United States Patent [19]

Yoshida

[11] **3,865,593**

[45] **Feb. 11, 1975**

[54] **PHOTOGRAPHIC FILM UNIT FOR A PHOTOGRAPHIC DIFFUSION TRANSFER COLOR PROCESS CONTAINING COUPLER-DEVELOPERS**

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[73] Assignee: **Fuji Photo Film Co. Ltd.**, Kanagawa, Japan

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[30] **Foreign Application Priority Data**

July 5, 1972 Japan 47-67244

[52] **U.S. Cl.** ..... **96/77**, 96/3, 96/29 D

[51] **Int. Cl.** **G03c 1/40**, G03c 7/00, G03c 5/54

[58] **Field of Search** ..... 96/3, 29 D, 77

[56] **References Cited**

UNITED STATES PATENTS

3,537,850	11/1970	Simon	96/29 D
3,537,852	11/1970	Bloom	96/29 D
3,728,113	4/1973	Becker et al.	96/77
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Primary Examiner—Ronald H. Smith
Assistant Examiner—Richard L. Schilling
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & MacPeak

[57] **ABSTRACT**

A non-stripping photographic film unit for a diffusion transfer color process which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members, comprising an image-receiving element having formed on a transparent support a mordant layer, a photosensitive element having at least one photosensitive silver halide emulsion layer, a water in-permeable sheet and a rupturable container retaining an alkaline processing solution, the unit containing in the photosensitive element or the rupturable container a colorless diffusible compound which develops silver halide and yields a dye by reaction with the oxidation product of an aromatic primary amino compound.

49 Claims, 12 Drawing Figures

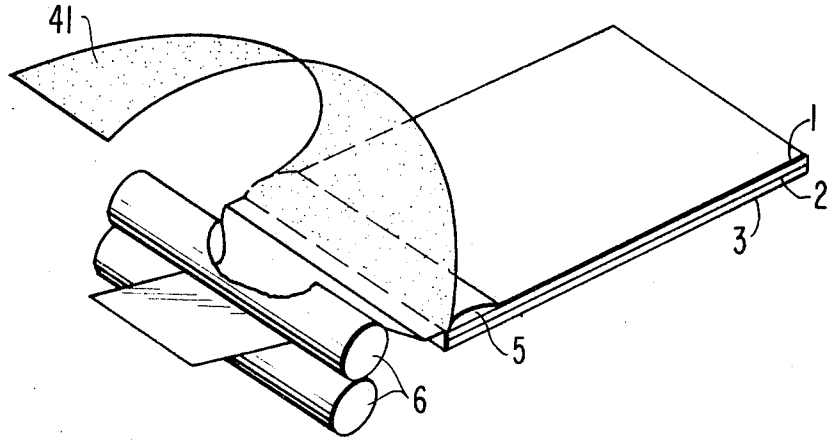


FIG. 1

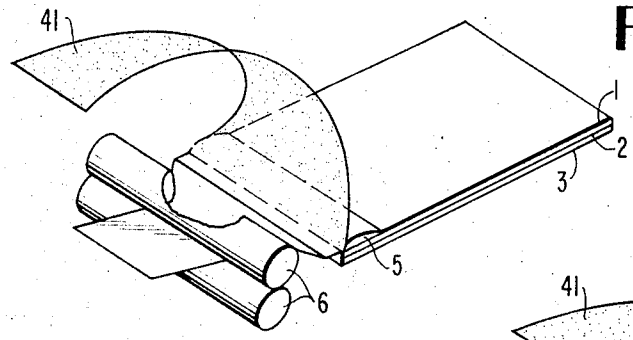
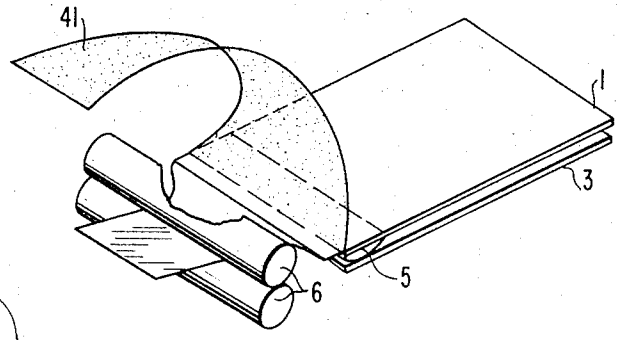


