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(54) Dye-fixing element.

(57) A dye-fixing element of a photographic element to which a mobile dye formed or released by development is transferred and fixed, especially by heat-development, has substantially no backing layer for curling balance. The element contains a mordant, a dispersion of a polymer having a glass transition point of 25 ° C or lower and a nonionic stabilizer for the polymer dispersion in the dye-fixing layer. The element is free from unfavorable side effects such as precipitation of salts, surface blocking and contact color migration when stored as a stack of elements under a wide range of ambient humidity conditions.

FIELD OF THE INVENTION

The present invention relates to a dye-fixing element, which is used in a method of forming a color photographic image by imagewise development, especially heat-development, followed by transfer and fixation of the formed image on the element.

BACKGROUND OF THE INVENTION

Since photographic methods using silver halides are superior to other photographic methods such as electro-photographic methods and diazo-photographic methods with regard to photographic characteristics such as sensitivity and gradation adjustment, they have heretofore been utilized most widely in the technical field.

Recently, a simple and rapid method of obtaining a photographic image in a silver halide photographic material has been developed in which the conventional wet processing treatment with a developer or the like is exchanged for a dry processing treatment by heating or the like.

As means of obtaining color images by heat-development, various methods have been proposed. For example, a method of forming a color image by the coupling of an oxidation product of a developing agent and a coupler has been proposed in U.S. Patents 3,531,286 and 3,761,270, Belgian Patent 802,519, Research Disclosure, pages 31 and 32 (September, 1975), and U.S. Patent 4,021,240.

The above method has a drawback in that the color image that is formed is often turbid because an image of reduced silver and a color image are formed simultaneously in the exposed and heat-developed area of the material.

Various methods have been proposed to overcome this drawback. These methods include a method of image-wise forming or releasing a mobile (diffusive) dye by heating, followed by transferring the mobile dye to a dye-fixing element having a mordant with a solvent such as water; a method of transferring the mobile dye to a dye-fixing element with a high boiling point organic solvent; a method of transferring the mobile dye to a dye-fixing element with a hydrophilic heat solvent that is incorporated into the element; and a method of transferring the mobile dye, which is a heat-diffusive or sublimable dye, to a dye-receiving element such as a support. (Refer to U.S. Patents 4,463,079, 4,474,867, 4,478,927, 4,507,380, 4,500,626 and 4,483,914; and JP-A-58-149046, JP-A-58-149047, JP-A-59-152440, JP-A-59-154445, JP-A-59-165054, JP-A-59-180548, JP-A-59-168439, JP-A-59-174832, JP-A-59-174833, JP-A-59-174834 and JP-A-59-174835. (The term "JP-A" as used herein means an "unexamined published Japanese patent application".)

Where a hydrophilic binder is employed in the dye-fixing layer of the dye-fixing element that is used in such image forming methods, the element often curls towards the dye-fixing layer under low humidity conditions. Therefore, in general, a backing layer consisting essentially of a hydrophilic binder is provided on the back surface of the element so as to attain curling balance in the element.

The provision of such a backing layer, however, causes the following problems:

(1) Where the dye-fixing layer contains a base or a base precursor and/or other film improving agents, it is difficult to obtain a satisfactory curling balance between the backing layer and the dye-fixing layer across the whole humidity range in accordance with fluctuation of the ambient humidity. As one means of overcoming this problem, a layer that has the same composition as the dye-fixing layer may be provided on the back side of the backing layer. This method, however, significantly increases the material cost. Moreover, where a plurality of such dye-fixing elements each having a color image formed therein are stored in a stack (pile) under high humidity conditions, the formed color image would often re-transfer to the adjacent backing layer.

(2) Where the dye-fixing layer contains a compound capable of diffusing in a hydrophilic binder, such as a base or a base precursor, and where a plurality of such dye-fixing elements are stored in a stack (pile) under high humidity conditions, the base or base precursor would migrate to the adjacent backing layer so that the distribution of the base or base precursor in the dye-fixing layer would become uneven. As a result, the color density of the developed and transferred image to be formed on the element would be uneven.

(3) Provision of a backing layer increases coating costs.

Apart from the above, incorporation of a water-soluble plasticizer such as glycerin into the coated layer has often been used to lower the elasticity of the coated layer and thereby reduce the coloring unbalance of the element. However, the effect of using a water-soluble plasticizer is not sufficient. In general, where the element contains a base or base precursor, the use of a water-soluble plasticizer tends to cause precipitation of the base or base precursor. It also tends to cause an increase in the stickiness of the surface of the element, and it may cause re-transfer of the once-transferred image when transferred prints are stored in a stack (pile). (Such re-transfer is hereinafter referred to as "contact color migration").

In sum, the use of a backing layer causes various problems which have not been resolved in the art.

SUMMARY OF THE INVENTION

A first object of the present invention is to provide a dye-fixing element which hardly curls under any humidity condition, which does not require a backing layer containing a hydrophilic binder for curling balance adjustment, and which is free from the above-mentioned problems in conventional elements.

A second object of the present invention is to provide a dye-fixing element which hardly curls under any humidity condition and which is free from various problems relating to precipitation of salts (for example, salts of the base or base precursor), stickiness of the coated surface, and contact color migration during storage.

These and other objects are attained by the present invention in accordance with which there is provided a dye-fixing element having a dye-fixing layer to which is transferred and fixed a mobile dye that is formed or released by development, especially heat-development, of a photographic element comprising a light-sensitive silver halide, a hydrophilic binder and a dye providing compound capable of forming or releasing a mobile dye in correspondence or reverse correspondence with the amount of exposure, after or simultaneously with imagewise exposure of the photographic element, in the presence of a base and/or a base precursor; the dye-fixing element being characterized in that the element does not have a backing layer composed of 1 g/m^2 or more of a hydrophilic binder on the side opposite to the dye-fixing layer, and in that the dye-fixing layer contains a mordant and a dispersion of a polymer having a glass transition point of 25 ° C or lower, and in that the polymer dispersion is stabilized with a nonionic stabilizer.

There is also provided in accordance with the present invention a dye-fixing element having a dye-fixing layer to which is transferred and fixed a mobile dye that is formed or released by heat-development of a photographic element comprising a light-sensitive silver halide, a hydrophilic binder and a dye providing compound capable of forming or releasing a mobile dye in correspondence or reverse correspondence with the amount of exposure, after or simultaneously with imagewise exposure of the photographic element, in the presence of a base and/or a base precursor; the dye-fixing element being characterized in that the element does not have a backing layer composed of 1 g/m^2 or more of a hydrophilic binder on the side opposite to the dye-fixing layer, and in that the dye-fixing layer contains a part or all of a base and/or a base precursor, a mordant, a nonionic water-soluble polysaccharide and a dispersion of a polymer having a glass transition point of 25 ° C or lower.

DETAILED DESCRIPTION OF THE INVENTION

The dye-fixing element of the present invention is used as an image-receiving material in the method of obtaining a color photographic image in which a silver halide photographic material is developed to form or release a diffusive dye and the dye is transferred to the image-receiving material.

This image forming method may be divided into a so-called wet color diffusion transfer method where development is effected with a processing solution at about room temperature, and a so-called heat-development diffusion transfer method where development is effected under heat. The dye-fixing element of the present invention is suitably applicable to both methods.

Especially preferably, the dye-fixing element of the present invention is used in the heat-development diffusion transfer method, which will be explained in detail below. The following explanation also applies to the wet color diffusion transfer method, except the parts intrinsic to heat-development, such as organic silver salts and the heat-development system itself.

The polymer dispersion for use in the present invention includes not only a so-called latex prepared by emulsion polymerization but also a dispersion prepared by dissolving a polymer in an organic solvent followed by emulsifying and dispersing the resulting solution and optionally removing the solvent from the dispersion.

To simplify the heat-development method of forming an image, it is effective to incorporate a base or base precursor into the photographic element or the dye-fixing element. In order to transfer to and fix the formed dye in the dye-fixing element, it is also effective to incorporate a mordant, described below, into the dye-fixing layer of the dye-fixing element. The mordant also helps prevent the formed color images from becoming blurred under high humidity conditions.

If a polymer dispersion is incorporated into the coating liquid composition containing the above-mentioned base or base precursor, coagulation of the liquid composition would often occur. In general, since a polymer dispersion is frequently stabilized by imparting anionic charges to the surface of the polymer, the polymer would often coagulate in the dye-fixing layer coating liquid composition containing a large amount of salts and/or cationic compounds (e.g., the mordant).

The present inventor investigated a method of preparing a coating composition which does not coagulate and, as a result, has found that the problem could be solved by employment of a polymer dispersion stabilized with a nonionic stabilizer such as a nonionic surfactant or a nonionic protective colloid.

In order to prevent curling of the dye-fixing element, it is preferred to minimize the amount of the hydrophilic binder in the dye-fixing layer and/or the adjacent layer(s) thereto. If the amount of hydrophilic binder is minimized, however, salts tend to precipitate. Precipitation of salts may be retarded somewhat by the addition of a polymer dispersion to the layers, but the effect of this is not sufficient. As another means of preventing precipitation of salts, the method of the present inventor's own prior JP-A-62-47639 (addition of nonionic water-soluble polysaccharides, especially dextran and pullulan to the dye-fixing layer and/or the adjacent layer(s) thereto has been shown to be effective. In general, however, addition of such polysaccharides to the layer often hardens the coated layer so much that the curling balance of the element is made worse.

Surprisingly, the present inventor has found that incorporation into the dye-fixing layer of a dispersion of a polymer having a glass transition temperature of 25 ° C or lower is effective for preventing precipitation of any base or base precursor in the layer without causing curling of the layer.

The polymer for use in the polymer dispersion desirably has a glass transition temperature of 25 ° C or lower. The polymer may have a glass transition temperature higher than 25 ° C, provided that the polymer is used in combination with an oily plasticizer and the polymer/plasticizer combination has a glass transition temperature of 25 ° C or lower. In cases where a plasticizer is used, it may be added to the system in which the polymer is produced. In general, however, an emulsion of the plasticizer is added to a polymer dispersion and stirred for a certain period of time.

Examples of a polymer dispersion for use in the present invention include polymer latex produced by emulsion homopolymerization or emulsion copolymerization of monomer systems of vinyl acetates, ethylene-vinyl acetates, acrylic substances, vinylidene chlorides, vinyl chlorides, butadienes or butadiene derivatives, and a polymer dispersion produced by dissolving the above-mentioned polymers, polyesters or polyurethanes in an organic solvent followed by emulsifying and dispersing the solution. Dispersions of polymers of vinyl acetates, ethylene-vinyl acetates, acrylic substances and styrene-butadienes are especially preferred, in view of the light fastness, heat stability, and dispersion stability of the coating compositions, and in view of their curling preventing effects and salt precipitation preventing effects.

Examples of monomers that may be used to make the polyemrs for the polymer dispersion for use in the present invention include acrylates, methacrylates, crotonates, vinyl esters, maleic acid diesters, fumaric acid diesters, itaconic acid diesters, acrylamides, methacrylamides, vinyl ethers, styrenes, dicarboxylic acids, and glycols.

Specific examples of such monomers are given below. Acrylates include, for example, methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, acetoxyethyl acrylate, phenyl acrylate, 2-methoxy acrylate, 2-ethoxy acrylate, and 2-(2-methoxyethoxy)ethyl acrylate.

Methacrylates include, for example, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate, and 2-ethoxyethyl methacrylate.

Crotonates include, for example, butyl crotonate and hexyl crotonate.

Vinyl esters include, for example, vinyl acetate, vinyl propionate, vinyl butyrate, vinylmethoxy acetate, and vinyl benzoate.

Maleic acid diesters include, for example, diethyl maleate, dimethyl maleate, and dibutyl maleate.

Fumaric acid diesters include, for example, diethyl fumarate, dimethyl fumarate, and dibutyl fumarate.

Itaconic acid diesters include, for example, diethyl itaconate, dimethyl itaconate, and dibutyl itaconate.

Acrylamides include, for example, acrylamide, methylacrylamide, ethylacrylamide, propylacrylamide, n-butylacrylamide, tert-butylacrylamide, cyclohexylacrylamdie, 2-methoxyethylacrylamide, dimethylacrylamide, diethylacrylamide, and phenylacrylamide.

Methacrylamides include, for example, methylmethacrylamide, ethylmethacrylamide, n-butylmethacrylamide, tert-butylmethacrylamide, 2-methoxymethacrylamide, dimethylmethacrylamide, and diethylmethacrylamide.

Vinyl ethers include, for example, methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, methoxyethyl vinyl ether, and dimethylaminoethyl vinyl ether.

