S. Patent No. 4,067,872. Those developing agents can be employed singly or in combination.

If necessary, the black and white developer may contain preservatives (e.g., sulfite, bisulfite), buffering agents (e.g., carbonate, boric acid, borate, alkanolamine), alkali agents (e.g., hydroxide, carbonate), soluble tablets (e.g., polyethylene glycols, esters thereof), softening agents for hard water (e.g., aminopolycarboxylic acids, organo phosphonic acid), pH adjusting agents (e.g., organic acid such as acetic acid), sensitizers (e.g., quaternary ammonium salt), development accelerators, surface active agents, anti-foam agents, film-hardening agents, antifogging agents (e.g., potassium iodide, potassium bromide, benzotriazole), viscosity-imparting agents, etc.

The black and white developer used in the invention needs to contain a compound serving as a solvent for silver halide, and in general, the above-mentioned sulfite added as a preservative serves as the solvent. Concrete examples of sulfites and other solvents for silver halide employable in the invention include KSCN, NaSCN, K_2SO_3 , Na_2SO_3 , $K_2S_2O_5$, $Na_2S_2O_5$, $K_2S_2O_8$, $Na_2S_2O_8$.

A pH value of the black and white developer is appropriately selected to obtain desired density and contrast, and the pH value thereof is in the range of about 8.5 to about 11.5.

In the present invention, the reversal process is preferably conducted by uniformly exposing to light the photographic material.

In place of the uniform exposure, a reversing bath can be used after the black and white development. The reversing bath may contain known fogging agents. Examples of the fogging agents include stannous ion complex salts such as stannous ion-organic phosphoric acid complex salt (U.S. Patent No. 3,617,282), stannous ion organic phosphonocarboxylic acid complex salt (Japanese Patent Publication No. 56(1981)-326161) and stannous ion-aminopolycarboxylic acid complex salt (U.K. Patent No. 1,209,050); and boron compounds such as hydrogenated boron compound (U.S. Patent No. 2,984,567) and heterocyclic amineboron compound (U.K. Patent No. 1,011,000).

A pH of the fogging bath (reversing bath) is within a wide range of from acidic side to alkaline side, and the pH value thereof is generally in the range of 2 to 12, preferably 2.5 to 10, more preferably 3 to 9. The reversing bath may be omitted, if the above-mentioned fogging agent is added to the color developing solution.

As aromatic primary amine color-developing agents used in the color developer of the invention, preferred are p-phenylenediamine derivatives. Representative examples of p-phenylenediamine derivatives are given below, but the invention is by no means restricted to the examples.

- D-1 N,N-diethyl-p-phenylenediamine
- D-2 2-amino-5-diethylaminotoluene
- D-3 2-amino-5-(N-ethyle-N-laurylamino)toluene
- D-4 4-[N-ethyl-N-(β -hydroxyethyl)amino]aniline
- D-5 2-methyl-4-[N-ethyl-N-(β -hydroxyethyl)amino]-aniline
- D-6 4-amino-3-methyl-N-ethyl-N-[β -(methanesulfonamide)ethyl]-aniline
- D-7 N-(2-amino-5-diethylaminophenylethyl)methanesulfonamide
- D-8 N,N-dimethyl-p-phenylenediamine
- D-9 4-amino-3-methyl-N-ethyl-N-methoxyethylaniline
- D-10 4-amino-3-methyl-N-ethyl-N- β -ethoxyethylaniline
- D-11 4-amino-3-methyl-N-ethyl-N- β -butoxyethylaniline

Among the above p-phenylenediamine derivatives, particularly preferred are the exemplified compounds D-2, D-4, D-5 and D-6.

These p-phenylenediamine derivatives may be salts such as sulfate, hydrochloride, sulfite and p-toluenesulfonate. The amount of the aromatic primary amine developing agent used in the developer is preferably in the range of about 0.1 g to about 20 g, more preferably in the range of about 0.5 g to about 15 g, per 1 l of the developer.

In the invention, a color developer substantially not containing benzyl alcohol is a color developer wherein a concentration of benzyl alcohol is not more than 3×10^{-2} mole per 1 l, and preferably is a color developer containing no benzyl alcohol.

Examples of sulfites contained in the color developer of the invention include sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite and potassium metabisulfite. Sulfite is

added to the color developer preferably in an amount of 1×10^{-5} mole to 5×10^{-2} mole, more preferably 1×10^{-4} mole to 5×10^{-2} mole, most preferably 1×10^{-4} mole to 2×10^{-2} mole, per 1 l of the color developer.

If necessary, to the developer may be also added preservatives such as various metals described in Japanese Patent Provisional Publications No. 57(1982)-44148 and No. 57(1982)-53749, salicylic acids described in Japanese Patent Provisional Publication No. 59(1984)-180588, alkanolamines described in Japanese Patent Provisional Publication No. 54(1979)-3532, polyethylene imines described in Japanese Patent Provisional Publication No. 56(1981)-94349, and aromatic polyhydroxy compounds described in U.S. Patent No. 3,746,544. Particularly, aromatic polyhydroxy compounds are preferably added.

The color developer employable in the invention preferably has a pH value of 9 to 14, more preferably 9 to 13. The color developer may also contain other compounds which are components of conventional color developers.

For keeping the above-mentioned pH, it is preferred to use a variety of buffers.

Concrete examples of the buffers include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, tribasic sodium phosphate, tribasic potassium phosphate, dibasic sodium phosphate, dibasic potassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate, (sodium 5-sulfosalicylate), and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate). However, the invention is by no means restricted to those examples.

The amount of the above-mentioned buffers added to the color developer is preferably not less than 0.1 mole/l, more preferably in the range of 0.1 mole/l to 0.4 mole/l.

In addition to the above-mentioned components, the color developer may further contain various chelating agents to prevent precipitation of calcium or magnesium or to enhance stability of the color developer.

As the chelating agents, preferred are organic acid compounds such as aminopolycarboxylic acids, organic phosphoric acids and phosphonocarboxylic acids. Concrete examples are given below, but those examples are given by no means to restrict the invention.

That is, there can be mentioned nitrilotriacetic acid, diethylenetriamine pentaacetic acid, ethylenediamine tetraacetic acid, N,N,N-trimethylene phosphonic acid, ethylenediamine-N,N,N,N'-tetramethylene phosphonic acid, transcyclohexanediamine tetraacetic acid, 1,2-diaminopropane tetraacetic acid, hydroxyethyliminodiacetic acid, glycol ether diamine tetraacetic acid, ethylenediamine orthohydroxyphenyl acetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, and N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid. These chelating agents can be employed in combination of two or more kinds, if necessary.

The chelating agent is added to the color developer in such an amount that the metallic ion in the color developer is blocked. For example, the amount thereof is in the range of 0.1 g to 10 g per 1 l of the color developer.

To the color developer may be added optional development accelerators, according to necessity. For example, there can be added p-phenylenediamine compounds described in Japanese Patent Provisional Publications No. 52(1977)-49829 and No. 50(1975)-15554; quaternary ammonium salts described in Japanese Patent Provisional Publication No. 50(1975)-137726, Japanese Patent Publication No. 44 (1969)-30074, and Japanese Patent Provisional Publications No. 56(1981)-156826 and No. 52(1977)-43429; amine compounds described in U.S. Patents No. 2,494,903, No. 3,128,182, No. 4,230,796 and No. 3,253,919, Japanese Patent Publication No. 41(1966)-11431, and U.S. Patents No. 2,482,546, No. 2,596,926 and No. 3,582,346; polyalkylene oxides described in Japanese Patent Publications No. 37(1962)-16088 and No. 42-(1967)-25201, U.S. Patent No. 3,128,183, Japanese Patent Publications No. 41(1966)-11431 and No. 42-(1967)-23883, and U.S. Patent No. 3,532,501; 1-phenyl-3-pyrazolidones; and imidazoles.

In the invention, optional antifogging agents can be added to the color developer according to necessity. As the antifogging agents, employable are alkali metal halides such as sodium chloride, potassium bromide and potassium iodide; and organic antifogging agents. Representative examples of the organic antifogging agents are nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chloro-benzotriazole, 2-thiazolyl-benzimidazole, 2-thiazolylmethyl-benzimidazole, indazole, hydroxyazaindolizine and adenine.

The color developer used in the invention may contain brightening agents. As the brightening agents, 4,4'-dimaino-2,2'-disulfostilbene type compounds are preferred. The amount of the brightening agent added to the color developer is in the range of 0 to 5 g/l, preferably 0.1 to 4 g/l.

Furthermore, various surface active agents such as alkylsulfonic acid, arylphosphonic acid, aliphatic carboxylic acid and aromatic carboxylic acid can be added to the color developer, if necessity.

In the invention, the temperature for treating the photographic material with the color developer is in the range of 20 to 50 °C, preferably 30 to 40 °C, and the time therefor is in the range of 20 seconds to 8 minutes, preferably 30 seconds to 6 minutes. It is preferred that the amount of the replenisher is as small as possible, and the amount thereof is generally in the range of 100 to 3,000 ml, preferably 100 to 2,500 ml, more preferably 100 to 2,000 ml, per 1 m² of the photographic material.

The color developing bath may be divided into two or more bath stages, if necessary, and the color developing replenisher may be replenished in the first bath or the last bath to shorten the developing time or to reduce the amount of the replenisher.