FIG. 2



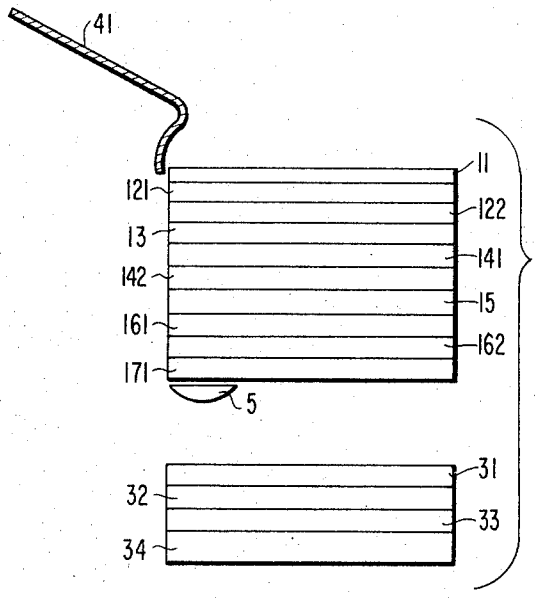


FIG. 3

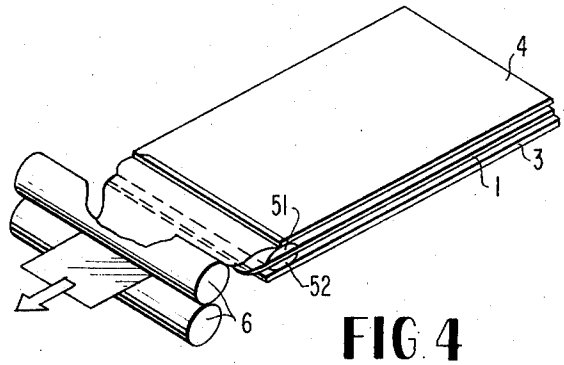


FIG. 4

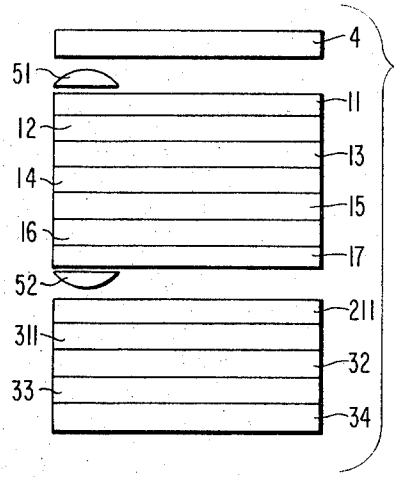


FIG. 5

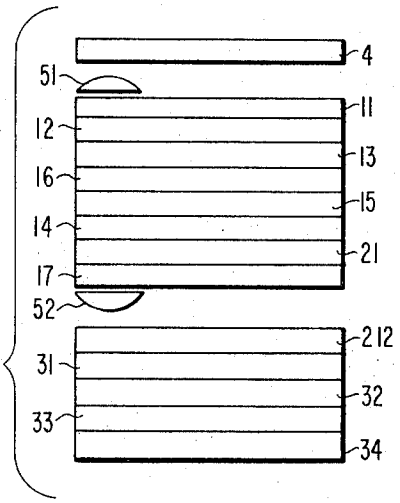


FIG. 6

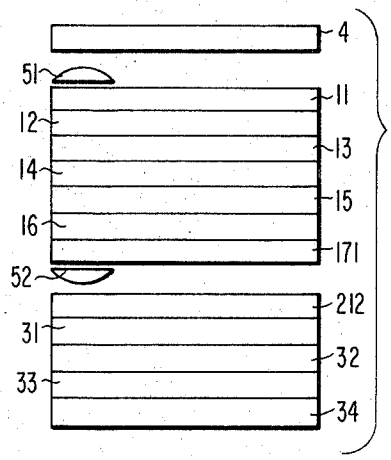


FIG. 7

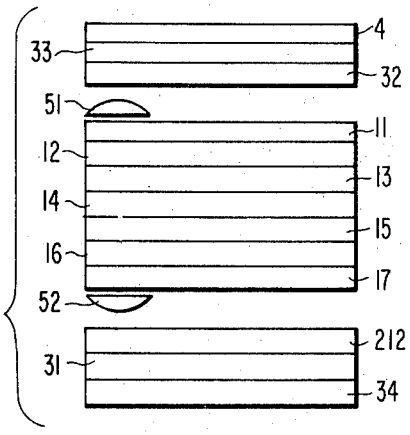


FIG. 8

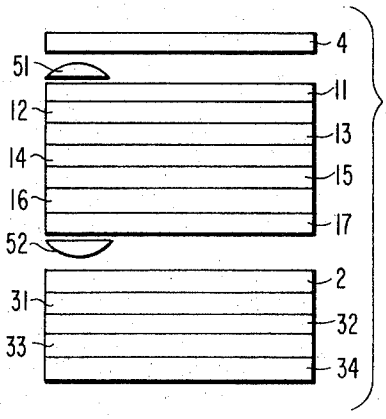


FIG. 9

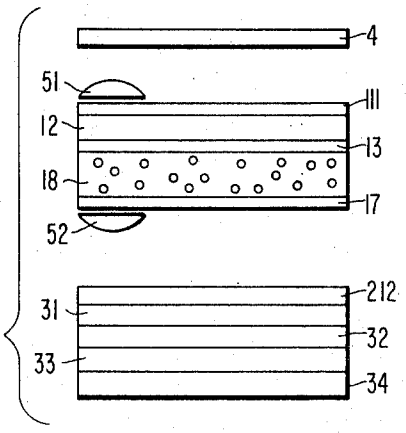
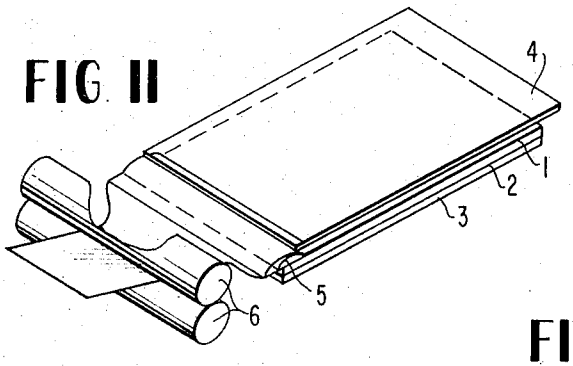


FIG. 10

FIG. 11



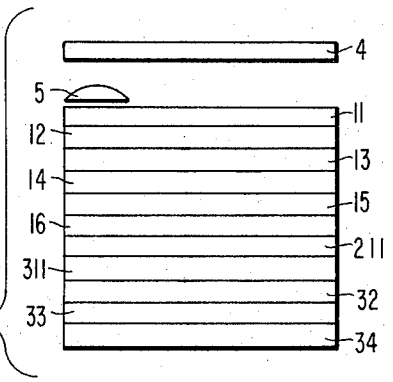


FIG. 12

PHOTOGRAPHIC FILM UNIT FOR A PHOTOGRAPHIC DIFFUSION TRANSFER COLOR PROCESS CONTAINING COUPLER-DEVELOPERS

BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a photographic film unit for a photographic diffusion transfer color process, particularly to a photographic film unit for a photographic diffusion transfer color process containing substantially colorless and diffusible compounds which are developers for silver halides and form dyes by the reaction with the oxidation products of aromatic primary amino compounds (hereinafter, these substantially colorless and diffusible compounds are called "coupler developers").

2. Description of the Prior Art

As is described in U.S. Pat. Nos. 3,415,644; 3,415,645; and 3,415,646, a color photographic diffusion transfer film unit containing a dye developer, that is, a dye which is a silver halide developing agent, provides a diffusion-transferred visible positive image of the dye developer on a mordant layer of the image-receiving element of the film unit without stripping the image-receiving element therefrom by processing the film unit, after exposure in a camera, with the dye developer upon withdrawing the film unit from the camera. However, the above-described system has the fault that since in the system a dye developer which is a colored material in the film unit is used in combination with a silver halide, the amount of light which can effect the silver halide is partially reduced due to light absorption by the dye developer when exposing the film unit. Thus the sensitivity of the film unit cannot be increased.