Styrenes include, for example, styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, isopropylstyrene, butylstyrene, chloromethylstyrene, methoxystyrene, butoxystyrene, acetoxystyrene, chlorostyrene, dichlorostyrene, bromostyrene, methyl vinylbenzoate, and 2-methylstyrene.

Dicarboxylic acids include, for example, terephthalic acid, isophthalic acid, succinic acid, sebacic acid, and adipic acid.

Glycols include, for example, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, neopentyl glycol, and bisphenol A-ethylene oxide adduct.

The polymers to be made from such monomers are preferably polymers of acrylates, copolymers of acrylates and methacrylates, copolymers of acrylates and acrylic acid or methacrylic acid, homopolymers or copolymers of vinyl acetate, styrene-butadiene copolymers, and polyurethanes.

Free radical polymerization of ethylenic unsaturated solid monomers is initiated by addition of free radicals formed by pyrolysis of a chemical initiator or by action of a reducing agent to an oxidative compound (redox initiator) or by physical action such as irradiation using ultraviolet rays or other high energy radiations of application of high frequency waves, to monomer molecules.

Typical chemical initiators usable for free radical polymerization include, for example, water-soluble compounds such as persulfates (e.g., ammonium or potassium persulfate), hydrogen peroxide and 4,4'-azobis(4-cyano-valerianic acid); and water-insoluble compounds such as azoisobutyronitrile, benzoyl peroxide, and chlorobenzoyl peroxide.

Ordinary redox initiators include hydrogen peroxide-iron(II) salts, potassium persulfate-potassium bisulfite, and cerium salts of alcohols.

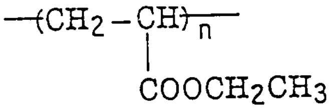
Initiators and their functions are described in F.A. Bovey, Emulsion Polymerization, (published by Interscience Publisher Inc., New York, 1955), pages 59 to 93.

Emulsifiers include surface-active anionic, nonionic, cationic or betaine compounds as well as high molecular weight protective colloids. Examples of these compounds and their functions are described in Belgische Chemische Industrie, Vol. 28, pages 16 to 20 (1963).

Especially preferred for use in the present invention is a latex of a polymer having a glass transition temperature of 25 ° C or lower.

Specific examples of polymer latexes for use in the present invention are mentioned below, which, however, are not limitative.

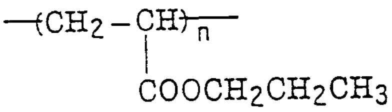
P－1



$$-\!\!\left(CH_2-\underset{COOCH_2CH_3}{\underset{|}{CH}}\right)_n\!\!-$$

Tg＝－21°C

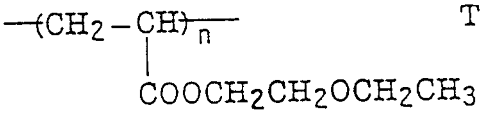
P－2



$$-\!\!\left(CH_2-\underset{COOCH_2CH_2CH_3}{\underset{|}{CH}}\right)_n\!\!-$$

Tg＝－36°C

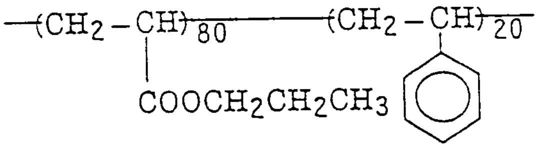
P－3



$$-\!\!\left(CH_2-\underset{COOCH_2CH_2OCH_2CH_3}{\underset{|}{CH}}\right)_n\!\!-$$

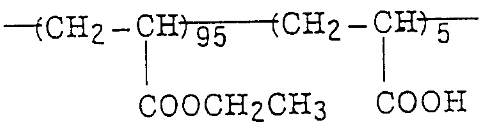
Tg＝－47°C

P－4



Tg＝－20°C

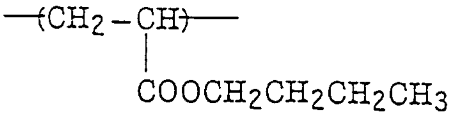
P－5



$$-\!\!\left(CH_2-\underset{COOCH_2CH_3}{\underset{|}{CH}}\right)_{95}\!\!\left(CH_2-\underset{COOH}{\underset{|}{CH}}\right)_5\!\!-$$

Tg＝－11°C

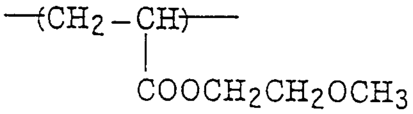
P-6



$$-\!\left(CH_2-\underset{\displaystyle COOCH_2CH_2CH_2CH_3}{\underset{|}{CH}}\right)\!-$$

Tg = −53°C

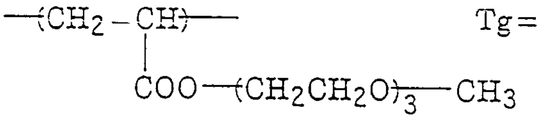
P-7



$$-\!\left(CH_2-\underset{\displaystyle COOCH_2CH_2OCH_3}{\underset{|}{CH}}\right)\!-$$

Tg = −45°C

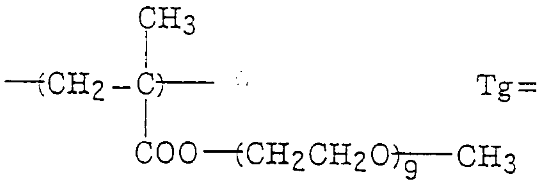
P-8



$$-\!\left(CH_2-\underset{\displaystyle COO-\!\left(CH_2CH_2O\right)_3\!-CH_3}{\underset{|}{CH}}\right)\!-$$

Tg = −36°C

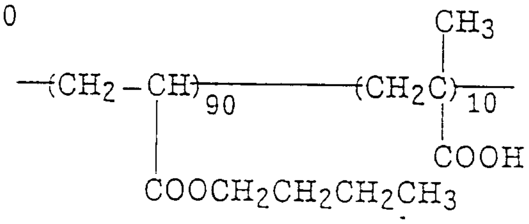
P-9



$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle COO-\!\left(CH_2CH_2O\right)_9\!-CH_3}{\underset{|}{C}}}}\right)\!-$$

Tg = −18°C

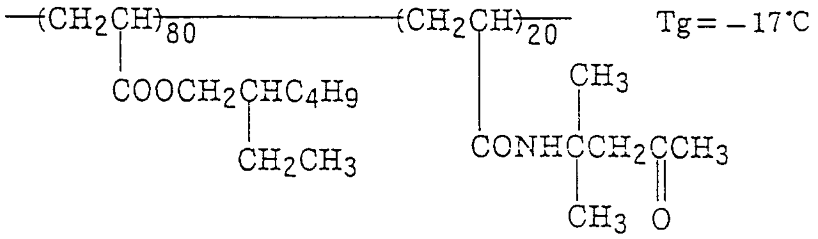
P-10



$$-\!\left(CH_2-\underset{\displaystyle COOCH_2CH_2CH_2CH_3}{\underset{|}{CH}}\right)_{90}\!-\!\left(CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle COOH}{\underset{|}{C}}}}\right)_{10}\!-$$

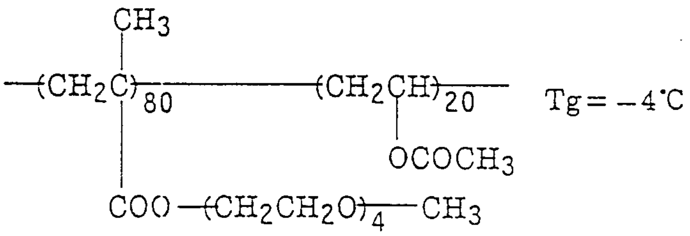
Tg = −26°C

P-11



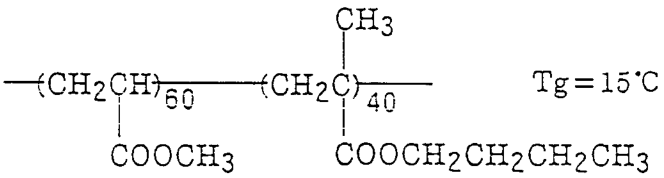
$$-(CH_2CH(COOCH_2CH(CH_2CH_3)C_4H_9))_{80}-(CH_2CH(CONHC(CH_3)_2CH_2C(=O)CH_3))_{20}- \quad Tg = -17°C$$

P-12



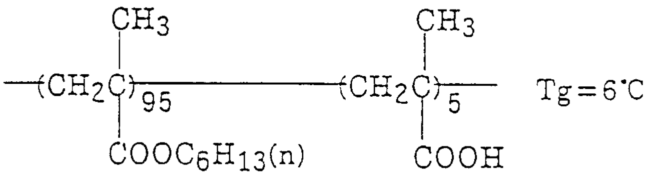
$$-(CH_2C(CH_3)(COO-(CH_2CH_2O)_4-CH_3))_{80}-(CH_2CH(OCOCH_3))_{20}- \quad Tg = -4°C$$

P-13



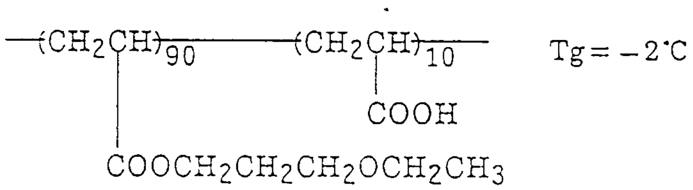
$$-(CH_2CH(COOCH_3))_{60}-(CH_2C(CH_3)(COOCH_2CH_2CH_2CH_3))_{40}- \quad Tg = 15°C$$

P-14



$$-(CH_2C(CH_3)(COOC_6H_{13}(n)))_{95}-(CH_2C(CH_3)(COOH))_{5}- \quad Tg = 6°C$$

P-15



$$-(CH_2CH(COOCH_2CH_2CH_2OCH_2CH_3))_{90}-(CH_2CH(COOH))_{10}- \quad Tg = -2°C$$

(Copolymerization ratio is represented by mol%.)

In addition, various other commercial latexes and emulsions may be used. These include Nipol LX811, 814, 820 to 823, 825, 826, 842, 851, 852, 854, 855, 857, 860, 874, 110, 112, 119, 139, 206, 209, 600, 415A, 426, 430, 432A, 433, 435, 436, 438C, 472, 473, 479, 511, 513, 517, 518, 531 and 407F (all products of Nippon Zeon Co., Ltd.); various latexes and emulsions of vinyl acetates, vinyl acetate/acrylic substances, acrylates, vinyl acetate/VeoVa, styrene/acrylic substances and ethylene/vinyl acetates, as sold commercially under the trade name Polysol by Showa Highpolymer Co.; and VONDIC 1040, 1050, 1310F, 1320NS, 1340, 1510, 1610NS, 1612NS, 1640, 1660, 1670(N), 1930N and 1980 (all products of Dai-Nippon Ink and Chemicals Inc.).

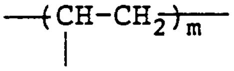
The amount of the polymer latex used in the dye-fixing layer is defined by the ratio of the total volume of the polymer in the latex added to the layer to the total volume of the hydrophilic binder in the same layer; and preferably, it is from 5 to 300 % by volume, more preferably from 10 to 200 % by volume. If it is less than 5 % by volume, the cracking preventing effect would be small. If, on the other hand, it is more than 300 % by volume, the film strength would be weak and the gloss of the surface would lower. Specifically, the amount of the polymer latex to be added is preferably from 0.5 g/m^2 to 10 g/m^2, and more preferably from 1 g/m^2 to 5 g/m^2, as the weight of the polymer in the latex.

The effect of the polymer latex used in the present invention is especially remarkable when it is combined with a polymer mordant having a high glass transition temperature, especially one having a glass transition temperature of 25 ° C or higher.

The nonionic surfactants which are used as a stabilizer for the polymer dispersion preferably contain a $-(CH_2CH_2O)_n-$ group, a $-(CH(CH_3)CH_2O)_n-$ group, a glycerol group or a saccharose group as a water-soluble component and an alkyl group or an aryl group as a hydrophobic component. n is an integer of 1 or more, preferably 5 or more. Ethylene oxide type nonionic surfactants where n is from 10 to 100 are especially preferred, as they display a large stabilizing effect.

Specific examples of nonionic surfactants usable in the present invention are described below.

W-1: $RCOO(CH_2CH_2O)_nH$
where
R = C_3-C_{22} alkyl, or



$-(\underset{|}{CH}-CH_2)_m-$;

n = 5 to 100;
m ≧ 10.

W-2: $R_1COO(CH_2CH_2O)_n$-$OCOR_2$
where
R_1, R_2 = C_3-C_{22} alkyl;
n = 5 to 100.

W-3: $RO(CH_2CH_2O)_nH$
where
R = C_3-C_{22} alkyl, cholesterin;
n = 3 to 100.