For the purpose of adjusting gradation, the color developer may contain compounds which react with oxidant of the color developing agent to produce colorless compound, so called, "competing compounds" such as citrazinic acid, J acid and H acid

After the color developing process, the photographic material of the invention is subjected to a bleaching process or a bleach-fix process. These processes can be carried out immediately after the color developing without conducting other processes, or can be carried out after other processes such as stopping, compensation and washing following the color developing.

A compensating liquid may contain bleaching accelerators such as aminopolycarboxylic acids (e.g., ethylenediamine tetraacetic acid and diethylenetriamine pentaacetic acid), sulfites (e.g., sodium sulfite and ammonium sulfite), thioglycerol, aminoethanethiol and sulfoethanethiol. Further, for the purpose of scum prevention, the compensating liquid preferably contains sorbitan esters of aliphatic acids substituted with ethylene oxides as described in U.S. Patent No. 4,839,262, and polyoxyethylene compounds as described in U.S. Patent No. 4,059,446 and *Research Disclosure*, vol. 191, No. 19104 (1980).

As bleaching agents used for the bleaching bath and/or bleach-fix bath, there can be employed ferric iron complex salts of aminopolycarboxylic acids, peroxides (e.g., sodium persulfate), etc. Preferred are ferric iron complex salts of aminopolycarboxylic acids. Examples of aminopolycarboxylic acids for the ferric iron complex salts include ethylenediaminetetraacetic acid, 1,3-diaminopropanetetraacetic acid, glycoletherdiaminetetraacetic acid, cyclohexanediaminetetraacetic acid, 1,4-diaminobutanetetraacetic acid, 1,2-propylenediaminetetraacetic acid, thioglycoletherdiaminetetraacetic acid, 1,3-butylenediaminetetraacetic acid and methyliminodiacetic acid.

The amount of the above-mentioned bleaching agent added to the bleaching bath or the bleach-fix bath is in the range of 0.05 to 1 mole, preferably 0.1 to 0.5 mole, per 1 l of the bleaching bath or the bleach-fix bath. The bleaching bath and/or the bleach-fix bath of the invention may also contain aminocarboxylates other than the aforementioned aminopolycarboxylic acid iron(III) complex salts.

The amount thereof is preferably in the range of 0.0001 to 0.1 mole/l, more preferably 0.003 to 0.05 mole/l.

In general, aminopolycarboxylic acids and their ferric iron complex salts are preferably used in the form of alkali metal salts or ammonium salts, and particularly ammonium salts are more preferred because they are excellent in solubility and bleaching power.

The bleaching bath and/or the bleach-fix bath may contain various bleaching accelerators.

The bleaching accelerators preferably are compounds having mercapto group or disulfide group as described in U.S. Patent No. 3,893,858, German Patent No. 1,290,812, U.K. Patent No. 1,138,842, Japanese Patent Provisional Publication No. 53(1988)-95630 and *Research Disclosure* No. 17129 (July 1978).

The amount of the bleaching accelerator is in the range of 0.01 to 20 g, preferably 0.1 to 10 g, per 1 l of a liquid having bleaching power.

The bleaching bath and/or the bleach-fix bath constituting the invention may further contain rehalogenating agents such as bromides (e.g., potassium bromide, sodium bromide, ammonium bromide) or chlorides (e.g., potassium chloride, sodium chloride, ammonium chloride), in addition to the bleaching agent and the above-mentioned compounds. The concentration of the rehalogenating agent in the bleaching bath is in the range of 0.1 to 5 moles, preferably 0.5 to 3 moles, per 1 l of the bleaching bath. Furthermore, the bleaching bath and/or the bleach-fix bath may contain other known additives which are generally used for conventional bleaching baths, for example, nitrates such as sodium nitrate and ammonium nitrate; one or more kinds of inorganic acids and organic acids having pH buffer power such as boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphoric acid, sodium phosphate, citric acid, sodium citrate and tartaric acid; and their salts.

In the bleach-fix bath and/or the fixing bath, thiosulfates can be used as fixing agents. The amount of thiosulfate is in the range of 0.1 to 3 mole/l, preferably 0.3 to 2 mole/l.

Examples of the thiosulfate compounds include ammonium thiosulfate, sodium thiosulfate, potassium thiosulfate, calcium thiosulfate and magnesium thiosulfate. Of these, ammonium thiosulfate is preferred because it has excellent solubility and the highest fixing speed.

As the fixing agent or fixing accelerator for the bleach-fix bath and/or the fixing bath of the invention, thiocyanic acid compound (particularly ammonium salt), thiourea, thioether, urea and the like can be also employed other than the above-mentioned thiosulfate compounds. The concentration of this auxiliary fixing agent or fixing accelerator together with the thiosulfate compound in the bleach-fix bath or the fixing bath is in the range of 1.11 to 3.0 mole/l, preferably 1.4 to 2.8 mole/l.

The bleach-fix bath and/or the fixing bath of the invention can contain sulfites (e.g., sodium sulfite, potassium sulfite and ammonium sulfite), hydroxylamine, hydrazine, etc. as preservatives, and further can contain various brightening agents, anti-foam agents, surface active agents, and organic solvents (e.g., polyvinyl pyrrolidone and methanol). Particularly, sulfinic acid compounds described in Japanese Patent Provisional Publication No. 62(1987)-143048 are preferably employed as preservative.

Furthermore, addition of a variety of aminopolycarboxylic acids and organic phosphonic acids to the bleach-fix bath and/or the fixing bath is preferred for the purpose of stabilizing the bath. The amount thereof is in the range of 0.01 to 0.3 mole/l, preferably 0.05 to 0.2 mole/l. They are effective especially when added to the fixing bath.

A pH value of the bleaching bath and/or the bleach-fix bath of the invention is generally in the range of 9 to 1, preferably 7.5 to 1.5, more preferably 7.0 to 2.0. Particularly, the bleaching bath preferably has a pH value of 5.0 to 2.0. When the pH value of the bath is within this preferred region, the photographic material hardly suffers bleach-fogging and shows excellent desilvering effect.

The fixing bath of the invention generally has a pH value of 9.0 to 5.0, preferably 7.5 to 5.5.

Water used in the washing process may contain known additives according to necessary. For example, employable are softening agents such as inorganic phosphoric acid, aminopolycarboxylic acid and organic phosphoric acid; antifungal agents or mildewproofing agents to prevent proliferation of various bacteria or algae (e.g., isothiazolone, organic chlorine type bactericide, benzotriazole, etc.); and surface active agents to prevent drying load and drying mark. Further, also employable are compounds described in L.E. West, "Water Quality Criteria", Phot. Sci. and Eng., vol. 9, No. 6, pp. 343-359 (1965).

As the stabilizing bath in the stabilizing process, processing liquids for stabilizing a dye image are employed. For example, a liquid having buffering power of pH 3 - 6 and a liquid containing aldehyde (e.g., glutaraldehyde) can be employed. Formalin is not preferred from the viewpoint of environmental pollution. The stabilizing bath may contain ammonium compounds, metallic compounds such as Bi and Al, brightening agents, chelating agents (e.g., EDTA, 1-hydroxyethylidene-1,1-diphosphonic acid), antifungal agents, mildewproofing agents, hardening agents, and surface active agents, depending on necessity. As the mildewproofing agents, thiazolone compounds such as 5-chloro-2-methyl-isothiazoline-3-one and 1,2-benzoisothiazoline-3-one are effective.

It is preferred to add alkanolamine to the stabilizing bath in order to prevent sulfide staining of thiosulfuric acid ion introduced with the photographic material into the bath.

The stabilizing bath of the invention generally has a pH value of 3 to 8, preferably 5 to 7. The temperature of the stabilizing bath is preferably in the range of 5 to 45 °C, more preferably 10 to 40 °C.

In the washing process or the stabilizing process, a multiplate counter current system is preferably employed, and the number of plates is preferably 2 to 4. Two or more kinds of stabilizing baths may be employed in the multiplate system. The ratio of the amount of replenisher to that of carried liquid of the prebath based on unit area of the photographic material is within a range of 1-50, preferably within a range of 2-30, more preferably within a range of 2-15.

The processing time for the washing process or the stabilizing process is made as short as possible, whereby the effect of the invention is markedly shown. From the viewpoint of rapid processing, the total time of the washing process and the stabilizing process is preferably in the range of 10 to 50 seconds, more preferably 10 to 30 seconds.

As water used in the washing process or the stabilizing process, preferable are tap water, water having been subjected to deionization using for example an ion exchange resin to have a content of Ca or Mg of not more than 5 mg/l, and water having been sterilized by means of halogen lamp or UV germicidal lamp.

EXAMPLE 1

Silver halide emulsions EM-1 to EM-4 according to the invention, each substantially not having photosensitivity, was prepared by a process comprising preparing silver halide grains according to a conventional neutral double jet method and then washing the grains to remove excessive ion according to a precipitation method. After the washing, each of the emulsions was subjected to addition of gelatin to make re-dispersing and subjected to pH-adjustment, but was not subjected to chemical ripening on the surface.

The obtained emulsions were shown in Table 3.