In U.S. Pat. No. 3,635,707 there is described a system in which a diffusion-transferred color positive image is formed on an image-receiving layer without stripping the image-receiving layer from the photosensitive element of the film unit by processing the film unit with a substantially non-diffusible compound which yields a diffusible dye by reaction with the oxidation product of a developing agent. However, this system essentially requires conductng reversal development in the photosensitive element of the film unit.

SUMMARY OF THE INVENTION

One object of this invention is, therefore, to provide a photographic film unit for a diffusion transfer color process which has high sensitivity and provides diffusion-transferred color positive images without the necessity of conducting reversal development in the film unit.

Another object of this invention is to provide a photographic film unit for a diffusion transfer color process which provides a visible diffusion-transferred color positive image on an image-receiving element without stripping the imagereceiving element from the photosensitive element of the film unit after processing.

As the result of various investigations, the inventors have succeeded in reaching the aforesaid objects of this invention, i.e., according to the present invention there is provided a photographic film unit for a diffusion transfer color process which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members and which comprises the combination, in sequence, of:

1. an image-receiving element having formed on a transparent support a mordant layer,
2. a photosensitive element having at least one photosensitive silver halide emulsion layer,
3. a water impermeable sheet, and
4. at least one of
   a. rupturable container capable of releasing, upon rupturing, its contents between the image-receiving element (1) and the photosensitive element (2), and
   b. a rupturable container capable of releasing, upon rupturing, its contents between the photosensitive element (2) and the water impermeable sheet, the photosensitive element (2) ship it comes containing a substantially colorless diffusible compound which develops silver halide and which is capable of forming a dye by reaction with the oxidation product of an aromatic primary amino compound, at least one of the rupturable containers containing an alkaline processing solution,

A. the film unit containing an aromatic primary amino compound and an oxidizing agent together or separately in one or more members of the image-receiving element (1), the photosensitive element (2), the water impermeable sheet (3) and at least one of the rupturable containers (a) and (b), and

B. the film unit containing a shading agent in

i. at least one of the following: a layer disposed between the photosensitive silver halide emulsion layer of the photosensitive element (2) most adjacent to the image-receiving element (1) and the mordant layer of the imagereceiving element and the rupturable container (a) or

ii. at least one of the water impermeable sheet (3) and the rupturable container (b).

DETAILED DESCRIPTION OF THE INVENTION

The film units of this invention are used for forming monochromatic or multicolor positive images. In a three color system, each silver halide emulsion layer of the photosensitive element used in this invention is combined with a coupler developer forming a complementary color dye to the main sensitive region of the silver halide emulsion. That is, a blue-sensitive emulsion layer is associated with a coupler developer forming a yellow dye, a green-sensitive silver halide emulsion layer is associated with a coupler developer forming a magenta dye, and a red-sensitive silver halide emulsion layer is associated with a coupler developer forming a cyan dye. Each coupler developer associated with each corresponding silver halide emulsion layer can be incorporated in the silver halide emulsion layer or in a layer adjacent thereto.

The silver halide emulsion layers of the multicolor photo sensitive emulsion layers are formed on the support in the order usually used in this art, that is, from the exposure side, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer. If desired, a yellow filter layer may be disposed between the blue-sensitive silver halide emulsion layer and the green-sensitive silver halide emulsion layer to absorb blue light transmitted through the blue-sensitive emulsion layer. An intermediate layer may also be disposed between any two silver halide emulsion layers. The

above-described layers may be formed on a proper transparent support or may be superposed on the image-receiving element which will be later described.

The silver halide emulsion of the photosensitive element used in this invention contains silver chloride, silver bromide, silver chlorobromide, silver iodobromide, silver chloroiodide, silver chlorobromoiodide or a mixture thereof. Such silver halide emulsions can be prepared by any well known method. For instance, there are single jet emulsion, double jet emulsions, Lipmann emulsions, emulsions formed by the ammonia method, emulsions formed by conversion method, etc., and they may be prepared according to the methods described in, e.g., U.S. Pat. Nos. 2,222,264; 3,320,069; 3,271,157; 2,592,250; 3,206,313; and 3,447,927.