W-4: $(ROOCCH_2)_2(ROOC)CO(CH_2CH_2O)_nH$
where
R = C_3-C_{22} alkyl;
n = 3 to 100.

W-5: $(ROOCCH_2)(ROOC)CHO(CH_2CH_2O)_nH$
where
R = C_3-C_{22} alkyl;
n = 3 to 100.

W-6: $RCH[COO(CH_2CH_2O)_nH]_2$
where
R = C_3-C_{22} alkyl;
n = 3 to 100.

W-7: $(R_1)(R_2)C_6H_3O(CH_2CH_2O)_nH$
where
R_1, R_2 = H, or C_1-C_{18} alkyl;
n = 3 to 100.

W-8: R-$N[(CH_2CH_2O)_pH][(CH_2CH_2O)_qH]$
where
R = C_3-C_{22} alkyl, phenyl, or naphthyl;
p, q = 3 to 100.

W-9: $RCON[(CH_2CH_2O)_pH][(CH_2CH_2O)_qH]$
where
R = C_3-C_{22} alkyl;
p, q = 3 to 100.

W-10: Sorbitan esters

e.g., Atlas "Span" 20, 80, 60, 40, 62, 65, 85 (all products of Kao Corporation)

W-11: Polyoxyethylene-sorbitan esters

e.g., polyoxyethylene-sorbitan monooleates (n = 5 to 50), Atlas "Tween" 65, 85 (both products of Kao Corporation)

W-12: Polyglycerins

e.g., $C_{12}H_{23}COO[CH_2CH(OH)CH_2O]_nH$ (n = 4).

Examples of nonionic protective colloids which may be used as a dispersion stabilizing agent for the polymer dispersion include polyvinyl alcohol, hydroxyethyl cellulose, methyl cellulose, polyamides, and polysaccharides such as dextran and pullulan. Polyvinyl alcohol, hydroxyethyl cellulose and methyl cellulose are especially preferred.

The dye-fixing element of the present invention is lapped over a photographic element at least for transfer of a diffusive dye to the former element from the latter element. Precisely, the dye-fixing element is to be kept in contact with the photographic element in such a way that the dye-fixing layer of the former element faces to the light-sensitive layer of the latter element, at least for transfer of a diffusive dye to the former from the later.

The dye-fixing element of the present invention may be either in a separate form where a dye-fixing element and a photographic element are separately coated on different supports or in a combined form where the two elements are coated on the same support. Regarding the relationship between the photographic element and the dye-fixing element, the relationship to the support, and the relationship to the dye-reflecting layer in the case of the present invention, the disclosure of column 57 of U.S. Patent 4,500,626 may be referred to. Preferably, the dye-fixing element of the present invention is in the separate form where it is coated on an independent (different) support separate from the photographic element.

The dye-fixing element of the present invention has a dye-fixing layer on a support, and if desired, it may have other auxiliary layers such as a protective layer, a peeling layer, a curling preventing layer or a subbing layer. Provision of a protective layer in the element is especially effective. One or more of these layers may contain a hydrophilic heat solvent, a plasticizer, an anti-fading agent, UV absorbent, a lubricant, a mat agent or an antioxidant.

In view of the objects of the present invention, the dye-fixing element of the present invention preferably does not have a backing layer containing a hydrophilic binder. However, even if a backing layer is coated on the element for the purpose of improving the antistatic property and the paper-feeding property (for easy conveyance of papers including the element), this would not cause problems provided that the amount of the hydrophilic binder coated in the backing layer is less than 1 g/m^2, preferably 0.5 g/m^2 or less, especially preferably 0.2 g/m^2 or less. If the amount of the hydrophilic binder coated in the backing layer is 1 g/m^2 or more, water-soluble low molecular weight compounds in the dye-fixing layer, such as bases or base precursors, would migrate to the adjacent backing layer, especially when a plurality of such dye-fixing elements are stored in a stack (pile) under high humidity conditions. As a result, because of the unevenness of the coated compound, any image formed on the element would be uneven also.

It is preferred that the dye-fixing element of the present invention contains a polymer mordant capable of fixing a mobile dye released by development.

The expression "polymer mordant" as used herein includes a polymer having tertiary amino groups and a polymer having nitrogen-containing heterocyclic moieties, as well as a polymer containing quaternary amino groups derived from them. These polymers are preferably combined with some other hydrophilic polymer (e.g., gelatin).

Above all, polymers having tertiary amino groups or heterocyclic moieties, especially polymers having imidazole groups, are preferred as a mordant, because the color image fixed with such a mordant has an excellent light fastness. In addition, these polymers have the advantage that dispersions of such polymers (e.g., latexes) do not tend to coagulate.

The polymer mordant, especially polymers having tertiary amino groups or tertiary imidazole groups, is preferably a water-soluble one, in view of the light fastness and the transferred density of the image fixed therewith and the easy producibility of the polymers.

Specific examples of polymers containing tertiary amine group-having vinyl monomer units are described in JP-A-60-60643 and 60-57836; and specific examples of polymers containing tertiary imidazole group-having vinyl monomer units are described in JP-A-60-118834, 60-122941, 62-244043 and 62-244036, and U.S. Patents 4,282,305, 4,115,124 and 3,148,061.

The molecular weight of the mordant is preferably from 1,000 to 1,000,000, especially preferably from 10,000 to 200,000.

The polymer mordant is incorporated into the dye-fixing layer of the dye-fixing element of the present invention, along with a hydrophilic colloid as a binder which will be described below.

The proportion of the polymer mordant to the hydrophilic colloid as well as the amount of the polymer mordant to be coated may be determined easily by anyone of ordinary skill in the art, in accordance with the amount of dye to be mordanted, the kind and composition of the polymer mordant used, and the image forming method in which the element is used. Suitably, the ratio of mordant/hydrophilic colloid may be from 20/80 to 80/20 (by weight); and the amount of the mordant to be coated may be from about 0.2 g/m^2 to about 15 g/m^2, preferably from 0.5 to 8 g/m^2.

The dye-fixing layer containing the polymer mordant may contain various surfactants to improve the coatability of the layer.

The dye-fixing element of the present invention contains a water-soluble base and/or base precursor, to enhance the simple and rapid processability of the element and to improve its storage stability.

Examples of bases usable in the present invention include inorganic bases of alkali metals or quaternary alkylammonium hydroxides, carbonates, bicarbonates, borates, secondary or tertiary phosphates and metaborates; and organic bases of aliphatic amines, aromatic amines, heterocyclic amines, amidines, cyclic amidines, guanidines and cyclic guanidines, as well as carbonates, bicarbonates, borates and secondary or tertiary phosphates of them.

Base precursors for use in the present invention include precursors of the above-mentioned organic bases. The expression "base precursor" as used herein means a substance capable of releasing a basic component by pyrolysis or electrolysis. For example, base precursors include salts of pyrolyzing organic acids, such as trichloroacetic acid, cyanoacetic acid, acetacetic acid or α-sulfonylacetic acid, and the above-mentioned organic bases; and salts with 2-carboxycarboxamides as described in U.S. Patent 4,088,496. In addition, the base precursors described in British Patent 998,945, U.S. Patent 3,220,846 and JP-A-50-22625 may also be used.

Compounds capable of releasing a base by electrolysis may also be used. For instance, electrolysis of various fatty acid salts is one example of using electrolytic oxidation. By the reaction, carbonates of alkali metals as well as those of organic bases such as guanidines or amidines may be obtained very efficiently. Examples of methods of using electrolytic reduction include formation of amines by reduction of nitro compounds or nitroso compounds; formation of amines by reduction of nitriles; and formation of p-aminophenols, p-phenylenediamines or hydrazines by reduction of nitro compounds, azo compounds or azoxy compounds. p-Aminophenols, p-phenylenediamines and hydrazines may be used not only as a base but also directly as a color image-forming substance. It is also possible to form alkali components by electrolysis of water in the presence of various inorganic salts.

In addition, it is also possible to utilize a method of forming a water-soluble base by reacting a compound, which may be complexed with a metal ion capable of forming a sparingly soluble metal salt compound (e.g., zinc oxide, basic zinc carbonate, calcium carbonate) and water, for example guanidine pyrophosphate or the like, and the sparingly soluble metal salt compound, as described in U.S. Patent 4,740,445. In accordance with this method, it is possible to conduct contact heat-treatment of a photographic element containing a dispersion of a sparingly soluble metal salt compound and a dye-fixing element containing a water-soluble salt capable of forming a complex with the metal ion of the metal salt compound, as a base precursor, in the presence of water to generate a base. This method is especially advantageous in view of the storage stability of the photographic element and the dye-fixing element.

The base and/or base precursor can be used either singly or in a combination of two or more of them.

The amount of base and/or base precursor to be used in the present invention is from 5×10^{-4} to 5×10^{-1} mol/m^2, preferably from 2.5×10^{-3} to 2.5×10^{-2} mol/m^2.

The photographic element to be used with the dye-fixing element of the present invention may be either a wet type that is processed at about room temperature under wet conditions or a heat-developing type processed under heat. In view of the effects of the present invention, the dye-fixing element of the present invention is preferably used with the heat-developing type photographic element. The photographic element which may be used with the dye-fixing element of the present invention basically contains a light-sensitive silver halide, a dye providing compound (which may be a reducing agent, as will be described below), and a binder on a support, and it may contain an organic metal salt oxidizing agent. These components are in most cases incorporated into the same layer, but they may be added separately to different layers provided that they are reactive with each other. For instance, if a colored dye providing compound is in the layer below a silver halide emulsion layer, it is effective for preventing lowering of the sensitivity of the emulsion layer. A reducing agent is preferably incorporated into the photographic element. Alternatively, it may be supplied to the photographic element from an external source such as the dye-fixing element by diffusing it thereinto from the dye-fixing element, as will be described below.

In order to obtain colors of a broad range in the chromaticity diagram by using the three primary colors of yellow, magenta and cyan, a combination of at least three silver halide emulsion layers each having a light-sensitivity in a different spectral region is used. For instance, a combination of a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer may be used, or a combination of a green-sensitive layer, a red-sensitive layer and an infrared sensitive layer may be used. The respective light-sensitive layers may be arranged in any desired sequence as generally employed in ordinary color photographic materials. These layers each may have two or more layers each having a different sensitivity.

The heat-developing photographic material may have various other auxiliary layers, such as a protective layer, a subbing layer, an interlayer, a yellow filter layer, an anti-halation layer, and a backing layer.

The silver halide for use in the present invention may be any one of silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloroiodide and silver chloroiodobromide.

The silver halide emulsion for use in the present invention may be either a surface latent image type emulsion or an internal latent image type emulsion. The internal latent image type emulsion is used as a direct reversal emulsion, in combination with a nucleating agent or with light fogging. The emulsion may also be a so-called core/shell emulsion in which the inside phase and the surface phase of each grain are different from each other. The silver halide emulsion may be either a monodispersed one or a polydispersed one. A mixture of monodispersed emulsions may also be used. The grain size of the emulsion grains may be from 0.1 to 2 μm, especially preferably from 0.2 to 1.5 μm. The crystal habit of the silver halide grains may be any one of a cubic, octahedral or tetradecahedral shape, or a tabular shape having a high aspect ratio.

Specifically, the silver halide emulsions described in U.S. Patents 4,500,626 (column 50) and 4,628,021, Research Disclosure (hereinafter referred to as RD), No. 17,029 (1978), and JP-A-62-253159 can be used in the present invention.

The silver halide emulsions may be used as primitive emulsions. In general, however, they are chemically sensitized before use. For instance, any known sulfur sensitization, reduction sensitization, noble metal sensitization or selenium sensitization, which are generally applied to emulsions of ordinary photographic materials, can be employed singly or in combination. Such chemical sensitization may also be effected in the presence of a nitrogen-containing heterocyclic compound (JP-A-62-253159).

The amount of light-sensitive silver halide to be coated in preparing the photographic material for use in the present invention may be from 1 mg/m^2 to 10 g/m^2 as silver.

The silver halides to be used in the present invention may be spectrally sensitized with methine dyes or other dyes. Suitable dyes include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes.

Specifically mentioned are the sensitizing dyes described in U.S. Patent 4,617,257, JP-A-59-180550 and JP-A-60-140335, and RD No. 17029 (1978), pages 12 and 13.

These sensitizing dyes may be used singly or in combination. Combinations of sensitizing dyes are often used for the purpose of supersensitization.

Dyes which do not have a spectral sensitizing activity by themselves or compounds which do not substantially absorb visible rays but which show a supersensitizing activity may be incorporated into the emulsions along with sensitizing dyes. Such dyes and compounds include those described in U.S. Patent 3,615,641 and JP-A-63-23145.