Table 3

Emulsion	Halogen composition	Mean grain diameter (μm)
EM-1	AgBr	0.04
EM-2	AgBr _{0.40} Cl _{0.60}	0.18
EM-3	AgBr _{0.02} Cl _{0.98}	0.18
EM-4	AgCl	0.18

Then, a paper was laminated with polyethylene on the both sides to prepare a paper support. On the surface of the paper support, the following first to twelfth layers were provided to prepare a color photographic material. The obtained photographic material (sample) was numbered as No. 101. Polyethylene positioned on the first layer side included 15 wt.% of anatase-type titanium oxide as a white pigment and an extremely small amount of ultramarine as a blue dye.

(Composition of layers)

The composition and its amount (g/m²) of each layer are set forth below. The values for the silver halide emulsions mean the coating amount of silver.

The first layer (Gelatin layer)	
Gelatin	1.30

The second layer (Antihalation layer)	
Black colloidal silver	0.10
Gelatin	0.70

The third layer (Low red sensitive layer)	
Silver chloriodobromide spectrally sensitized with red sensitizing dye (mixture of ExS-1, 2, 3 in the ratio of 1:1:1) [silver chloride: 1 mole %; silver iodide: 4 mole %; mean grain size: 0.3 μm ; size distribution: 10 %; cubic; iodine core-type core shell]	0.06
Silver iodobromide spectrally sensitized with red sensitizing dye (mixture of ExS-1, 2, 3 in the ratio of 1:1:1) [silver iodide: 4 mole %; mean grain size: 0.5 μm ; size distribution: 15 %; cubic]	0.10
Gelatin	1.00
Cyan coupler (ExC-1)	0.14
Cyan coupler (ExC-2)	0.07
Discoloration inhibitor (mixture of Cpd-2, 3, 4 in the ratio of 1:1:1)	0.12
Coupler dispersion medium (Cpd-6)	0.03
Coupler solvent (mixture of Solv-1, 2, 3 in the ratio of 1:1:1)	0.06
Development accelerator (Cpd-13)	0.05

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The fourth layer (High red sensitive layer)	
Silver iodobromide spectrally sensitized with red sensitizing dye (mixture of ExS-1, 2, 3 in the ratio of 1:1:1) [silver iodide: 6 mole %; mean grain size: 0.8 μ m; size distribution: 20 %; tabular (aspect ratio = 8, iodine core type)]	0.15
Gelatin	1.00
Cyan coupler (ExC-1)	0.20
Cyan coupler (ExC-2)	0.10
Discoloration inhibitor (mixture of Cpd-2, 3, 4 in the ratio of 1:1:1)	0.15
Coupler dispersion medium (Cpd-6)	0.03
Coupler solvent (mixture of Solv-1, 2, 3 in the ratio of 1:1:1)	0.10

The fifth layer (Intermediate layer)		
5	Magenta colloidal silver	0.02
	Gelatin	1.00
	Color stain inhibitor (mixture of Cpd-7, 16 in the ratio of 1:1)	0.08
	Color stain inhibitor solvent (mixture of Solv-4, 5 in the ratio of 1:1)	0.16
	Polymer latex (Cpd-8)	0.10

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The sixth layer (Low green sensitive layer)	
Silver chloriodobromide spectrally sensitized with green sensitizing dye (ExS-4) [silver chloride: 1 mole %; silver iodide: 2.5 mole %; mean grain size: 0.28 μm ; size distribution: 8 %; cubic; iodine core-type core shell]	0.04
Silver iodobromide spectrally sensitized with green sensitizing dye (ExS-4) [silver iodide: 2.5 mole %; mean grain size: 0.48 μm ; size distribution: 12 %; cubic]	0.06
Gelatin	0.80
Magenta coupler (mixture of ExM-1, 2 in the ratio of 1:1)	0.10
Discoloration inhibitor (Cpd-9)	0.10
Stain inhibitor (mixture of Cpd-10, 11 in the ratio of 1:1)	0.01
Stain inhibitor (Cpd-5)	0.001
Stain inhibitor (Cpd-12)	0.01
Coupler dispersion medium (Cpd-5)	0.05
Coupler solvent (mixture of Solv-4, 6 in the ratio of 1:1)	0.15

The seventh layer (High green sensitive layer)	
Silver iodobromide spectrally sensitized with green sensitizing dye (ExS-4) [silver iodide: 3.5 mole %, mean grain size: 1.0 μm ; size distribution: 21 %; tabular (aspect ratio = 9, iodine homogeneously-dispersed type)]	0.10
Gelatin	0.80
Magenta coupler (mixture of ExM-1, 2 in the ratio of 1:1)	0.10
Discoloration inhibitor (Cpd-9)	0.10
Stain inhibitor (mixture of Cpd-10, 11, 22, in the ratio of 1:1:1)	0.01
Stain inhibitor (Cpd-5)	0.001
Stain inhibitor (Cpd-12)	0.01
Coupler dispersion medium (Cpd-6)	0.05
Coupler solvent (mixture of Solv-4, 6)	0.15

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The eighth layer (Yellow filter layer)		
	Yellow colloidal silver	0.20
	Gelatin	1.00
	Color stain inhibitor (Cpd-7)	0.06
	Color stain inhibitor solvent (mixture of Solv-4, 5 in the ratio of 1:1)	0.15
	Polymer latex (Cpd-8)	0.10

The ninth layer (Low blue sensitive layer)	
Silver chloriodobromide spectrally sensitized with blue sensitizing dye (mixture of ExS-5, 6 in the ratio of 1:1) [silver chloride: 2 mole %; silver iodide: 2.5 mole %; mean grain size: 0.38 μm ; size distribution: 8 %; cubic; iodine core-type core shell]	0.07
Silver iodobromide spectrally sensitized with blue sensitizing dye (mixture of ExS-5, 6 in the ratio of 1 : 1) [silver iodobromide: 2.5 mole %; mean grain size: 0.55 μm ; size distribution: 11 %; cubic]	0.10
Gelatin	0.50
Yellow coupler (ExY-1)	0.20
Stain inhibitor (Cpd-5)	0.001
Discoloration inhibitor (Cpd-14)	0.10
Coupler dispersion medium (Cpd-6)	0.05
Coupler solvent (Solv-2)	0.05

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The tenth layer (High blue sensitive layer)	0.25
Silver iodobromide spectrally sensitized with blue sensitizing dye (mixture of ExS-5, 6 in the ratio of 1:1) [silver iodide: 2.5 mole %; mean grain size: 1.4 μ m; size distribution: 21 %; tabular (aspect ratio = 14)]	1.00
Gelatin	0.40
Yellow coupler (ExY-1)	0.002
Stain inhibitor (Cpd-5)	0.10
Discoloration inhibitor (Cpd-14)	0.15
Coupler dispersion medium (Cpd-6)	0.10
Coupler solvent (Solv-2)	

The eleventh layer (Protective layer containing ultraviolet absorbent)

5	Gelatin	1.50
	Ultraviolet absorbent (mixture of Cpd-1, 2, 4, 15 in the ratio of 1:1:1:1)	1.00
10	Color stain inhibitor (mixture of Cpd-7, 16)	0.06
	Dispersion medium (Cpd-6)	
15	Ultraviolet absorbent solvent (mixture of Solv-1, 2 in the ratio of 1:1)	0.15
	Irradiation inhibiting dye (mixture of Cpd-17, 18 in the ratio of 1:1)	0.02
20	Irradiation inhibiting dye (mixture of Cpd-19, 20 in the ratio of 1:1)	0.02

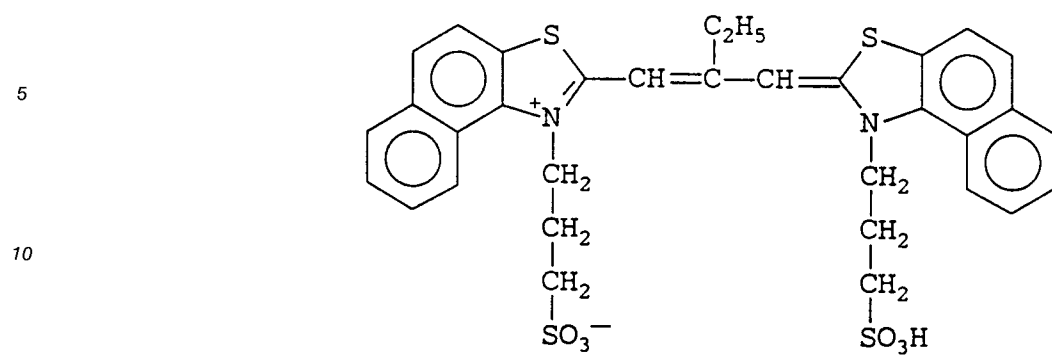
The twelfth layer (Protective layer)

25	EM-3	0.13 (in terms of silver halide)
	Modified POVAL	0.02
	Gelatin	1.50
	Gelatin hardening agent (mixture of H-1, 2 in the ratio of 1:1)	0.17
30	Block copolymer of polyvinyl alcohol and acrylic acid (23 % of polyvinyl alcohol is denatured, and molecular weight is 30,000) (P-2)	0.02

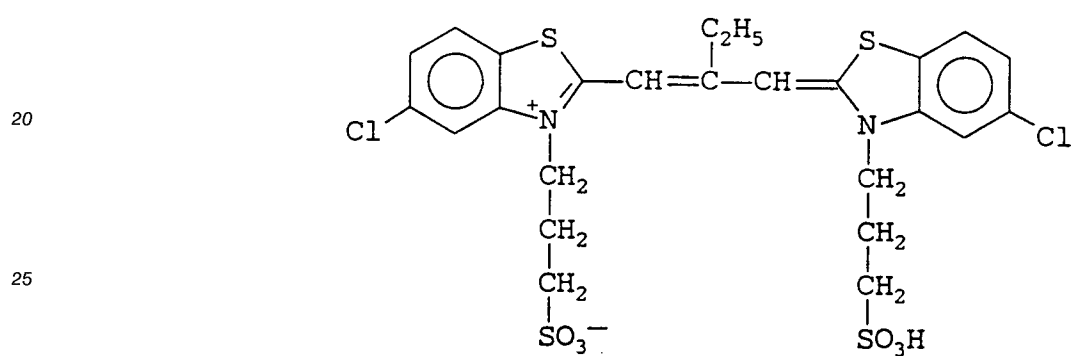
Further, emulsifying dispersion aids of Alkanol XC (available from Du Pont) and sodium alkylbenzene sulfonate, and coating aids of succinic acid ester and Magefac F120 (available from Dainippon Ink & Chemicals Inc.) were also added to each layer. Stabilisers of Cpd-21, 22 and 23 were added to each of the layers containing silver halide or colloidal silver.