The silver halide emulsions used in this invention may further be chemically ripened with sulfur, gold, platinum, palladium, or tellurium compounds as described in U.S. Pat. Nos. 1,623,497; 2,399,083; 3,297,447; and 3,297,446; if desired.

The color sensitization of the silver halide emulsions of this invention can be conducted by any known method. For instance, as disclosed in U.S. Pat. No. 1,154,781, the silver halide emulsion can be color-sensitized by adding a solution of a sensitizing dye in an organic solvent to the emulsion and after stirring, allowing the mixture to stand.

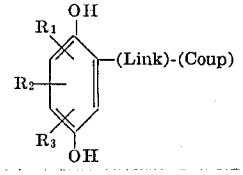
Examples of the sensitizing dyes useful for color sensitizing silver halide emulsions are cyanines, merocyanine, styryl, hemicyanine, and hemioxonole as disclosed in U.S. Pat. Nos. 2,526,632; 2,503,776; 2,493,748; and 3,384,486. The sensitizing dyes as described above can be used individually or, if desired, as a mixture of two or more thereof.

Examplary useful cyanine dyes are, for example, in F. M. HAMER, "The Cyanine Dyes and Related Compounds" published by Interscience, and P. Glafkides "Chimie Photographique" 2nd Edition 1957, published by Paul Montel, Paris, Chapters 35 to 41.

The silver halide emulsions used in this invention may further contain a development accelerator, such as polyalkylene glycol, a cationic surface active agent or a thioether. Moreover, to prevent an increase in fog and a reduction in sensitivity while the silver halide emulsion is stored, it may contain a stabilizer such as the thiazonium compounds as disclosed in U.S. Pat. Nos. 2,131,038 and 2,694,716, the azaindenes as disclosed in U.S. Pat. Nos. 2,886,437 and 2,444,605, the mercury salts as disclosed in U.S. Pat. No. 2,728,663, the urazols as disclosed in U.S. Pat. No. 3,287,135, the sulfocatechols as disclosed in U.S. Pat. No. 3,236,652, the oximes as disclosed in British Pat. No. 623,448, the nitroindazole mercaptotetrazoles as disclosed in U.S. Pat. Nos. 2,403,927; 3,266,897 and 3,397,987, the polyvalent metal salts as disclosed in U.S. Pat. No. 2,839,405, and the palladium salts, platinum salts, and gold salts as disclosed in U.S. Pat. Nos. 2,566,263 and 2,597,915.

The coupler developer, which is the most characteristic component of this invention, is a developer for silver halides and forms a dye by reaction with the oxidation product of an aromatic primary amino compound. The coupler developer is diffusible in an alkaline processing solution but reduces in diffusibility when the coupler developer develops silver halide. When a coupler developer develops silver halide, the coupler developer changes to the quinone form from the hydroquinone form, and the quinone form of the coupler developer is substantially insoluble in an aqueous solution and is nondiffusible. Further, the quinone form of the coupler developer hardens gelatin binder. Such a coupler developer is substantially colorless and is completely different from the dye developers described in U.S. Pat. Nos. 3,415,644; 3,415,645; 3,415,646; 3,473,925; and 2,983,606. The coupler developer used in this invention further has the property that it is dissolved and diffused in an alkaline processing solution and thus is completely different from the compounds disclosed in U.S. Pat. No. 3,635,707 which are essentially non-diffusible in an alkaline processing solution (which is most preferably at a pH above 12).

The coupler developers used in this invention include the compounds represented by the general formula



wherein

1. (Coup) stands for a coupler compound well known in color photographic process, which has a structure capable of forming a dye by the reaction with the oxidation product of an aromatic primary amino compound, said dye having, preferably, its main absorption region in a blue, green, or red region, and can be selected from
   a. phenols and naphthols;
   b. active methylene-containing compounds such as benzoylacetanilides and 1-phenyl-5-pyrazolones and
   c. cyanoacetyls, phenylacetonitriles pyrazolos, pyrazolo-benzimidazoles and indazoline-3-ons.

The main nucleus of the coupler is essentially a phenol, aniline or chain or cyclic radical having an active methylene group and such are described in detail "The Theory of the Photographic Process" by C. E. K. Mees 3rd Edition pages 383 to 394, and by W. Pelz in "Farb K uppler" AGFA Mittelungen Lever Kusen Vol. 3 page 111–175 (1961).