The time of adding such sensitizing dyes into the emulsions may be before or after chemical ripening of the emulsions. As the case may be, it may be before or after the formation of nuclei of the silver halide grains, in accordance with U.S. Patents 4,183,756 and 4,225,666. The amount of the dyes to be added is generally from about 10^{-8} to 10^{-2} mol, per mol of silver halide.

Where the dye-fixing element of the present invention is applied to a heat-developing system, the photographic element in the system may contain an organic metal salt, as an oxidizing agent, along with a light-sensitive silver halide. As such an organic metal salt, organic silver salts are especially preferred.

Organic compounds to be used for forming such organic silver salt oxidizing agents include benzotriazoles, fatty acids and other compounds described in U.S. Patent 4,500,626 (columns 52 to 53). In addition, silver salts of alkynyl group-containing carboxylic acids such as silver phenylpropiolate, as described in JP-A-60-113235, as well as acetylene silver as described in JP-A-61-249044 are also useful. Two or more kinds of organic silver salts may be employed in combination.

The organic silver salt may be added to the emulsion in an amount of from 0.01 to 10 mols, preferably from 0.01 to 1 mol, per mol of the light-sensitive silver halide in the emulsion. The total amount of the light-sensitive silver halide and the organic silver salt to be coated is suitably from 50 mg/m^2 to 10 g/m^2, as silver.

Various antifoggants and photographic stabilizers may be used in the present invention. Examples include the azoles and azaindenes described in RD No. 17643 (1978), pages 24 and 25; the nitrogen-containing carboxylic acids and phosphoric acids described in JP-A-59-168442; the mercapto compounds and metal salts thereof described in JP-A-59-11166; and the acetylene compounds described in JP-A-62-87957.

As the reducing agent for use in the present invention, any one which is known in the field of photographic materials can be employed. The reducing agents include the dye providing compounds having a reducing property, which will be described below. In this case, any other reducing agent can be used, if desired, in combination with such a reducing dye providing compound. In addition, reducing agent precursors which do not have a reducing property by themselves but which exhibit a reducing capacity with the aid of a nucleophilic reagent or under heat during development procedures may also be employed.

Examples of the reducing agents which can be employed in the present invention include the reducing agents and reducing agent precursors described in U.S. Patents 4,500,626 (columns 49 and 50), 4,483,914 (columns 30 and 31), 4,330,617 and 4,590,152, JP-A-60-140355 (pages 17 and 18), JP-A-57-40245, JP-A-56-138736, JP-A-59-178458, JP-A-59-53831, JP-A-59-182449, JP-A-59-182450, JP-A-60-119555, JP-A-60-128436 through JP-A-60-128439, JP-A-60-198540, JP-A-60-181742, JP-A-61-259253, JP-A-62-244044, JP-A-62-131253 through JP-A-62-131256 and European Patent 220,746A2 (pages 78 to 96).

Combinations of various reducing agents as described in U.S. Patent 3,039,869 can also be employed.

Where non-diffusive reducing agents are used in accordance with the present invention, an electron transfer agent and/or an electron transfer agent precursor can be used, if desired, in combination with the reducing agent to accelerate the movement of electrons between the non-diffusive reducing agent and the developable silver halide.

The electron transfer agent or precursor thereof can be selected from the above-mentioned reducing agents and precursors thereof. The electron transfer agent or precursor thereof preferably has a higher mobility than the non-diffusive reducing agent (electron donor). Especially useful electron transfer agents are 1-phenyl-3-pyrazolidones and aminophenols.

An electron transfer agent is an easily diffusive and mobile compound. Therefore, such an electron transfer agent is especially effective for preventing unfavorable coloration of the dye-fixing element of the present invention because of the rapid movement of the agent to the element.

The non-diffusive reducing agent (electron donor) to be employed in combination with the electron transfer agent may be any one of the above-mentioned reducing agents which are not substantially mobile in the layers of a photographic element. Preferred examples of electron donors include hydroquinones, sulfonamidophenols, sulfonamidonaphthols, and the compounds described in JP-A-53-110827, as well as the non-diffusive and reducing dye providing compounds which will be described below.

In accordance with the present invention, the amount of the reducing agent to be added preferably is from 0.01 to 20 mols, especially preferably from 0.1 to 10 mols, per mol of silver.

In the practice of the present invention, a dye providing compound capable of forming or releasing a mobile dye in correspondence or reverse correspondence with the amount of exposure is used.

Examples of dye providing compounds which can be employed in the present invention include compounds (couplers) capable of forming a dye by an oxidation-coupling reaction. The coupler may be either a 4-equivalent one or a 2-equivalent one. 2-Equivalent couplers which have a non-diffusive group as the split-off group and which form a diffusive dye by oxidation-coupling reaction are preferred. The non-diffusive group may be in the form of a polymer chain. Examples of color developing agents and couplers for use in the present invention are described in detail in T.H. James, The Theory of the Photographic Process, 4th Ed., pages 291 to 334 and 354 to 361 and in JP-A-58-123533, JP-A-58-149046, JP-A-58-149047, JP-A-59-111148, JP-A-59-124399, JP-A-59-174835, JP-A-59-231539, JP-A-59-231540, JP-A-60-2950, JP-A-60-2951, JP-A-60-14242, JP-A-60-23474 and JP-A-60-66249.

A further example of a dye providing compound which can be used is a compound adapted to imagewise release or form a diffusive dye. Compounds of this type can be represented by the formula (LI):

$$(\mathrm{Dye} - \mathrm{Y})_{n} \!-\!\!-\!\!- \mathrm{Z} \qquad (\mathrm{LI})$$

wherein Dye represents a dye group, or a dye group or dye precursor group whose wavelength has been shortened temporarily;

Y represents a chemical bond or a linking group;

Z represents a group which either causes an imagewise differential in the diffusibility of the compound

$$(\mathrm{Dye\text{-}Y})_n\text{—}\mathrm{Z}$$

in correspondence or reverse correspondence with the light-sensitive silver salt carrying a latent image or releases the Dye and causes a differential in diffusibility between the released Dye and

$$(\mathrm{Dye\text{-}Y})_n\text{—}\mathrm{Z};$$

; and n represents 1 or 2, and when n is equal to 2, the two Dye-Y groups may be same as or different from each other.

As specific examples of the dye providing compounds of formula (LI), the following compounds (1) through (5) are mentioned. Compounds (1) through (3) are those capable of forming a diffusive color image (positive color image) in reverse correspondence with development of silver halide; and compounds (4) and (5) are those capable of forming a diffusive color image (negative color image) in correspondence with the development of silver halide.

(1) Color-developing agents comprising a combination of a hydroquinone developing agent and a dye component, as described in U.S. Patents 3,134,764, 3,362,819, 3,597,200, 3,544,545 and 3,482,972. The color-developing agents are diffusive under alkaline conditions but become non-diffusive after reaction with a silver halide.

(2) Non-diffusive compounds which may release a diffusive dye under alkaline conditions but which lose that capacity when reacted with a silver halide can also be used, as described in U.S. Patent 4,503,137. Examples of such compounds include compounds capable of releasing a diffusive dye by intramolecular nucleophilic displacement reaction, as described in U.S. Patent 3,980,479; and compounds capable of releasing a diffusive dye by intramolecular rearrangement reaction of the isoxazolone ring in the molecule, as described in U.S. Patent 4,199,354.

(3) Non-diffusive compounds capable of reacting with a reducing agent which has remained without being oxidized by development to release a diffusive dye can also be used, as described in U.S. Patent 4,559,290, European Patent 220,746A2, U.S. Patent 4,783,396, and Kokai Giho 87-6199.

Examples of such compounds include compounds capable of releasing a diffusive dye by an intramolecular nucleophilic displacement reaction after reduction, as described in U.S. Patent 4,139,389 and 4,139,379 and JP-A-59-185333 and JP-A-57-84453; compounds capable of releasing a diffusive dye by an intramolecular electron-migrating reaction after reduction, as described in U.S. Patent 4,232,107, JP-A-59-101649 and JP-A-61-88257 and RD No. 24025 (1984); compounds capable of releasing a diffusive dye by cleavage of the single bond after reduction, as described in German Patent 3,003,588A, JP-A-56-142530, and U.S. Patents 4,343,893 and 4,619,884; nitro compounds capable of releasing a diffusive dye after electron reception, as described in U.S. Patent 4,450,223; and compounds capable of releasing a diffusive dye after electron reception, as described in U.S. Patent 4,609,610.

More preferably, exampels of such compounds include compounds having an N-X bond (where X means an oxygen, sulfur or nitrogen atom) and an electron-attracting group in one molecule, as described in European Patent 220,746A2, Kokai Giho 87-6199, U.S. Patent 4,783,396, and JP-A-63-201653 and JP-A-63-201654; compounds having a SO_2-X bond (where X has the same meaning as mentioned above) and an electron-attracting group in one molecule, as described in JP-A-1-26842; compounds having a PO-X bond (where X has the same meaning as mentioned above) and an electron-attracting group in one molecule, as described in JP-A-63-271344; and compounds having a C-X' bond (where X' has the same meaning as mentioned above for X or means $-SO_2-$) and an electron-attracting group in one molecule, as described in JP-A-63-271341. In addition, compounds capable of releasing a diffusive dye by cleavage of the single bond in the molecule after reduction owing to the π-bond capable of conjugating with an electron-receiving group, as described in JP-A-1-161237 and JP-A-1-161342, may also be used.

Above all, especially preferred are compounds having an N-X bond and an electron-attracting group in one molecule. Specific examples of such compounds include Compounds (1) to (3), (7) to (10), (12), (13), (15), (23) to (26), (31), (32), (35), (36), (40), (41), (44), (53) to (59), (64) and (70) described in European Patent 220,746A2 and U.S. Patent 4,783,396, and Compounds (11) to (23) described in Kokai Giho 87-6199.

(4) Compounds (DDR couplers) which have a diffusive dye as the split-off group and which release the

diffusive dye by reaction with an oxidation product of a reducing agent may also be used. Examples of such compounds are described in British Patent 1,330,524, JP-B-48-39165 and U.S. Patents 3,443,940, 4,474,877 and 4,483,914.

(5) Compounds (DRR compounds) which have the property of reducing silver halides and organic silver salts and which release a diffusive dye after having reduced the halides or salts can also be used. As the compounds of this type may function even in the absence of any other reducing agent, they can advantageously solve the problem of image staining caused by the oxidized and decomposed product of the reducing agent. Specific examples of such compounds are described in U.S. Patents 3,928,312, 4,053,312, 4,055,428 and 4,336,322, JP-A-59-65839, JP-A-59-69839, JP-A-53-3819 and JP-A-51-104343, RD No. 17645, U.S. Patents 3,725,062, 3,728,113 and 3,443,939, JP-A-58-116537 and JP-A-57-179840, and U.S. Patent 4,500,626. Preferred examples of such DRR compounds include the compounds described in the above-mentioned U.S. Patent 4,500,626, columns 22 to 44. Above all, Compounds (1) to (3), (10) to (13), (16) to (19), (28) to (30), (33) to (35), (38) to (40) and (42) to (64) described in U.S. Patent 4,500,626 are preferred. In addition, the compounds described in U.S. Patent 4,639,408, columns 37 to 39 are also useful.

Dye providing compounds other than the above-mentioned couplers and the compounds of the formula (LI) include dye-silver compounds comprising an organic silver salt and a dye bonded to each other (RD of May 1978, pages 54 to 58), azo dyes employable in a heat-developing silver dye bleaching method (U.S. Patent 4,235,957, RD of April 1976, pages 30 to 32) and leuco dyes (U.S. Patents 3,985,565 and 4,022,617). These dye donor compounds can also be employed in the present invention.

The dye providing compound, non-diffusive reducing agent and other hydrophobic additives are incorporated into the layers of the photographic material by any known method, for example, by the method described in U.S. Patent 2,322,027. In this method, high boiling point organic solvents such as those described in JP-A-59-83154, JP-A-59-178451, JP-A-59-178452, JP-A-59-178453, JP-A-59-178454, JP-A-59-178455 and JP-A-59-178457 can be used optionally together with low boiling point organic solvents having a boiling point of from 50 ° C to 60 ° C.

The amount of the high boiling point organic solvent to be used in the above method is 10 g or less, preferably 5 g or less, per gram of the dye providing compound used. It is suitably one cc or less, more suitably 0.5 cc or less, especially suitably 0.3 cc or less, per gram of the binder.

In addition, a dispersion method with a polymer, as described in JP-B-51-39853 and JP-A-51-59943, may also be employed.

Where the compound to be incorporated into the layers is substantially insoluble in water, it may be dispersed in the binder in the form of fine grains, apart from the above-mentioned methods.