Followings are compounds used in the example.

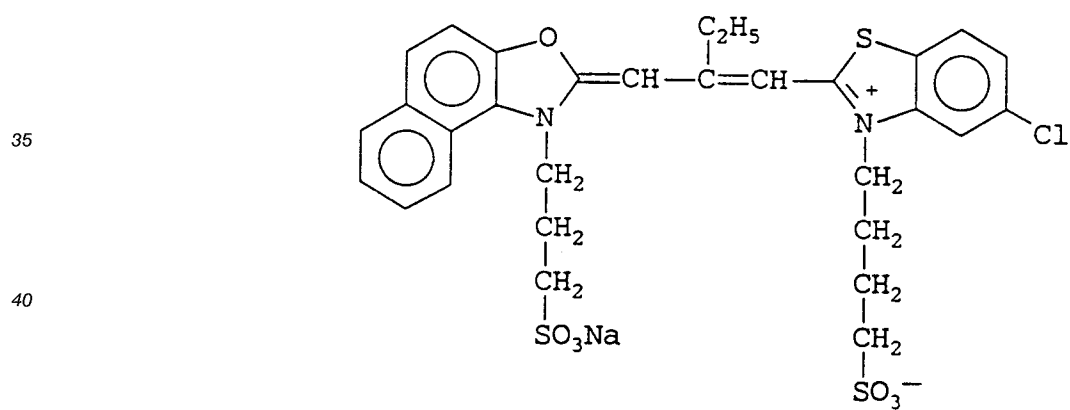
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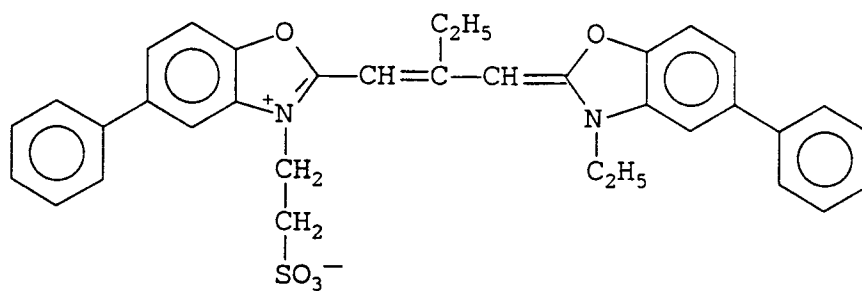
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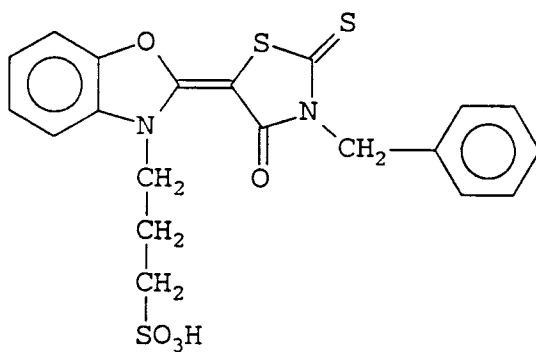
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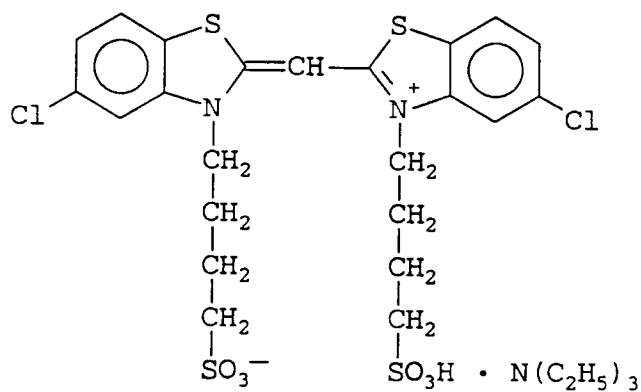
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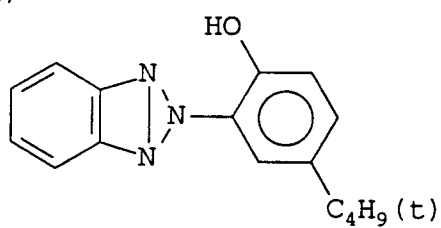
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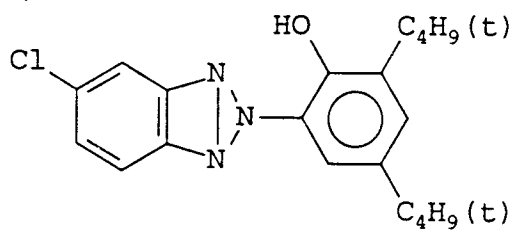
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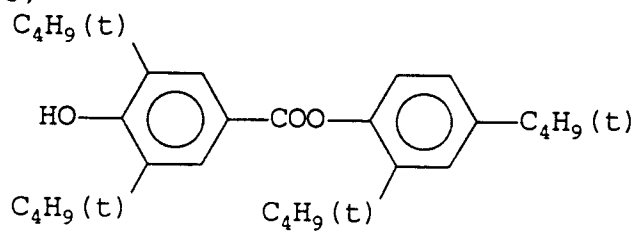
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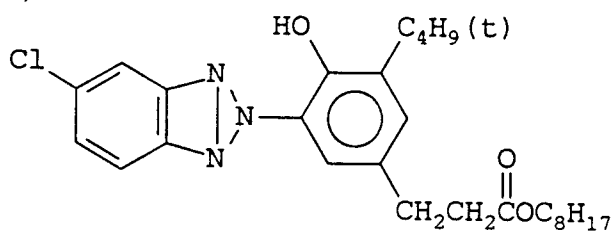
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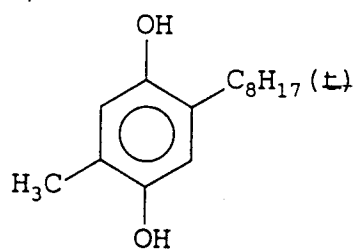
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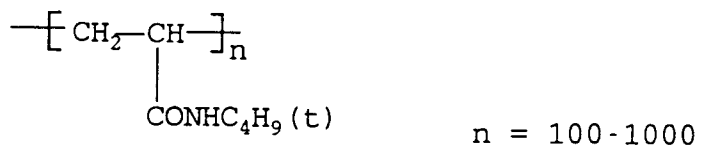
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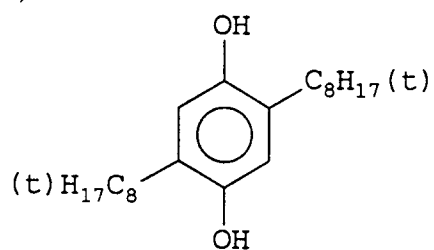
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(Cpd - 6)



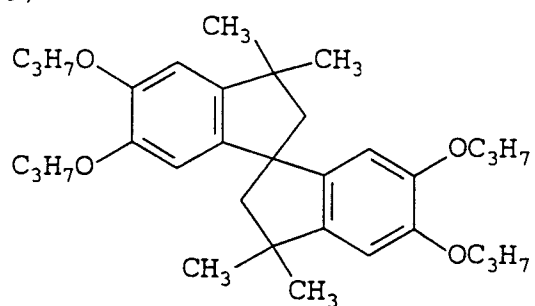
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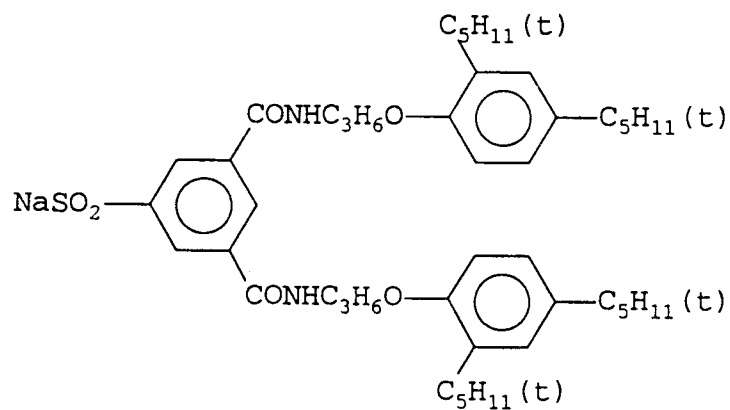
(Cpd-8)