2. (Link) stands for the group connecting (Coup) and hydroquinone, and can be selected from alkylene, most preferably C_1–C_3 alkylene, the connecting group being connected to (Coup) at a position other than the coupling site.

3. R_1, R_2 and R_3 each represent a hydrogen atom, a hydroxyl group, a halogen atom, an alkyl group, or an alkoxyl group, the latter two most preferably being of C_1–C_3.

The coupler developer can have a catechol nucleus (bonding at the 4-position) in place of a hydroquinone nucleus as the developer nucleus, but it is preferred that the developing nucleus be a hydroquinone nucleus.

The coupler developers used in this invention can be prepared by various methods. For instance, they can be easily prepared by the reaction of the hydroquinone derivatives as described in the examples of U.S. Pat. Nos. 3,134,764; 3,134,765; 3,173,906; 3,208,991; 3,218,312; 3,135,734; 3,201,384; 3,262,924; 3,252,969 and 3,297,441 with the compounds known as color couplers described in the examples Belgian

Pat. No. 616,867; German Pat. Nos. 1,124,356 and 1,187,479; British Pat. Nos. 873,125 and 856,158; U.S. Pat. No. 3,062,653; British Pat. Nos. 872,886 and 918,128; German Pat. No. 1,103,761; British Pat. No. 890,305; Belgian Pat. Nos. 644,330 and 643,146; U.S. Pat. Nos. 2,311,082 and 2,619,419; German Pat. No. 1,101,429; U.S. Pat. No. 2,983,608; British Pat. No. 956,261; German Pat. Nos. 1,176,478 and 1,187,478; U.S. Pat. No. 2,964,402; German Pat. No. 1,111,505; British Pat. No. 837,360; U.S. Pat. Nos. 2,350,812; 2,293,004 and 2,976,146; French Pat. No. 1,323,977; German Pat. Nos. 1,163,144; 1,109,522 and 1,137,311; U.S. Pat. Nos. 3,002,836 and 2,589,004; British Pat. No. 833,596; Belgian Pat. Nos. 613,328 and 590,403; British Pat. No. 858,564; U.S. Pat. No. 3,056,674; British Pat. No. 808,276; Belgian Pat. Nos. 636,700 and 611,885; British Pat. No. 865,492; German Pat. No. 1,176,479; and Japanese Pat. Nos. 4085/59; 18,333/60; 21,711/61; 18,145/63; 6030/65; 27,563/64 and 2/64.

It is preferred that the coupler developer used in this invention be diffusible in the presence of an alkaline processing solution but non-diffusible in the photosensitive element before processing by the alkaline processing solution (i.e., in the photosensitive element in which an alkaline processing solution is not present). If the coupler developer present in the photosensitive element before processing by an alkaline processing solution is diffusible, another coupler developer which is not the coupler developer forming a dye absorbing light in the range of the complementary color to the main photosensitive region of the emulsion layer containing the aforesaid coupler developer partially enters the above-described emulsion layer by diffusion, which results in color mixing or reducing the color reproducibility. In order to prevent the occurence of such a fault, it is preferred that the coupler developer be dissolved in a high boiling solvent and the solution be dispersed in a hydrophilic colloid to confine the coupler developer in the fine particles of the high boiling solvent in the dissolved state. Preferable solvents have a boiling point above 120°C. For example, alkyl phthalates whose alkyl group has 1–6 carbon atoms such as methyl phthalate, ethyl phthalate, propyl phthalate, n-butyl phthalate, propyl phthalate, di-n-butyl phthalate, anyl phthalate, iso-amyl phthalate and dioctyl phthalate, phosphoric acid esters such as triphenyl phosphate, tricresyl phosphate, diphenyl-mono-p-tert-butylphenyl phosphate, alkylamides or acetoanilides such as N-n-butylacetanilide, n-methyl-p-methylacetanilide, etc. Preferred hydrophilic colloids are gelatin, polyvinyl alcohol, etc.

While not especially limitative, in each layer silver is usually $0.1–10\times10^{-4}$ mole/100 cm^2, the coupler developer is usually $0.5–50\times10^{-5}$ mole/100 cm^2 and the ratio of Ag/coupler developer is usually 1–10 (molar ratio).