Where the hydrophobic compound is dispersed in a hydrophilic colloid, various surfactants may be used. For instance, the surfactants mentioned in JP-A-59-157636, pages 37 to 38 may be used for this purpose.

The photographic material of the present invention can contain a compound having a function of activating the developability thereof and of stabilizing the image formed. Examples of such compounds which can preferably be employed in the present invention are described in U.S. Patent 4,500,626, columns 51 to 52.

The binder to be used in the layers constituting the photographic element and the dye-fixing element of the present invention is preferably a hydrophilic one. Examples of usable hydrophilic binders include those mentioned in JP-A-62-253159 (pages 26 to 28). Specifically, transparent or semi-transparent hydrophilic binders are preferred, which include natural compounds, for example, proteins such as gelatin and gelatin derivatives, polysaccharides such as cellulose derivatives, starch, gum arabic, dextran and pullulan; and other synthetic high molecular weight compounds such as polyvinyl alcohol, polyvinylpyrrolidone, and acrylamide polymers. In addition, the highly water-absorbing polymers described in JP-A-62-245260, such as homopolymers of vinyl monomers having -COOM or -SO_3M groups (where M is a hydrogen atom or an alkali metal), or copolymers of such vinyl monomers or copolymers of such vinyl monomers along with other vinyl monomers (e.g., sodium methacrylate, ammonium methacrylate, Sumikagel L-5H produced by Sumitomo Chemical Co., Ltd.) may also be used. Such binders may be used in combinations of two or more of them.

Where a method of heat-developing a photographic material while applying a slight amount of water thereto is employed in carrying out the present invention, the photographic material preferably contains a highly water-absorbing polymer whereby absorption of the water may be effected rapidly. It is preferred to incorporate the said highly water-absorbing polymer into the dye-fixing layer and the protective layer therefor, whereby re-transfer of the once-transferred dye to any other material from the dye-fixing element is prevented.

In accordance with the present invention, the amount of the binder to be coated is preferably 20 g or less, especially 10 g or less, more preferably 7 g or less, per m^2.

The layers constituting the light-sensitive photographic element and the dye-fixing element can contain a hardening agent. Examples of hardening agents are described in U.S. Patent 4,678,739 (column 41) and JP-A-59-116655, JP-A-62-245261 and JP-A-61-18942. Specifically, there are mentioned aldehyde hardening agents (e.g., formaldehyde), aziridine hardening agents, epoxy hardening agents, vinylsulfone hardening agents (e.g., N,N'-ethylene-bis(vinylsulfonylacetamino)ethane), N-methylol hardening agents (e.g., dimethylolurea) and high molecular weight hardening agents (e.g., compounds described in JP-A-62-234157).

Of the above-mentioned hardening agents, epoxy hardening agents are especially preferred in view of the coatability (precisely, an epoxy hardening agent-containing composition is stable for a long period of time and an epoxy hardening agent is reactive with the adjacent layer), the quality of the hardened film (precisely, the storage stability of raw films is good when an epoxy hardening agent is used and the quality of the hardened film is also good when the agent is used), and the photographic properties (precisely, the transferred density of the image formed is high when an epoxy hardening agent is used).

As specific examples of usable epoxy hardening agents, those described in JP-A-62-91942 are referred to.

In accordance with the present invention, the light-sensitive photographic element and/or the dye-fixing element can contain an image formation accelerator. The image formation accelerators include those which promote the redox reaction between a silver salt oxidizing agent and a reducing agent, those which promote the reactions of forming a dye from a dye providing substance or decomposing a dye or releasing a diffusive dye, and those which promote the migration of a dye from the light-sensitive layer to the dye-fixing layer. Classified by physico-chemical function, the image formation accelerators can be classified into bases or base precursors, nucleophilic compounds, high boiling point organic solvents (oils), heat solvents, and surfactants and compounds which interact with silver or silver ions, for instance. However, each of these substances generally has plural functions and provides several of the above-mentioned effects. A detailed discussion on these substances can be found in U.S. Patent 4,678,739, columns 38 to 40.

The light-sensitive photographic element and/or the dye-fixing element of the present invention can contain various development stopping agents for the purpose of always obtaining constant images despite fluctuation of the development temperature and the processing time in development.

The expression "development stopping agent" as used herein means a compound which, after proper development, quickly neutralizes a base or reacts with a base to lower the base concentration in the layer and thereby stops the development, or a compound which interacts with silver and a silver salt to arrest development. Specifically, there are mentioned acid precursors which release an acid under heat, electrophilic compounds which react with the existing base by displacement reaction under heat, as well as nitrogen-containing heterocyclic compounds, mercapto compounds and precursors thereof. More precisely, specific examples of these compounds are described in JP-A-62-253159 (pages 31 to 32).

Layers (including the backing layer) constituting the light-sensitive photographic element may contain various polymer latexes for the purpose of improving the film properties of the element, for example, for preventing curling, surface blocking, cracking and formation of pressure marks (due to decrease or increase of sensitivity under pressure) on the element. Specifically, polymer latexes usable for these purposes are the polymer latexes described in JP-A-62-245258, JP-A-62-136648 and JP-A-62-110066, as well as the above-mentioned polymer dispersions to be used in the dye-fixing element of the present invention.

The layers constituting the light-sensitive photographic element and the dye-fixing element can contain a high boiling point organic solvent as a plasticizer, a sliding agent, or an agent to improve peeling apart of the photographic element and the dye-fixing element. Specifically, the compounds described in JP-A-62-253159, page 25, and JP-A-62-245253 are referred to.

In addition, for the purposes stated in the preceding paragraph, various kinds of silicone oils (which may be all types of silicone oils including dimethylsilicone oil and modified silicone oils formed by introducing various organic groups into dimethylsiloxane) can be used. Eamples of such silicone oils include the various modified silicone oils described in Technical Reference of Modified Silicone Oils (published by Shin-Etsu Silicone Co., Ltd.), page 6-18B. Above all, carboxy-modified silicone oil (trade name: X-22-3701) is effective.

Further, the silicone oils described in JP-A-62-215958 and JP-A-63-46449 are also useful.

The light-sensitive photographic element and the dye-fixing element can contain an anti-fading agent. Such anti-fading agents include antioxidants and ultraviolet absorbents as well as various kinds of metal complexes.

Examples of antioxidants include chroman compounds, coumaran compounds, phenol compounds (e.g., hindered phenols), hydroquinone derivatives, hindered amine derivatives and spiroindane compounds. The compounds described in JP-A-61-159644 are also effective.

Examples of the ultraviolet absorbent include benzotriazole compounds (U.S. Patent 3,533,794), 4-thiazolidone compounds (U.S. Patent 3,352,681), benzophenone compounds (JP-A-46-2784) and other compounds described in JP-A-54-48535, JP-A-62-136641 and JP-A-61-88256. Further, the ultraviolet-absorbing polymers described in JP-A-62-260152 are also effective.

Examples of the metal complexes include the compounds described in U.S. Patents 4,241,155, 4,245,013 (columns 3 to 36) and 4,254,195 (columns 3 to 8), JP-A-62-174741 and JP-A-61-88256 (pages 27 to 29), JP-A-63-199248, JP-A-1-75568 and JP-A-1-74272.

Examples of useful anti-fading agents are described in JP-A-62-215272 (pages 125 to 137).

The anti-fading agent for preventing the dye which has been transferred to the dye-fixing element from fading may previously be incorporated into the dye-fixing element or, alternatively, it maybe supplied to the dye-fixing element from a source external to the light-sensitive photographic material.

The above-mentioned antioxidant, ultraviolet absorbent and metal complex can be employed in the present invention in the form of a combination thereof.

The light-sensitive photographic element and the dye-fixing element can contain a fluorescent brightening agent. In particular, it is preferred to incorporate a fluorescent brightening agent in the dye-fixing element or to supply it to the dye-fixing element from a source external to the light-sensitive photographic element. As examples of brightning agents, the compounds described in K. Veenkataraman, The Chemistry of Synthetic Dyes, Vol. V, Chap. 8, and JP-A-61-143752 are referred to. Specifically, there are mentioned stilbene compounds, coumarin compounds, biphenyl compounds, benzoxazolyl compounds, naphthalimide compounds, pyrazoline compounds and carbostyryl compounds.

The fluorescent brightening agent can be employed in combination with an anti-fading agent.

The layers constituting the light-sensitive photographic element and the dye-fixing element can contain various surfactants for various purposes, such as to aid coating, improve peeling properties, improve slide properties, prevent static charges, and enhance developability. Specific examples of such surfactants are described in JP-A-62-173463 and JP-A-62-183457.

The layers constituting the light-sensitive photographic element and the dye-fixing element can contain organic fluorine compounds to improve sliding properties, prevent static charges, and improve peeling properties. Specific examples of such organic fluorine compounds include the fluorine surfactants described in JP-B-57-9053 (columns 8 to 17) and JP-A-61-20944 and JP-A-62-135826, as well as hydrophobic fluorine compounds such as fluorine oils and similar oily fluorine compounds, tetrafluoroethylene resins, and similar solid fluorine compound resins.

The light-sensitive photographic element and the dye-fixing element can contain a mat agent. As the mat agent, there are mentioned silicone dioxide and the compounds described in JP-A-61-88256 (page 29) such as polyolefins or polymethacrylates, as well as the compounds described in JP-A-63-274944 and JP-A-63-274952 such as benzoguanamine resin beads, polycarbonate resin beads and AS resin beads.

In addition, the layers constituting the light-sensitive photographic element and the dye-fixing element may further contain a heat solvent, a defoaming agent, a microbicidal, fungicidal agent, a colloidal silica and other additives. Examples of such additives are described in JP-A-61-88256 (pages 26 to 32).

The support which may be used to prepare the light-sensitive photographic element and the dye-fixing element of the present invention may be any support that withstands the processing temperature. In general, paper and synthetic high molecular weight films are used as the support. Specifically, the support includes films of polyethylene terephthalate, polycarbonates, polyvinyl chloride, polystyrene, polypropylene, polyimide, celluloses (e.g., triacetyl cellulose) and those films containing a pigment such as titanium oxide; synthetic paper made of polypropylene by filming method; mixed paper made of a synthetic resin pulp (e.g., polyethylene) and a natural pulp; as well as Yankee paper, baryta paper, coated paper (especially cast-coated paper), metals, cloths and glasses.

These supports may be used directly as they are or they may be coated with a synthetic high molecular weight substance (e.g., polyethylene) on one surface or both surfaces.

In addition, the supports described in JP-A-62-253159, pages 29 to 31 can also be employed in the present invention.

The surface of the support may be coated with a hydrophilic binder and a semiconductive metal oxide (e.g., alumina sol or tin oxide) or an antistatic agent such as carbon black.

For imagewise exposing and recording the photographic element of the present invention, various methods can be employed, which include, for example, a method of directly photographing the scene or portrait with a camera; a method of exposing an image through a reversal film or negative film by the use of a printer or an enlarger; a method of scanning and exposing an original through a slit by the use of an exposing device of a duplicator; a method of exposing the image information via the corresponding electric signal by emitting the information with an emitting diode or various lasers; and a method of outputting the image information with an image display device such as a CRT, a liquid crystal display, an electroluminescence display or a plasma display and then exposing the same directly or via some optical system.

As the light source to be used for recording an image on the photographic element, those described in U.S. Patent 4,500,626 (column 56), such as natural light, tungsten lamps, light-emitting diodes, laser rays and CRT rays can be employed, as mentioned above.

The image information applied to the photographic material of the present invention may include image signals obtained from a video camera or an electronic still camera; television signals standardized by Nippon Television Signal Standard Code (NTSC); image signals obtained by dividing an original into pixels with a scanner; and image signals formed by the use of a computer such as CG or CAD.

The heating temperature in the heat-development step varies, depending upon the film pH value to be adjusted by the base or base precursor therein and it may be from about 25 ° C to about 250 ° C. Preferably, it is from about 50 ° C to about 200 ° C, especially preferably from about 70 ° C to about 180 ° C. The step of diffusing and transferring the dye formed by the development may be effected simultaneously with the heat-development step or after it. In the latter case, the heating temperature in the transfer step may be from the temperature in the previous heat-development step to room temperature. Preferably, it is from 50 ° C to a temperature lower than the temperature in the heat-development step by about 10 ° C.

Migration of the dye formed may be effected only by heat, but a solvent may be used for the purpose of accelerating the migration of the dye. Further, as described in detail in JP-A-59-218443 and JP-A-61-238056, a method where development and transfer are carried out in the presence of a small amount of a solvent (especially, water) under heat, either at the same time or in a continuous sequence, can be advantageously utilized. In this method, the heating temperature is preferably not lower than 50 ° C and not higher than the boiling point of the solvent used. For instance, where the solvent is water, the temperature is desirably from 50 ° C to 100 ° C.