Polyethyl acrylate (MW = 10,000 - 100,000)

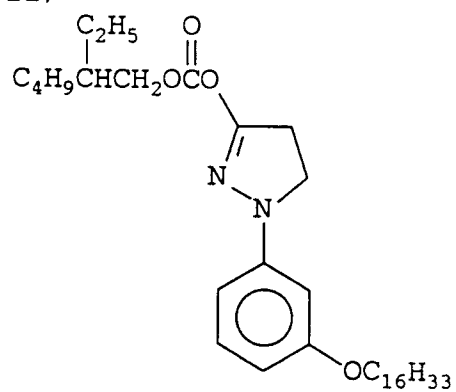
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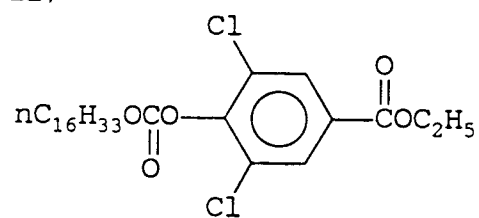
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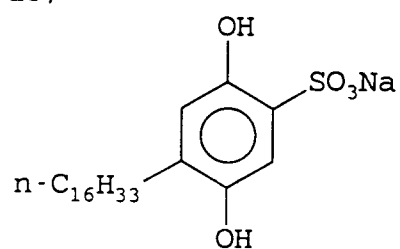
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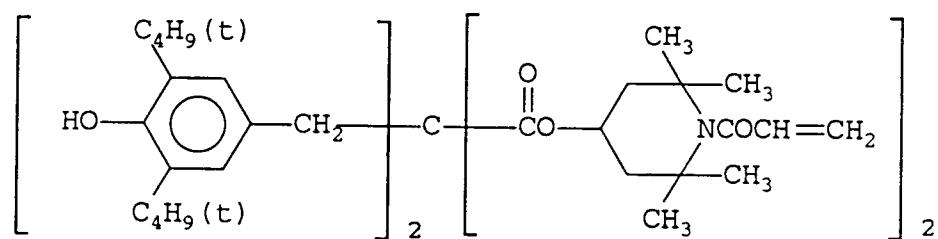
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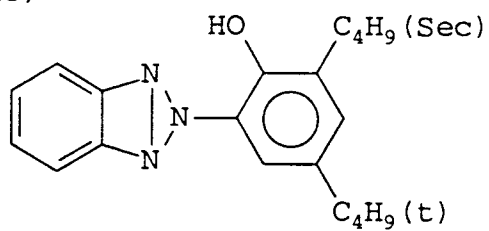
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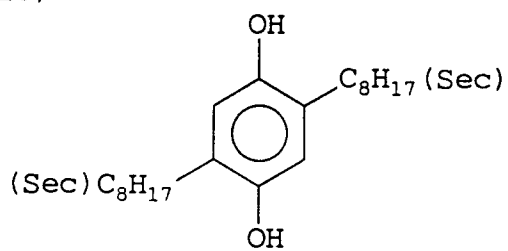
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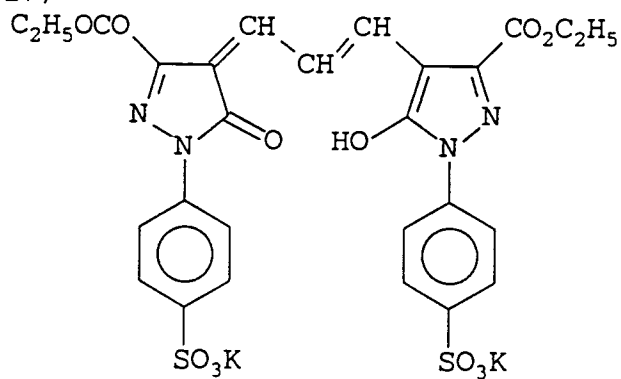
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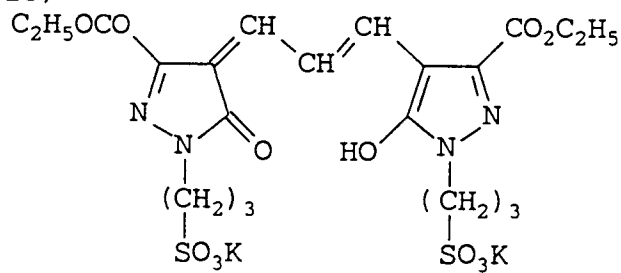
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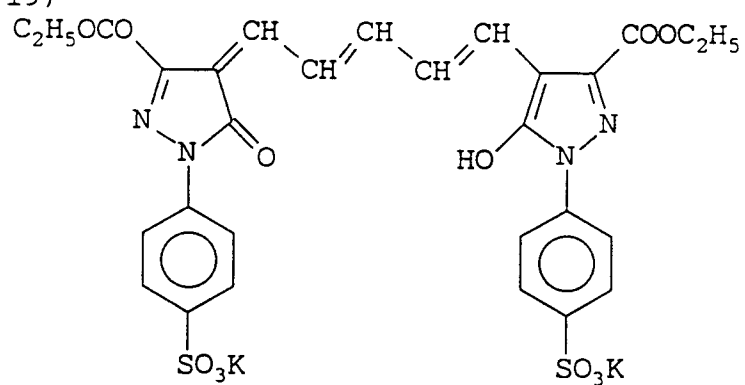
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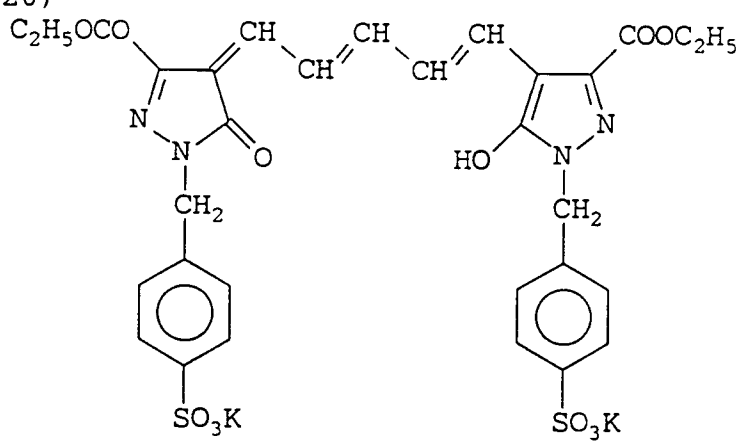
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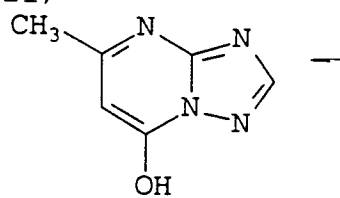
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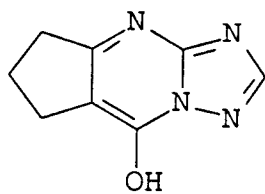
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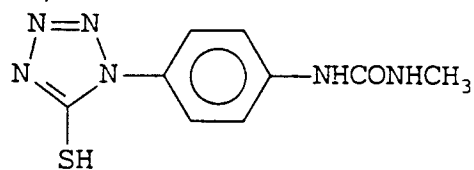
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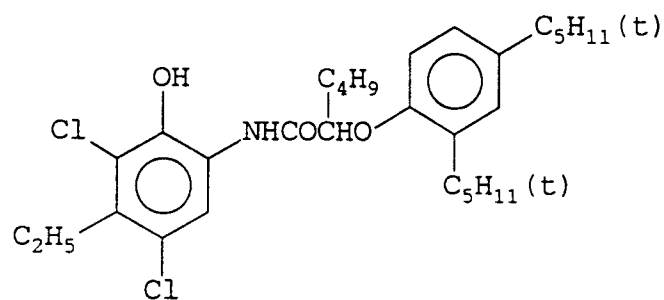
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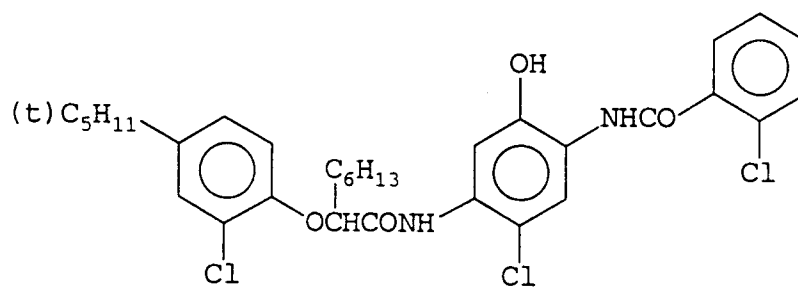
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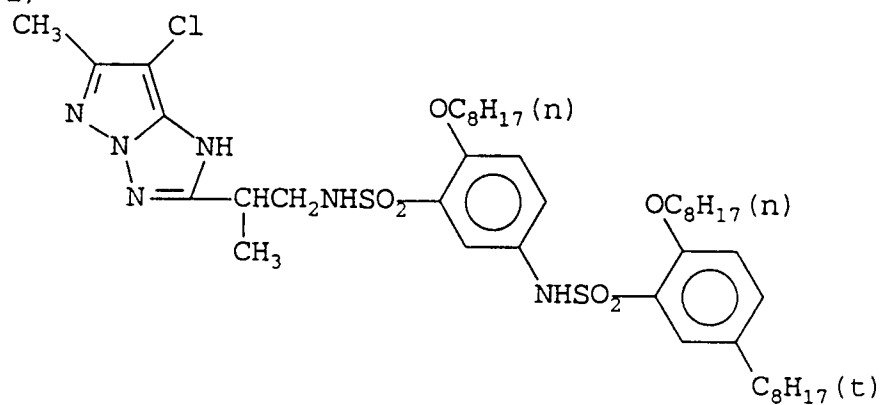
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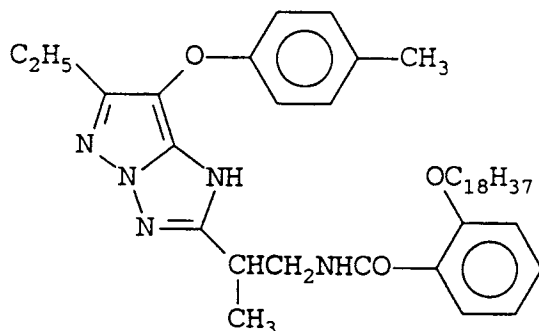
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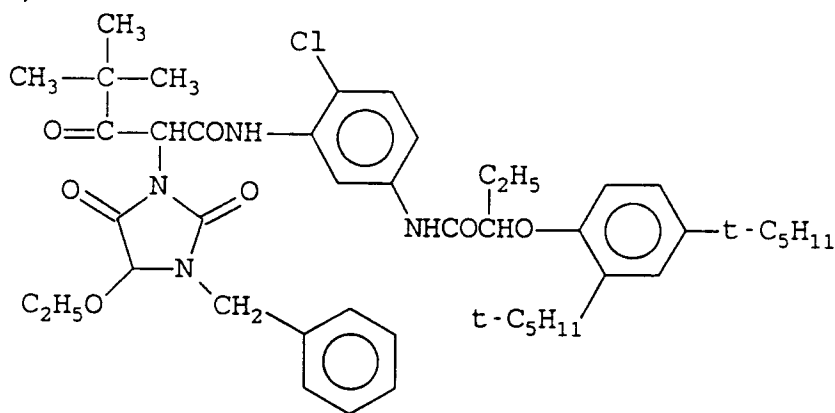
(ExM - 1)