Examples of the solvents to be used to accelerate development and/or migration of the diffusive dye formed to the dye-fixing element include water and an aqueous basic solution containing an inorganic alkali metal salt or an organic base. As the bases, those mentioned hereinbefore for the image formation accelerators can be employed. In addition, a low boiling point solvent, or a mixed solution comprising a low boiling point solvent and water or an aqueous basic solution can also be used. Further, surfactants and antifoggants as well as sparingly soluble metals and complex-forming compounds can be incorporated into the solvents.

The solvent can be used by applying it to either the dye-fixing element or the light-sensitive photographic element or to both of them. The amount of solvent used may be a small amount. A small amount means an amount less than the weight of the solvent corresponding to the maximum swollen volume of the total coated layers (especially less than the amount obtained by subtracting the weight of the total coated layers from the weight of the solvent corresponding to the maximum swollen volume of the total coated layers).

As a method of applying the solvent to the light-sensitive layer or the dye-fixing layer, for example, the method described in JP-A-61-147244 (page 26) can be employed. Apart from this, the solvent can be incorporated into either the light-sensitive photographic element or the dye-fixing element or into both of them in the form of solvent-containing microcapsules.

In order to accelerate migration of the dye formed, a method of incorporating a hydrophilic heat solvent which is solid at room temperature but may melt at a high temperature into the light-sensitive photographic element or into the dye-fixing element may also be employed in the present invention. In employing such a method, the hydrophilic heat solvent may be incorporated into either the light-sensitive photographic element or the dye-fixing element or into both of them. The layer to which the solvent is added may be any of the emulsion layer, interlayer, protective layer and dye-fixing layer, but the solvent is preferably added to the dye-fixing layer and/or the adjacent layer(s).

Examples of the heat solvent to be employed in the method include ureas, pyridines, amides, sulfonamides, imides, alcohols, oximes and other heterocyclic compounds.

Also for accelerating migration of the dye formed, a high boiling point organic solvent may be incorporated into the light-sensitive photographic material and/or the dye-fixing element.

For heating the material and/or the element in the development step and/or the transfer step, the material and/or the element may be contacted with a heated block or plate, or heated with a hot plate, hot presser, hot roller, halogen lamp heater or infrared or far-infrared lamp heater, or the material may be passed through a high temperature atmosphere. If desired, the photographic element and/or the dye-fixing element of the present invention may have a heating element layer provided therein, in which the layer is electrically charged so as to heat the elements. Regarding such a heating element, the one disclosed in JP-A-61-145544 may be referred to.

Where the light-sensitive photographic element is attached to the dye-fixing element and they are combined together under pressure, the method described in JP-A-61-174244 (page 27) is applicable with respect to the pressure conditions and the means of pressing the combined elements together.

For processing the photographic elements of the present invention, any general heat-developing apparatus can be utilized. For instance, the apparatus described in JP-A-59-75247, JP-A-59-177547, JP-A-59-181353 and JP-A-60-18951, JP-U-A-62-25944 are preferably employed.

The present invention will be explained in more detail with reference to the following examples, which, however, are not intended to restrict the scope of the invention.

EXAMPLE 1

A photographic element sample having the layer constitution stated below was prepared and designated Photographic Element Sample No. 01.

Layer Constitution of Sample No. 01:

Support:

Polyethylene Terephthalate (96 µm), with backing layer coated with carbon black.

First Layer: Red-Sensitive Emulsion Layer	
Red-sensitive Silver Halide Emulsion	230 mg/m^2 as Ag
Cyan Dye Providing Compound (3)	343 mg/m^2
Gelatin	330 mg/m^2
Electron Donor (1)	163 mg/m^2
High Boiling Point Solvent (1)	172 mg/m^2
Electron Transfer Agent (1)	28 mg/m^2
Electron Transfer Agent Precursor (1)	17 mg/m^2
Antifoggant (3)	0.7 mg/m^2

Second Layer: Interlayer	
Gelatin	790 mg/m^2
Zinc Hydroxide	300 mg/m^2
Electron Donor (2)	130 mg/m^2
High Boiling Point Solvent (1)	73 mg/m^2
Surfactant (2)	100 mg/m^2
Active Charcoal	25 mg/m^2

Third Layer: Green-Sensitive Emulsion Layer	
Green-Sensitive Silver Halide Emulsion	220 mg/m^2 as Ag
Magenta Dye Providing Compound (2)	365 mg/m^2
Gelatin	310 mg/m^2
Electron Donor (1)	158 mg/m^2
High Boiling Point Solvent (1)	183 mg/m^2
Electron Transfer Agent (1)	27 mg/m^2
Electron Transfer Agent Precursor (1)	15 mg/m^2
Antifoggant (2)	0.3 mg/m^2

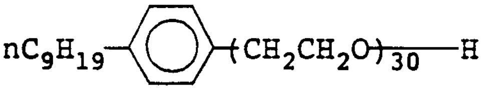
Fourth Layer: Interlayer	
Gelatin	700 mg/m^2
Electron Donor (2)	130 mg/m^2
High Boiling Point Solvent (1)	48 mg/m^2
Surfactant (2)	61 mg/m^2
Electron Transfer Agent (1)	27 mg/m^2
Electron Transfer Agent (2)	36 mg/m^2
Hardening Agent (1)	37 mg/m^2

Fifth Layer: Blue-Sensitive Emulsion Layer	
Blue-Sensitive Silver Halide Emulsion	380 mg/m^2 as Ag
Yellow Dye Providing Compound (1)	400 mg/m^2
Gelatin	600 mg/m^2
Electron Donor (1)	303 mg/m^2
High Boiling Point Solvent (1)	200 mg/m^2
Electron Transfer Agent Precursor (1)	15 mg/m^2
Zinc Hydroxide	330 mg/m^2
Antifoggant (1)	0.6 mg/m^2

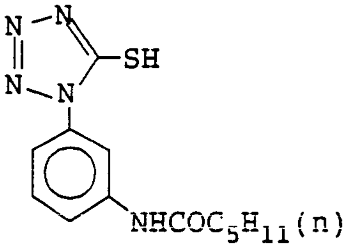
Sixth Layer: Protective Layer	
Gelatin	900 mg/m^2
Silica (grain size 4 µm)	40 mg/m^2
Zinc Oxide	600 mg/m^2
Surfactant (1)	130 mg/m^2

The compounds used in preparing Sample No. 101 are shown below.

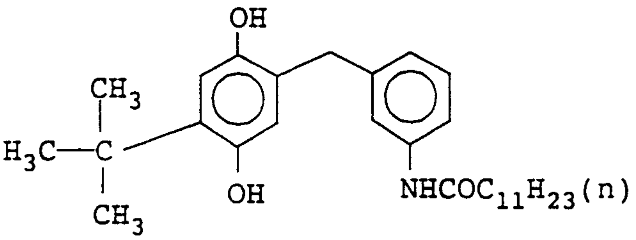
Surfactant (1)



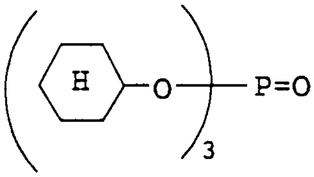
Anti-foggant (1)



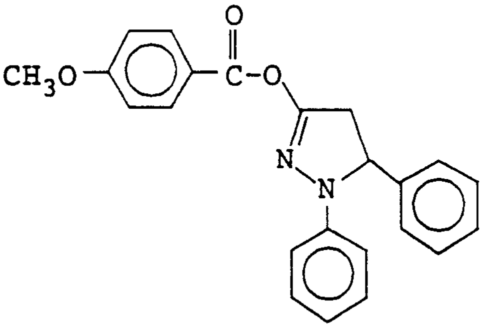
Electron Donor (1)



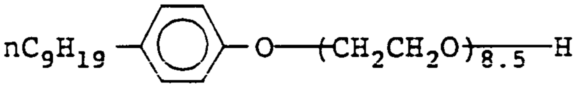
High Boiling Point Solvent (1)



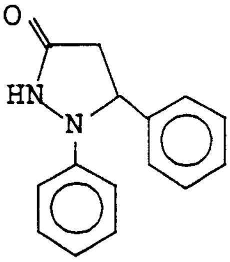
Electron Transfer Agent Precursor (1)



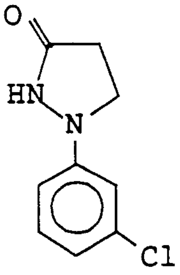
Surfactant (2)



Electron Transfer Agent (1)



Electron Transfer Agent (2)



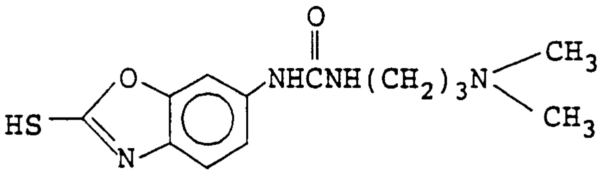
Hardening Agent (1)

3/1 Mixture (by weight) of (1)-1/(1)-2

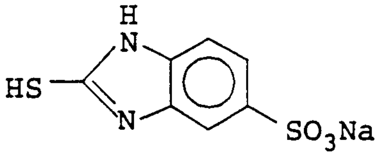
$CH_2 = CHSO_2CH_2CONH(CH_2)_2NHCOCH_2SO_2CH = CH_2$ (1)-1

$CH_2 = CHSO_2CH_2CONH(CH_2)_3NHCOCH_2SO_2CH = CH_2$ (1)-2

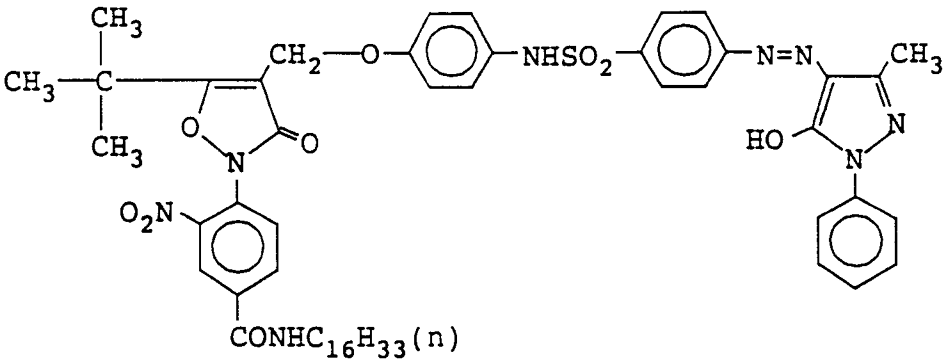
Anti-foggant (2)



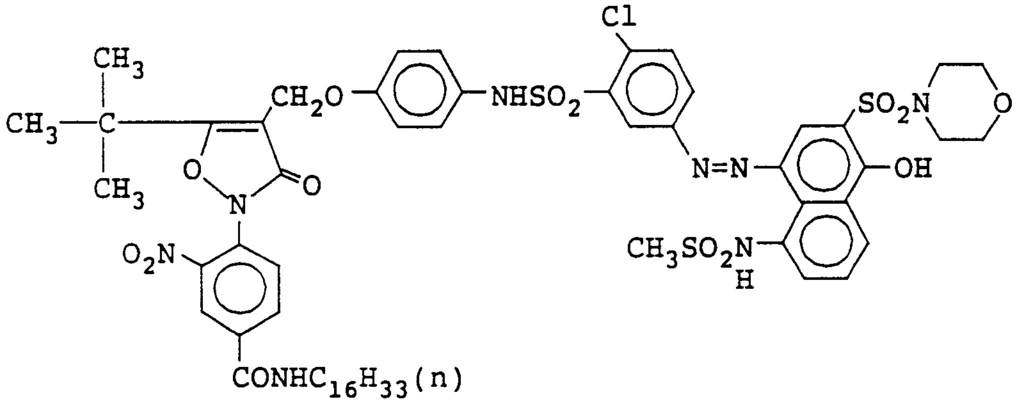
Anti-foggant (3)



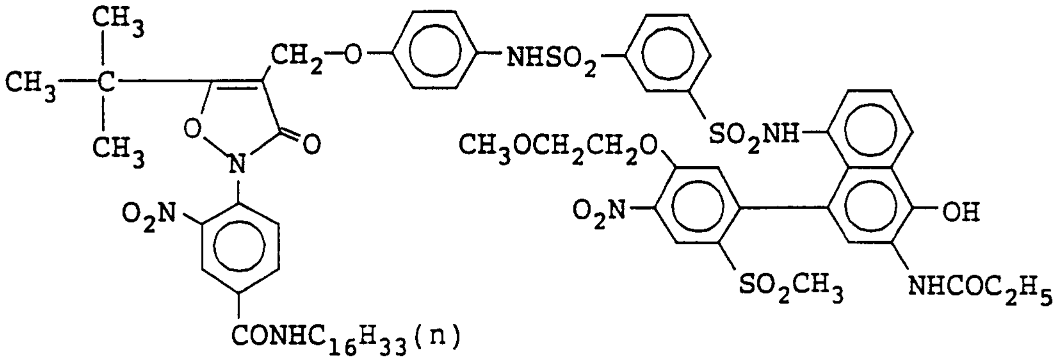
Yellow Dye Providing Compound (1)



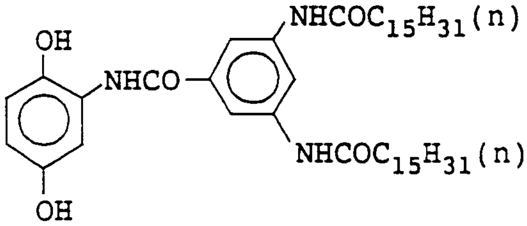
Magenta Dye Providing Compound (2)



Cyan Dye Providing Compound (3)



Electron Donor (2)



A dye-fixing element sample having the layer constitution mentioned in Table 1-A below was prepared, in which a support having the layer constitution given in Table 1-D was coated with a surface layer described in Table 1-B and a backing layer described in Table 1-C. The fluorescent brightening layer in the surface layer was introduced thereinto by an oil-protect method using high boiling point solvent (1), ethyl acetate and sodium dodecylbenzenesulfonate in the same layer. The sample thus prepared was designated dye-fixing element Sample No. 01.