(ExM-2)



(ExY-1)



- (Solv-1) Di(2-ethylhexyl) phthalate
 (Solv-2) Trinonyl phosphate
 (Solv-3) Di(3-methylhexyl) phthalate
 (Solv-4) Tricresyl phosphate
 (Solv-5) Dibutyl phthalate
 (Solv-6) Trioctyl phosphate
 (H-1) CH₂ = CH-SO₂-CH₂-CONH-CH₂-CH₂-CONH-CH₂-SO₂-CH = CH₂
 (H-2) Sodium salt of 4,6-dichloro-2-hydroxy-1,3,5-triazine

The obtained sample was numbered as No. 101. The procedures of preparation of No. 101 were repeated except that the amounts of the yellow couplers in the ninth and tenth layers, the amounts of the color stain inhibitors (Cpd-7, Cpd-16) in the eleventh layer and the kind and the amount of the emulsion in the twelfth layer were varied to those set forth in Table 4, and between the eleventh layer and the twelfth layer was further provided the eleventh-middle, to prepare samples of No. 102 to No. 109 as shown in Table 4.

Table 4

Sample No.	Yellow Coupler in 9th layer and 10th layer	Amount of Color Stain Inhibitor in 11th layer (Cpd-7, Cpd-16)
101 (Comp.Ex)	ExY-1	0.06 g/m ²
102 (Comp.Ex)	Y-2	0.06 g/m ²
103 (Example)	Y-2	0.06 g/m ²
104 (Example)	Y-2	0.06 g/m ²
105 (Comp.Ex)	Y-2	0.0 g/m ²
106 (Example)	Y-2	0.06 g/m ²
107 (Example)	Y-2	0.06 g/m ²
108 (Example)	Y-2	0.06 g/m ²
109 (Comp.Ex)	Y-2	0.06 g/m ²

Table 4 (Continued)

Sample No.	11th-b layer (newly provided)		12th layer	
	Emulsion	Amount	Emulsion	Amount
101 (Comp.Ex)	not provided		EM-3	20 mg/m ₂
102 (Comp.Ex)	not provided		EM-3	20 mg/m ₂
103 (Example)	EM-3	20 mg/m ²	—	—
104 (Example)	EM-3	10 mg/m ²	—	—
105 (Comp.Ex)	EM-3	20 mg/m ²	—	—
106 (Example)	EM-4	20 mg/m ²	—	—
107 (Example)	EM-2	20 mg/m ²	—	—
108 (Example)	EM-1	20 mg/m ²	—	—
109 (Comp.Ex)	—	—	—	—

Note: The amount of the emulsion in the 11th-b layer and the amount of the emulsion in the 12th layer are shown in terms of silver halide. The 11th-b layer newly provided in the samples No. 103 to No. 109 contained gelatin in addition to the emulsion, and the thickness of the layer was 0.3 μ m.

The obtained samples were subjected to practical exposure or sensitometry exposure using a light source of 3,200 °K, and then subjected to the following reversal process, to obtain images. Followings are processing stages and processing liquids used in the reversal process.

Process

Black and white development	38 °C	75 seconds
Washing	38 °C	90 seconds
Reversal exposure	100 lux or more	60 seconds or more
Color development	38 °C	135 seconds
Washing	38 °C	45 seconds
Bleach-fix	38 °C	120 seconds
Washing	38 °C	135 seconds
Drying		

Composition of processing liquid

(Black and white developer)		
	Pentasodium nitrilo-N,N,N-trimethylenephosphonate	0.6 g
	Pentasodium diethylenetriaminepentaacetate	4.0 g
5	Potassium sulfite	30.0 g
	Potassium thiocyanate	1.2 g
	Potassium carbonate	35.0 g
	Potassium hydroquinonemonosulfonate	25.0 g
10	Diethylene glycol	15.0 ml
	1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone	2.0 g
	Potassium chloride	0.5 g
	Potassium iodide	5.0 mg
	Water to make up to 1 l	(pH: 9.70)

(Color developer)		
	Benzyl alcohol	15.0 ml
20	Diethylene glycol	12.0 ml
	3,6-Dithia-1,8-octanediol	0.2 g
	Pentasodium nitrilo-N,N,N-trimethylenephosphonate	0.5 g
	Pentasodium diethylenetriaminepentaacetate	2.0 g
	Sodium sulfite	2.0 g
25	Potassium carbonate	25.0 g
	Hydroxylaminesulfate	3.0 g
	N-ethyl-N-(β -methanesulfonamideethyl)-3-methyl-4-aminoanilinesulfate	5.0 g
	Potassium bromide	0.5 g
	Potassium iodide	1.0 mg
30	Water to make up to 1 l	(pH: 10.40)

(Bleach-fix bath)		
35	2-Mercapto-1,3,4-triazole	1.0 g
	Disodium ethylenediaminetetraacetate dihydrate	5.0 g
	Ammonium ethylenediaminetetraacetate Fe(III) monohydrate	80.0 g
	Sodium sulfite	15.0 g
	Ammonium thiosulfate (700 g/l liquid)	160.0 ml
40	Glacial acetic acid	5.0 ml
	Water to make up to 1 l	(pH: 6.50)

The results are set forth in Table 5.

Table 5

Sample No.	Reproduction of lemon yellow		Streak	Yellow stain Dmin(B)
	M density	Organo-leptic evaluation		
101 (Comp.Ex)	0.45	BB	BB	0.11
102 (Comp.Ex)	0.42	AA	CC	0.11
103 (Example)	0.42	AA	AA	0.11
104 (Example)	0.42	AA	AA	0.11
105 (Comp.Ex)	0.42	AA	AA	0.14
106 (Example)	0.42	AA	AA	0.11
107 (Example)	0.42	AA	AA	0.11
108 (Example)	0.42	AA	AA	0.11
109 (Comp.Ex)	0.42	AA	AA	0.11

Table 5 (Continued)

Sample No.	Inclusion of bleach accelerator $\Delta D_{0.6}(B)$	Agitation dependence $\Delta S_{0.6}(R)$
101 (Comp.Ex)	-0.01	-0.02
102 (Comp.Ex)	-0.02	-0.02
103 (Example)	-0.01	-0.02
104 (Example)	-0.04	-0.04
105 (Comp.Ex)	-0.01	-0.02
106 (Example)	-0.01	-0.02
107 (Example)	-0.01	-0.03
108 (Example)	-0.01	-0.04
109 (Comp.Ex)	-0.08	-0.10

In Table 5, reproduction of lemon yellow was carried out as follows. An object containing lemon yellow was photographed using a commercially available color reversal film, and the image of the object was printed onto each of the samples. Thus treated each sample was processed using a reversal paper sheet

processor (HOPE 2010V), to obtain a color image. With respect to all of the samples No. 101 to No. 109, the lemon yellow-developed portions were measured on yellow (Y) density and magenta (M) density on the same portions. As a result, all of the samples had Y densities of the lemon yellow-developed portions within a range of 1.20 ± 0.04 . The M density in this case was expressed as a degree of magenta stain in the lemon yellow-developed portion.