Table 1-A : Layer Constitution of Sample No. 01

Surface Layer (1) having the layer constitution shown in Table 1-B

Support (1) having the layer constitution shown in Table 1-D

Backing layer (1) having the layer constitution shown in Table 1-C

Table 1-B

Constitution of Surface Layer (1)		
Layer Number	Additives	Amount Coated (g/m^2)
3rd Layer	Water-soluble Polymer (1)	0.25
	Water-soluble Polymer (2)	0.07
	Guanidine Picolinate	0.45
	Surfactant (1)	0.01
	Surfactant (2)	0.10
	Surfactant (3)	0.03
2nd Layer	Gelatin	1.40
	Water-soluble Polymer (1)	0.20
	Water-soluble Polymer (3)	0.60
	Mordant (1)	2.40
	Guanidine Picolinate	2.20
	Fluorescent Brightening Agent (1)	0.055
	Stain Inhibitor (1)	0.060
	High Boiling Point Organic Solvent (1)	1.40
	Surfactant (4)	0.025
1st Layer	Gelatin	0.25
	Water-soluble Polymer (1)	0.02
	Surfactant (1)	0.005
	Surfactant (2)	0.005
	Hardening Agent (1)	0.16

Table 1-C

Constitution of Backing Layer (1)		
Layer Number	Additives	Amount Coated (g/m^2)
1st Backing Layer	Gelatin Water-soluble Polymer (4) Surfactant (1) Hardening Agent (1)	3.00 0.04 0.05 0.13
2nd Backing Layer	Gelatin Water-soluble Polymer (4) Surfactant (1) Surfactant (5) Mat Agent (1)	0.37 0.005 0.045 0.011 0.03

Table 1-D

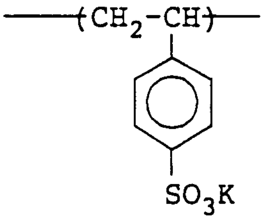
Constitution of Support (1)		
Layer	Composition	Thickness (µm)
Surface Subbing Layer	Gelatin	0.1
Surface PE Layer (Glossy)	Low Density Polyethylene (density 0.923); 89.2 parts Surface-treated Titanium Oxide; 10.0 parts Ultramarine; 0.8 parts	20.0
Pulp Layer Back PE Layer (Mat)	Wood-free Paper (LBKP/NBKP = 1/1 (by weight), density 1.080) High Density Polyethylene (density 0.960)	73.0 18.0
Back Subbing Layer	Gelatin Colloidal Silica	0.05 0.05
	Total	111.2

Table 1-E

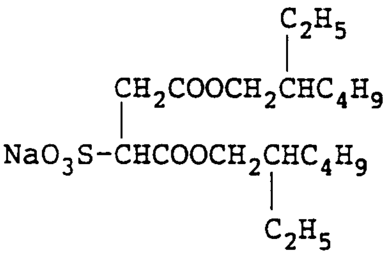
Physical Properties of Support (1)			
Item	Unit	Physical Value	Method of Measurement
Toughness (length/width)	g	4.40/3.15	Taper Toughness Meter
Whiteness		L* 94.20 a* +0.12 b* -2.75	CLE L*a*b*

Compounds used in preparing Sample No. 01 are shown below.

Water-soluble Polymer (4)

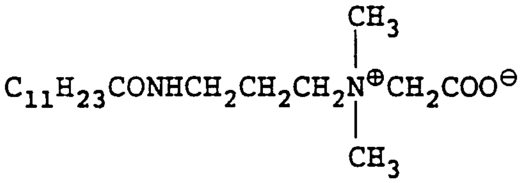


Surfactant (1)



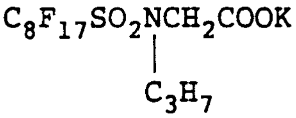
$NaO_3S\text{-}CH(COOCH_2CH(C_2H_5)C_4H_9)CH_2COOCH_2CH(C_2H_5)C_4H_9$

Surfactant (2)



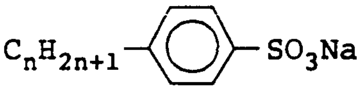
$C_{11}H_{23}CONHCH_2CH_2CH_2N^{\oplus}(CH_3)_2CH_2COO^{\ominus}$

Surfactant (3)



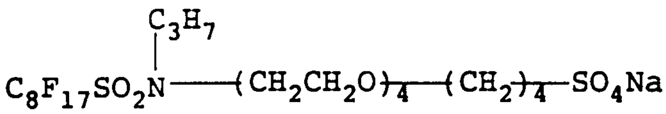
$C_8F_{17}SO_2N(C_3H_7)CH_2COOK$

Surfactant (4)



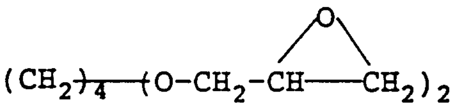
(n≒12.6)

Surfactant (5)

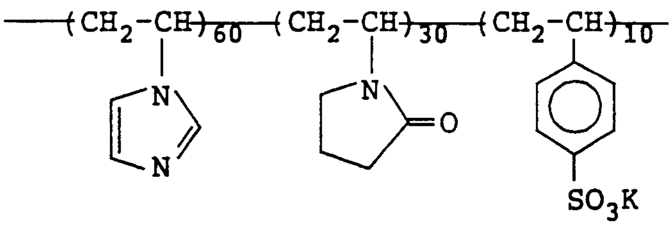


$C_8F_{17}SO_2N(C_3H_7)\text{—}(CH_2CH_2O)_4\text{—}(CH_2)_4\text{—}SO_4Na$

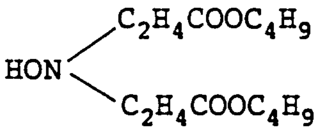
Hardening Agent (1)



Mordant (1)



Stain Inhibitor (1)



Mat Agent (1):

Benzoguanamine Resin (mean grain size 15 µm) Water-soluble Polymer (1):
Sumikagel L5-H (product of Sumitomo Chemical Co., Ltd.)

Water-soluble Polymer (2):

K-Carrageenan (product of Taito Co.)

Water-soluble Polymer (3):

Dextran (molecular weight: 70,000)

Fluorescent Brightening Agent (1):

2,5-Bis(5-t-benzoxazol(2))thiophene

High Boiling Point Organic Solvent (1):

Enpara 40 (product of Ajinomoto Co., Inc.)

Next, dye-fixing element Sample No. 02 was prepared in the same manner as Sample No. 01, except that no backing layer was provided.

Further, dye-fixing element Sample Nos. 03 to 16 were prepared in the same manner as Sample No. 02, except that the second layer (mordant layer) of the surface layer (1) (Table 1-B) was changed described below.

Second layer of Dye-fixing Element Sample No. 03:

Gelatin	1.40 g/m^2
Mordant (1)	2.40 g/m^2
Guanidine Picolinate	2.20 g/m^2
Fluorescent Brightening Agent (1)	0.055 g/m^2
Stain Inhibitor (1)	0.06 g/m^2
High Boiling Point Organic Solvent (1)	1.40 g/m^2
Surfactant (4)	0.025 g/m^2

Second Layer of Dye-Fixing Element Sample No. 04:

This was same as the second layer of Sample No. 03, except that an acrylic latex of Nipol LX 814 (product of Nippon Zeon Co., Ltd.: Tg = 17°C) was added in an amount of 2.0 g/m^2 as a solid content.

Second Layer of Dye-Fixing Element Sample No. 05:

Gelatin	0.8 g/m^2
Water-soluble Polymer (3)	0.6 g/m^2
Nipol LX814 (as solid)	2.0 g/m^2
Mordant (1)	2.40 g/m^2
Guanidine Picolinate	2.20 g/m^2
Fluorescent Brightening Agent (1)	0.055 g/m^2
Stain Inhibitor (1)	0.06 g/m^2
High Boiling Point Organic Solvent (1)	1.40 g/m^2
Surfactant (4)	0.025 g/m^2

Second Layer of Dye-Fixing Element Sample No. 06:

This was same as the second layer of Sample No. 04, except that the Nipol LX814 was replaced with the same amount of an acrylic latex of Nipol LX811 (product of Nippon Zeon Co., Ltd.: Tg = -18°C).

Second Layer of Dye-Fixing Element Sample Nos. 07 and 08:

Samples Nos. 07 and 08 were same as Sample Nos. 05 and 06, respectively, except that a nonionic surfactant $C_6H_5O(CH_2CH_2O)_{30}H$ was added.

Second Layer of Dye-Fixing Element Sample Nos. 09, 10 and 11:

Sample Nos. 09, 10 and 11 were prepared in the same manner as Sample No. 05, except that the Nipol LX814 was replaced by Nipol LX438C (a styrene-butadiene latex stabilized with the same nonionic surfactant as that used in Sample No. 07, product of Nippon Zeon Co., Ltd.: Tg = 0°C), Polysol PS-10 (a vinyl acetate latex stabilized with polyvinyl alcohol, product of Showa Highpolymer Co.) and Denka EVA-Tex 30 (an ethylene-vinyl acetate latex stabilized with polyvinyl alcohol, product of Denki Kagaku Kogyo K.K.; Tg = 0°C), respectively.

Second Layer of Dye-Fixing Element Sample No. 12:

This was same as Sample No. 05, except that the Nipol LX814 was replaced with Denka EVA-Tex 27 (an ethylene-vinyl acetate latex with no protective colloid, product of Denki Kagaku Kogyo K.K.: Tg = -5°C).

Second Layer of Dye-Fixing Element Sample No. 13:

This was same as Sample No. 12, except that hydroxyethyl cellulose (HEC) was used as a protective colloid for the latex.

Second Layer of Dye-Fixing Element Sample Nos. 14 and 15:

Sample Nos. 14 and 15 were prepared in the same manner as Sample No. 05, except that the amount of Nipol LX814 (as solids content) was changed to 4.0 g/m^2 and 0.5 g/m^2, respectively.

Second Layer of Dye-Fixing Element Sample No. 16:

This was same as Sample No. 05, except that pullulan was used in place of dextran. The above-mentioned photographic element Sample No. 101 was combined with each of these dye-fixing element samples and processed with an image recording processor as described in Japanese Patent Application No. 63-137104.

Specifically, the photographic element sample was exposed with an original (a test chart with wedges of yellow, magenta, cyan and gray each having a continuously varying color density) through a slit by a scanning exposure, the exposed sample was dipped in water kept at 35°C for about 5 seconds, this was squeezed with rollers and then immediately attached to a dye-fixing element sample in such a way that the coated top surfaces of the two faced each other, and the combined samples were heated with heat rollers for 15 seconds in such a way that the water-applied surfaces were heated up to 80°C. Then, the photographic element sample was peeled apart from the dye-fixing element sample, whereupon a sharp color image well corresponding to the original was formed on the dye-fixing element sample.

In addition, the properties of each of the abovementioned dye-fixing element samples were evaluated as described below, and the results are shown in Table 2 below.

Curling:

The developed and transferred dye-fixing element sample was cut into a size of 10 cm x 10 cm, which was then stored under one of the following conditions (A) to (C) for 2 hours whereupon the degree of curling of the sample was measured in such a way that the curled sample was put on a flat rack and the height (unit: mm) of each of the four edges of the sample (from the surface of the rack) was measured and the four measured values were averaged.