Separately from the above-mentioned density measurement, an object containing lemon yellow was photographed and the resulting image was subjected to organoleptic evaluation. The results were classified into AA (superior), BB and CC (inferior).

Evaluation on occurrence of streaks was conducted as follows. Each sample was subjected to running-process for 1 month using the above-mentioned HOPE 2010V processor, and then the exposed sample was processed until the sample became grey having a density of 0.7. The occurrence of streaks was evaluated by means of visual judgement. The results are classified as follows.

AA: Any streak was not observed.

BB: Some streaks were observed.

CC: Many streaks were observed.

Each value of "yellow stain" in Table 5 is a value of minimum density ($D_{min}(B)$) obtained when the sample was measured using a blue filter after the sensitometry exposure and the reversal process. The value of minimum density preferably is not more than 0.11. The value of minimum density exceeding 0.13 is undesirable from the viewpoint of practical use.

Each value of "inclusion of bleaching agent" in Table 5 is a change value ($\Delta D_{0.6}(B)$) of a sensitivity of the blue sensitive layer in the case where the development is inhibited when 1 mg/l of 2-mercapto-1,3,5-triazole (bleach accelerator) is included by accident into the black and white developer. This value preferably is a value closer to 0.

The terms "agitation dependence" in Table 5 mean photographic stability to agitation of a processing liquid in the black and white development. Each value thereof is a change value ($\Delta S_{0.6}(R)$) of a sensitivity of the red sensitive layer in the case where 2 l of the black and white developing bath is agitated using a nitrogen gas and the change of the sensitivity is completely terminated. This value is also preferably a value closer to 0.

It has been confirmed that the samples of No. 103, No. 104, and No. 106 to No. 108 according to the present invention are satisfactory in all of the above properties. Also confirmed is that the samples of No. 103 and No. 106 are most excellent among those samples.

EXAMPLE 2

Samples of No. 201 to 206 were prepared in the same manner as in preparation of the sample of No. 103 in Example 1, except that the block copolymer (P-2) used in the twelfth layer was changed according to the Table 6. The samples was treated in the same manner as in Example 1 except that the samples were not imagewise exposed to light.

Each of the dried samples was preserved at 25 °C and the relative humidity of 50 % for one week, and placed at 25 °C and the relative humidity of 82 % for 5 minutes. The surface luster of each of the samples were then observed. The results are set forth in Table 6.

Table 6

Sample No.	Polymer Contained in 12th Layer		Surface Luster
	Kind	Amount (mg/m ²)	
201	(P-2)	20	A
202	(P-2)	50	A
203	(P-2)	100	A
204	(P-2)	5	B
205	(P-1)	50	A
206	Polyvinyl Alcohol	50	C
	(Molecular weight: 20,000)		

As is evident from the results shown in Table 6, the block copolymer has a function of showing an

excellent surface luster.

EXAMPLE 3

5 The samples No. 103, No. 105 and 109 used in Example were subjected to sensitometry exposure using a light source of 3,200 °K, and then subjected to the following reversal process, to obtain images. Followings are processing stages and processing liquids used in the reversal process.

Process (1)

10 The same as Example 1

Process (2)

15	Black and white development	38 °C	60 seconds
	First Washing	33 °C	60 seconds
	Color development	38 °C	60 seconds
20	Bleaching	38 °C	60 seconds
	Bleach-fix	38 °C	60 seconds
	Second Washing	33 °C	60 seconds
25	Total processing time (except drying process)		
			6 minutes 30 seconds

Composition of processing liquid

30

(Black and white developer)		
	Mother liquid	Replenisher
35	Pentasodium nitrilo-N,N,N-trimethylenephosphonate	1.0 g
	Pentasodium diethylenetriaminepentaacetate	3.0 g
	Potassium sulfite	30.0 g
	Potassium thiocyanate	1.2 g
40	Potassium carbonate	35.0 g
	Potassium hydroquinonemonosulfonate	25.0 g
	1-Phenyl-3-pyrazolidone	2.0 g
	Potassium bromide	0.5 g
	Potassium iodide	5.0 mg
45	Water	to make up to 1 l
	pH	9.60
		9.70
(pH was adjusted by hydrochloric acid or potassium hydroxide)		

50

55

(First washing)	Mother liquid	Replenisher
Ethylenediamine tetramethylenephosphonic acid		
	2.0 g	Same as
Disodium phosphate	5.0 g	mother
		liquid
Water	to make up to 1 l	
pH	7.00	
(pH was adjusted by hydrochloric acid or sodium hydroxide)		

(Color developer)		
	Mother liquid	Replenisher
Benzyl alcohol	15.0 ml	18.0 ml
Diethylene glycol	12.0 ml	14.0 ml
3,6-Dithia-1,8-octane	2.00 g	2.50 g
Tetrasodium nitrilo-N,N,N-trimethylenephosphonate	0.5 g	0.5 g
Pentasodium diethylenetriaminepentaacetate	2.0 g	2.0 g
Sodium sulfite	2.0 g	2.5 g
Hydroxylaminesulfate	3.0 g	3.6 g
N-ethyl-N-(β -methanesulfonamideethyl)-3-methyl-4-aminoanilinesulfate	6.0 g	9.0 g
Ethylenediamine	10.0 ml	12.0 ml
Diaminostilbene brightening agent	1.0 g	1.2 g
Potassium bromide	0.5 g	
Potassium iodide	1.0 mg	
Water	to make up to 1 l	
pH	10.60	11.00

(pH was adjusted by hydrochloric acid or potassium hydroxide)

(Bleaching bath)		
	Mother liquid	Replenisher
Disodium ethylenediaminetetraacetate	10.0 g	Same
Ammonium ethylenediaminetetraacetate Fe(III) dihydrate	120 g	as
Ammonium bromide	100 g	mother
Ammonium nitrate	10 g	liquid
Water	to make up to 1 l (pH: 6.30)	
(pH was adjusted by acetic acid or ammonium hydroxide)		

(Bleach-fix bath)		
	Mother liquid	Replenisher
Disodium ethylenediaminetetraacetate dihydrate	5.0 g	Same as mother liquid
Ammonium ethylenediaminetetraacetate Fe(III) monohydrate	80.0 g	
Sodium sulfite	15.0 g	
Ammonium thiosulfate (700 g/l liquid)	160.0 ml	
2-Mercapto-1,3,4-triazole	0.5 g	
Water	to make up to 1 l (pH: 6.5)	
(pH was adjusted by acetic acid or ammonium hydroxide)		

(Second washing including mother liquid and replenisher)

Water was deionized through a mixed-bed system column charged with strongly acidic cation exchange resin of H type (Amberlite IR-120B available from Rohm & Haas Co.) and anion exchange resin of OH type (Amberlite IR-400 available from Rohm & Haas Co.) to contain calcium and magnesium ions in an amount of not more than 3 mg/l. To the resulting deionized water, 20 mg/l of sodium dichloroisocyanurate and 1.5 g/l of sodium sulfate were added. The pH value of the obtained water was within a range of 6.5 - 7.5.

Process (3)

Process	Temperature	Time	Replenisher (Amount at morning)
Black and white	38 °C	40 seconds	200 ml
First Washing	20-30 °C	40 seconds	15 l or more
Color development (1)	38 °C	40 seconds	100 ml
Color development (2)	38 °C	40 seconds	100 ml
Bleaching	38 °C	40 seconds	100 ml
Bleach-fix	38 °C	40 seconds	100 ml
Second Washing	20-30 °C	40 seconds	15 l or more
Total processing time (except drying process)			4 minutes 30 seconds

The volume of each tank was 1 l.

Composition of porocessing liquid

(Black and white developer)		
	Mother liquid	Replenisher
Pentasodium nitrilo-N,N,N-trimethylenephosphonate	1.0 g	1.0 g
Pentasodium diethylenetriaminepentaacetate	3.0 g	3.0 g
Potassium sulfite	30.0 g	30.0 g
Potassium thiocyanate	1.2 g	1.2 g
Potassium carbonate	35.0 g	35.0 g
Potassium hydroquinonemonosulfonate	25.0 g	25.0 g
1-Phenyl-3-pyrazolidone	2.0 g	2.0 g
Potassium chloride	0.5 g	
Potassium iodide	5.0 mg	
Water	to make up to 1 l	
pH	9.60	9.70
(pH was adjusted by hydrochloric acid or potassium hydroxide)		

(First washing)	Mother liquid	Replenisher
Ethylenediamine tetramethylenephosphonic acid		
	2.0 g	Same as
Disodium phosphate	5.0 g	mother
		liquid
Water	to make up to 1 l	
pH	7.00	
(pH was adjusted by hydrochloric acid or potassium hydroxide)		

(Color developer)		
	Mother liquid	Replenisher
Benzyl alcohol	15.0 ml	18.0 ml
Diethylene glycol	12.0 ml	14.0 ml
3,6-Dithia-1,8-octane	2.00 g	2.50 g
Tetrasodium nitrilo-N,N,N-trimethylenephosphonate	0.5 g	0.5 g
Pentasodium diethylenetriaminepentaacetate	2.0 g	2.0 g
Sodium sulfite	2.0 g	2.5 g
Hydroxylaminesulfate	3.0 g	3.6 g
N-ethyl-N-(β -methanesulfonamideethyl)-3-methyl-4-aminoanilinesulfate	6.0 g	9.0 g
Ethylenediamine	10.0 ml	12.0 ml
Diaminostilbene brightening agent	1.0 g	1.2 g
Potassium bromide	0.5 g	
Potassium iodide	1.0 mg	
pH	10.60	11.00
(pH was adjusted by hydrochloric acid or potassium hydroxide)		

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(Bleaching bath)		
	Mother liquid	Replenisher
Disodium ethylenediaminetetraacetate	10.0 g	Same
Ammonium ethylenediaminetetraacetate Fe(III) dihydrate	120 g	as
Ammonium bromide	100 g	mother
Ammonium sulfate	10 g	liquid
Water	to make up to 1 l (pH: 6.30)	
(pH was adjusted by acetic acid or ammonium hydroxide)		

(Bleach-fix bath)		
	Mother liquid	Replenisher
Disodium ethylenediaminetetraacetate dihydrate	5.0 g 80.0 g 15.0 g	Same as mother liquid
Ammonium ethylenediaminetetraacetate Fe(III) monohydrate		
Sodium sulfite		
Ammonium thiosulfate (700 g/l liquid)	160.0 ml	to make up to 1 l (pH: 6.50) (pH was adjusted by acetic acid or ammonium hydroxide)
2-Mercapto-1,3,4-triazole	0.5 g	
Water		

(Second washing including mother liquid and replenisher)

Water was deionised through a mixed-bed system column charged with strongly acidic cation exchange resin of H type (Amberlite IR-120B available from Rohm & Haas Co.) and anion exchange resin of OH type (Amberlite IR-400 available from Rohm & Haas Co.) to contain calcium and magnesium ions in an amount of not more than 3 mg/l. To the resulting deionized water, 20 mg/l of sodium dichloroisocyanurate and 1.5 g/l of sodium sulfate were added. The pH value of the obtained water was within a range of 6.5 - 7.5.

The results are set forth in Table 7 and Table 8.

Table 7

Sample No.	Yellow Stain Dmin (B)		
	Process (1)	Process (2)	Process (3)
105	0.14	0.16	0.17
103	0.11	0.11	0.12

Table 8

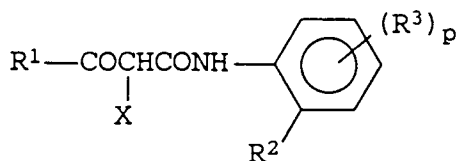
Sample No.	Inclusion of bleach accelerator $\Delta D_{0.6}(B)$		
	Process (1)	Process (2)	Process (3)
109	- 0.08	- 0.09	- 0.10
103	- 0.01	- 0.02	- 0.02

As is evident from the results shown in Tables 7 and 8, the effect of the present invention is remarkable when the time of the black and white development or the total time of the processes is shortened.

Claims

1. A silver halide color reversal image forming method comprises the steps of:
 - imagewise exposing to light a silver halide color photographic material which comprises a support, a silver halide emulsion layer containing a cyan coupler, a silver halide emulsion layer containing a magenta coupler and a silver halide emulsion layer containing a yellow coupler;
 - subjecting the material to a black and white development process;
 - subjecting the material to a reversal process;
 - subjecting the material to a color development process; and
 - subjecting the material to a desilvering process,
 wherein the black and white development process is completed for a time of not longer than 80 seconds after the photographic material is imagewise exposed to light; the yellow coupler is represented by the formula [I]; the layer containing the yellow coupler is the uppermost silver halide emulsion layer containing a coupler; the photographic material further comprises at least three protective layers provided on the layer containing the yellow coupler; the lower protective layer contains a scavenger of an oxidation product of a developing agent in an amount of not less than 0.1 mg/m²; the middle protective layer contains non-photosensitive silver halide grains in an amount of not less than 0.001 mg/m²; and the upper protective layer is a colloidal layer:

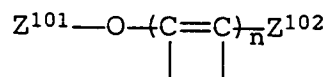
[I]



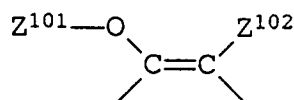
wherein R¹ is an aryl group or a tertiary alkyl group; R² is fluorine, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a dialkylamino group, an alkylthio group or an arylthio group; R³ is a substituent group of the benzene ring; X is hydrogen or a group capable of being eliminated by a coupling reaction with an oxidation product of an aromatic primary amine developing agent; p is an integer of 0 to 4; and when p is two or more, the groups represented by R³ may be different from each other.

2. The image forming method as claimed in claim 1, wherein the photographic material comprises a support, a silver halide emulsion layer containing a cyan coupler, a silver halide emulsion layer containing a magenta coupler, a silver halide emulsion layer containing a yellow coupler, the lower protective layer, the middle protective layer and the upper protective layer in the order
3. The image forming method as claimed in claim 1, wherein the black and white development process is completed for a time of not longer than 60 seconds after the photographic material is imagewise exposed to light.
4. The image forming method as claimed in claim 3, wherein the black and white development process is completed for a time of not longer than 40 seconds after the photographic material is imagewise exposed to light.
5. The image forming method as claimed in claim 1, wherein the total time of the black and white development, reversal, color development and desilvering processes other than the time required for drying the photographic material is not longer than 6 minutes and 30 seconds.
6. The image forming method as claimed in claim 5, wherein the total time of the black and white development, reversal, color development and desilvering processes other than the time required for drying the photographic material is not longer than 4 minutes and 40 seconds.
7. The image forming method as claimed in claim 1, wherein the reversal process is conducted by uniformly exposing to light the photographic material.
8. The image forming method as claimed in claim 1, wherein the scavenger contained the lower protective layer has a partial structure represented by the formula [XI]:

[XI]



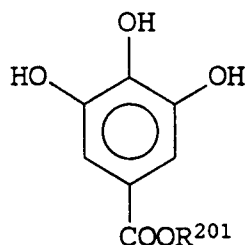
wherein n is an integer of 1 to 4; each of Z¹⁰¹ and Z¹⁰² independently is -OH, -NH₂, -NHR¹⁰¹, -NR¹⁰²R¹⁰³ or -NHSO₂R¹⁰⁴; R¹⁰¹ is an alkyl group; each of R¹⁰² and R¹⁰³ is an alkyl group, or a combination of R¹⁰² and R¹⁰³ forms a nitrogen-containing heterocyclic ring; R¹⁰⁴ is an alkyl group or an aryl group; and when n is 1,



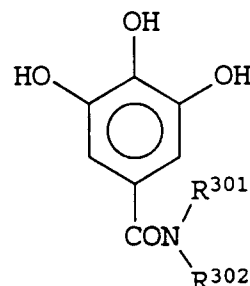
may be a partial structure of a benzene ring or a naphthalene ring.

9. The image forming method as claimed in claim 1, wherein the scavenger contained the lower protective layer represented by the formula [XII] or [XIII]:

[XII]



[XIII]



wherein R²⁰¹ is an alkyl group having 1 - 18 carbon atoms; each of R³⁰¹ and R³⁰² independently is hydrogen, an aliphatic group, an aromatic group or a heterocyclic group, or a combination of R³⁰¹ and R³⁰² may form a ring; and at least one of R³⁰¹ and R³⁰² is a group other than hydrogen.

10. The image forming method as claimed in claim 1, wherein the non-photosensitive silver halide grains contain silver chloride in an amount of not less than 70 % by mole.
11. The image forming method as claimed in claim 1, wherein the middle protective layer contains the non-photosensitive silver halide grains in an amount of 0.001 mg/m² to 0.5 mg/m².
12. The image forming method as claimed in claim 1, wherein the average grain size of the non-photosensitive silver halide grains is in the range of 0.02 μm to 0.5 μm.
13. The image forming method as claimed in claim 1, wherein the total thickness of the protective layers is not more than 6 μm.
14. The image forming method as claimed in claim 1, wherein the thickness of the middle protective layer is not more than 30 % of the total thickness of the protective layers.
15. The image forming method as claimed in claim 1, wherein the thickness of the lower protective layer is not less than 20 % of the total thickness of the protective layers.
16. The image forming method as claimed in claim 1, wherein at least one of the protective layers further contains a block copolymer of polyvinyl alcohol and a polymer having an ionic group.
17. The image forming method as claimed in claim 1, wherein the upper protective layer further contains a block copolymer of polyvinyl alcohol and a polymer having an ionic group.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 10 1339

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-2 100 303 (EASTMAN KODAK CO.) * claims 1-5 * ---	1	G03C5/50 G03C1/76 G03C7/30
A	DE-A-1 925 391 (FUJI PHOTO FILM CO.) * page 5, line 4 - page 7, line 2 * ---	1	
A	US-A-4 960 685 (A. T. BOWNE) * column 1, line 46 - column 11, line 24 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 04 MAY 1992	Examiner Volker Markowski
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			