(A) 25°C, 20% RH
(B) 25°C, 50% RH
(C) 25°C, 80% RH

All the non-processed dye-fixing element samples were tempered under the condition of 25°C and 80% RH for 2 hours, and they were stacked (piled up) in such a way that the front surface (with dye-fixing layer) of one sample was kept in contact with the back surface of another sample. A weight of 20 g/cm^2 was applied to the stack (pile), which was thus stored for 3 days under an ambient condition of 60°C and 80% RH. Each of the thus stored dye-fixing element samples was combined with the previously prepared photographic element Sample No. 01 and processed with an image recording processor as described in the above-mentioned Japanese Patent Application No. 63-137104 using an original of a completely uniformly black paper.

The degree of unevenness of the thus formed black image was evaluated on the basis of the following three ranks A, B and C.

A : Image was uniform and was not uneven.
B : Image was somewhat uneven.
C : Image was noticeably uneven.

Surface Gloss:

The surface gloss of each sample was measured on the basis of JIS-Z-8741 (reflection to 20 degreemirror surface).

Contact Color Migration:

A non-exposed photographic element Sample No. 01 or a photographic element Sample No. 01 fully exposed with a white light was combined with one of the prepared dye-fixing element samples and then processed to form developed samples each with a black solid image or a white solid image. These were tempered under the condition of 25 ° C and 80% RH for 1 hour and then stacked (piled up) in such a way that the front surface (with black image) of one sample was kept in contact with the front surface (with white image) of another sample, under a load of 500 g/200 cm^2 and an ambient condition of 25 ° C and 80% RH for 3 days. Then, the two samples were peeled apart, whereupon the degree of the dye re-transferred from the black image sample to the white image sample was measured. The contact color migration of the tested samples was evaluated on the basis of the following three ranks A, B and C.

A : Almost no color migration was noted.
B : Some color migration was noted.
C : Color migration was great.

Precipitation of Base Precursor:

Non-processed dye-fixing element samples were subjected to an alternating heat cycle of 40 ° C-80% RH-8 hours and 0 ° C-20% RH-12 hours 14 times, whereupon the crystalline precipitate, if any, formed on the surface of the sample was checked. The sample was then evaluated on the basis of the following three ranks A, B and C.

A : No precipitate.
B : Some precipitate formed.
C : Much precipitate formed.

Surface Blocking (Adhesion):

Non-processed dye-fixing element samples were tempered under the condition of 25 ° C and 60% RH and then stacked (piled up) in such a say that the front surface (with dye-fixing layer) of one sample was kept in contact with the back surface of another sample under a load of 500 g/100 cm^2 and an ambient condition of 60 ° C and 60% RH for 3 days. Then, the samples were peeled apart, whereupon the degree of surface blocking (adhesion) was examined. The tested sample was then evaluated on the basis of the following three ranks A, B and C.

A : No surface blocking.
B : Some surface blocking was noted.
C : Surface blocking was great.

Table 2

Dye-Fixing Element Sample	Curling (25°C) (mm)			Storage Stability of Stacked Samples	Contact Color Migration	Surface Gloss	Precipi-tation	Surface Blocking	Remarks
	20% RH	50% RH	80% RH						
01 (Comparative sample)	12	0	0	B to C	A	80	A	A	This has a backing layer.
02 (Comparative sample)	>40 (cylindrical)	4	0	A	A	80	A	A	This is same as No. 01, but has no backing layer.
03 (Comparative sample)	31	0	0	A	B	73	C	B	This is same as No. 02, but the amount of the binder was decreased. (This has no dextran.)
04 (Comparative sample)	15	0	0	A	B	65	B to C	B	This is same as No. 03, but has a latex (acrylic latex, Tg 17°C).
05 (Sample of the invention)	18	0	0	A	A	70	A	A	This is same as No. 04, but has dextran.
06 (Comparative sample)	24	0	0	A	B	45	B to C	B	This is same as No. 04, but the latex therein has a Tg of -17°C.
07 (Sample of the invention)	17	0	0	A	A	81	A	A	This is same as No. 05, but has a nonionic surfactant.
08 (Sample of the invention)	16	0	0	A	B	75	A	A	This is same as No. 06, but has a nonionic surfactant.

Dye-Fixing Element Sample	Curling (25°C) (mm)			Storage Stability of Stacked Samples	Contact Color Migration	Surface Gloss	Precipitation	Surface Blocking	Remarks
	20% RH	50% RH	80% RH						
09 (Sample of the invention)	18	0	0	A	A	79	A	A	This is same as No. 07, but has a styrene-butadiene latex.
10 (Sample of the invention)	19	0	0	A	A	78	A	A	This is same as No. 05, but has a PVA-stabilized vinyl acetate latex.
11 (Sample of the invention)	20	0	0	A	A	80	A	A	This is same as No. 05, but has a PVA-stabilized EVA latex.
12 (Sample of the invention)	16	0	0	A	A	69	A	A	This is same as No. 05, but has an EVA latex.
13 (Sample of the invention)	18	0	0	A	A	73	A	A	This is same as No. 12, but has an HEC-stabilized EVA latex.
14 (Sample of the invention)	14	0	0	A	A	65	A	A	This is same as No. 05, but the amount of latex coated was changed to 4.0 g/m^2.
15 (Sample of the invention)	26	0	0	A	A	75	A	A	This is same as No. 05, but the amount of latex coated was changed to 0.5 g/m^2.
16 (Sample of the invention)	18	0	0	A	A	68	A	A	This is same as No. 05, but has pullulan in place of dextran.

From the results in Table 2 above, the following conclusions may be drawn:

(1) The storage stability of a stack (pile) of dye-fixing element samples under high humidity conditions was improved by removal of the backing layer from the samples, but the samples curled noticeably under low humidity conditions.

Curling resistance of the dye-fixing element samples could be improved somewhat by decreasing the amount of binder in the dye-fixing layer (removal of water-soluble polymer (1) or (3)) therein, but the improvement was insufficient. The decrease caused rather noticeable precipitation of the base precursor on the surface of the sample. However, curling resistance was greatly improved and precipitation of the base precursor was retarded by addition of a polymer dispersion (latex) having a low Tg value to the dye-fixing layer.

(2) Where a latex stabilized with a nonionic surfactant or nonionic protective colloid was used, coagulation of the latex in the coating composition was inhibited. As a result, deterioration of the surface gloss of the dye-fixing element caused by addition of a latex thereto could be prevented.

(3) Substitution of a latex for the water-soluble binder in the dye-fixing element augmented precipitation of the base precursor in the element. However, by adding a latex having a low Tg value and by further adding dextran or pullulan thereto, precipitation of the base precursor could be completely prevented. Adding dextran or pullulan did not interfere to any significant degree with the curling resistance of the element under low humidity conditions.

The results make clear that curling of a dye-fixing element under low humidity conditions may be inhibited by incorporating a low Tg polymer dispersion (latex, etc.) stabilized with a nonionic surfactant or nonionic protective colloid into a mordant-containing dye-fixing layer, even though the element does not have a curling-resistant backing layer containing a hydrophilic binder.

In addition, by incorporating both a low Tg polymer dispersion and an anionic group-free water-soluble polysaccharide, especially dextran or pullulan, into the dye-fixing layer of the dye-fixing element, all the problems associated with dye-fixing elements, including precipitation of diffusive low molecular weight substances (salts), such as base precursors, contained in the dye-fixing layer, surface blocking of elements stacked up for storage, and contact color migration of processed elements stacked up for storage under high humidity conditions, may be solved, without lowering the curling resistance of the elements to any significant extent.

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

Claims

1. A dye-fixing element for receiving and fixing a mobile dye that is formed or released by development of a photographic element, where the photographic element comprises a light-sensitive silver halide, a hydrophilic binder and a dye providing compound capable of forming or releasing a mobile dye in correspondence or reverse correspondence with the amount of exposure of the light-sensitive silver halide, and where the mobile dye is transferred and fixed, during or after imagewise exposure of the photographic element, in the presence of a base and/or a base precursor,

said dye-fixing element comprising a dye-fixing layer that includes a mordant, a dispersion of a polymer having a glass transition temperature of 25 ° C or lower, and a nonionic stabilizer for the polymer dispersion; and said dye-fixing element not comprising a backing layer composed of 1 g/m^2 or more of a hydrophilic binder on the side opposite to the dye-fixing layer.

2. A dye-fixing element for receiving and fixing a mobile dye that is formed or released by heat-development of a photographic element, where the photographic element comprises a light-sensitive silver halide, a hydrophilc binder and a dye providing compound capable of forming or releasing a mobile dye in correspondence or reverse correspondence with the amount of exposure of the light-sensitive silver halide, and where the mobile dye is transferred and fixed, during or after imagewise exposure of the photographic element, in the presence of a base and/or a base precursor,

said dye-fixing element comprising a dye-fixing layer that includes a mordant, a dispersion of a polymer having a glass transition temperature of 25 ° C or lower, and a nonionic stabilizer for the polymer dispersion; and said dye-fixing element not comprising a backing layer composed of 1 g/m^2 or more of a hydrophilic binder on the side opposite to the dye-fixing layer.

3. A dye-fixing element having a dye-fixing layer to which a mobile dye formed or released by heat-development of a photographic element comprising a light-sensitive silver halide, a hydrophilic binder and a dye providing compound capable of forming or releasing a mobile dye in correspondence or reverse correspondence with the amount of exposure is transferred and fixed, during or after imagewise exposure of the photographic element, in the presence of a base and/or a base precursor; the dye-fixing element being characterized in that the element does not have a backing layer composed of 1 g/m^2 or more hydrophilic binder on the side opposite to the dye-fixing layer, and further characterized in that the dye-fixing layer includes a part or all of the base and/or the base precursor, a mordant, a nonionic water-soluble polysaccharide, and a dispersion of a polymer having a glass transition temperature of 25 ° C or lower.

4. The dye-fixing element of claim 3, in which the polymer dispersion is stabilized with a nonionic stabilizer.

5. The dye-fixing element as in claim 1, in which the mordant is a polymer containing tertiary salt amino groups or imidazole groups

6. The dye-fixing element as in claim 2, in which the mordant is a polymer containing tertiary salt amino groups or imidazole groups.

7. The dye-fixing element as in claim 3, in which the mordant is a polymer containing tertiary salt amino groups or imidazole groups.

8. The dye-fixing element as in claim 1, in which the nonionic stabilizer is a nonionic surfactant.

9. The dye-fixing element as in claim 2, in which the nonionic stabilizer is a nonionic surfactant.

10. The dye-fixing element as in claim 4, in which the nonionic stabilizer is a nonionic surfactant.

11. The dye-fixing element as in claim 1, in which the nonionic stabilizer is a nonionic protective colloid.

12. The dye-fixing element as in claim 2, in which the nonionic stabilizer is a nonionic protective colloid.

13. The dye-fixing element as in claim 4, in which the nonionic stabilizer is a nonionic protective colloid.

14. The dye-fixing element of claim 13, in which the nonionic protective colloid is polyvinyi alcohol or hydroxyethyl cellulose.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

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Page 1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	PATENT ABSTRACTS OF JAPAN vol. 12, no. 119 (P-689)(2966) 14 April 1988 & JP-A-62 245 258 (FUJI PHOTO FILM) 26 October 1987 * page 512 * * abstract * ---	1-14	G03C8/40 G03C8/56 G03C1/81
Y	PATENT ABSTRACTS OF JAPAN vol. 10, no. 358 (P-522)(2415) 2 December 1986 & JP-A-61 156 045 (FUJI PHOTO FILM) 15 July 1986 * abstract * ---	1-14	
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 93 (P-838)(3441) 6 March 1989 & JP-A-63 274 953 (FUJI PHOTO FILM) 11 November 1988 * abstract * ---	1-3	
Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 230 (P-599)(2677) 28 July 1987 & JP-A-62 043 641 (FUJI PHOTO FILM) 25 February 1987 * abstract * ---	1,2,4, 8-10	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C
Y	EP-A-0 219 101 (KONISHIROKU PHOTO INDUSTRY) * claims * ---	1-3	
Y	RESEARCH DISCLOSURE. no. 308, December 1989, HAVANT GB pages 993 - 1015; 'Photographic silver halide emulsions, preparation' * page 1003, paragraph IX - page 1004 * * page 1005, paragraph XI - page 1006 * ---	1-14	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 JUNE 1992	PHILOSOPH L.

CATEGORY OF CITED DOCUMENTS

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)

A	EP-A-0 123 166 (FUJI PHOTO FILM) * page 109, line 1 - page 110, line 4; claims; example 1 *	1,5-7, 11-14	

			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

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THE HAGUE	29 JUNE 1992	PHILOSOPH L.

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