Furthermore, in order to prevent the dispersed fine particles of the high boiling solvent containing the coupler developer from being associated in the binder (dispersed oil coagulutes) of the photosensitive element, to prevent the coupler developer from being crystallized in the coating and to improve the ease of coating of the coating composition containing the coupler developer, various conventional additives can be used. For instance, there can be used a surface active agent such as saponin; an anionic compound such as the alkylarylsulfonic acids described in U.S. Pat. No. 2,600,831; the amphoteric compounds described in U.S. Pat. No. 3,133,816; and the water-solubilizing additives of glycidol and an alkylphenol as described in U.S. Pat. No. 3,133,816. Moreover, to adjust the pH thereof, citric acid, boric acid, etc., can be added,

The photosensitive element used in this invention may be provided with if desired a protective layer, intermediate layers, a filter layer, an antihalation layer, an ultraviolet absorption layer, etc.

In the film unit of this invention a compound called an auxiliary developing agent can be used, for example a benzenoid-type silver halide developing agent, i.e., a silver halide developing agent having a benzene nucleus or a naphthalene nucleus having at least two substituents selected from the class a hydroxyl group, an amino group, and an alkylamino group capable of forming an oxidation product of a quinoid-type silver halide developing agent by developing the exposed silver halide. Examples of such an auxiliary silver halide developing agent are hydroxyphenyl hydroquinone, phenyl hydroquinone, 4′-methylphenyl hydroquinone p-(t)-butylcatechol, (t)butyl hydroquinone, etc. Examples of other auxiliary developing agents are 3-pyrazolidones, and preferred examples thereof are 1-phenyl-3-pyrazolidone and 1-(p-methyl)-phenyl-3-pyrazolidone. The auxiliary developing agent can be incorporated in a protective layer, a silver halide emulsion layer, a coupler developer layer, an intermediate layer, or in more than one of such layers, etc., of the photosensitive element as described in U.S. Pat. Nos. 3,266,842 and 1,243,539 and Japanese Pat. Nos. 17,383/60 and 393/64. The main purpose of using such an auxiliary developing agent is to accelerate the development of the exposed silver halide by the coupler developer. The use of the auxiliary developing agent also results in a reduction of the minimum density of the positive image formed on the mordant layer, an increase of the maximum density thereof and an improvement in color separation. See also British Pat. Nos. 1,243,539, and Japanese Pat. Publications Nos. 4839/60, 10240/69, 2241/62, 29130/64 and 13837/68. Usually from 10 to 1/100 mole of auxiliary developing agent/mole of coupler developer is used.

As the binder for the protective layer, the silver halide emulsion layer, the coupler developer layer, the intermediate layer, etc., of the photosensitive element in this invention, there are illustrated gelatin, gelatin containing calcium alginate and gelatin phthalate. Examples of other binders are those described in U.S. Pat. No. 3,384,483 and also polyvinylamide, polyacrylamide, polyvinyl alcohol, polyvinyl pyrrolidone, cellulose derivatives, polysaccharide, etc. The above-described binders may be used individually or as a mixture thereof. The binder or binders may further be used together with various hardening agents.

In the photosensitive element of this invention, the silver halide emulsion layer or layers each associated with each coupler developer may be formed on an alkali-permeable support such as a transparent or opaque sheet of polyvinyl alcohol or gelatin, i.e., coupler developer is incorporated in a silver halide emulsion layer or an adjacent layer thereof.

Also, as illustrated in FIG. 2 of the accompanying drawings, in the embodiment of the film unit of this invention where a photosensitive element is faced to an image-receiving element with a space between them so that an alkaline processing solution can be spread be-

tween the elements, the support for the photosensitive element need not necessarily be an alkali-permeable support but can be a transparent support if the support is not positioned at the side facing the image-receiving element. Any supports known in photographic field can be used as such a transparent support, e.g., polyethylene terephthalate film, cellulose triacetate film, polycarbonate film, etc.

The silver halide emulsion layers may be coated in multi-layers on the support or may be incorporated in one layer as microcapsules containing each if them separately, as described in U.S. Pat. Nos. 2,800,457; 2,800,458; and 2,907,682. The technique of producing such microcapsules for photosensitive elements is described practically in U.S. Pat. Nos. 3,466,662 and 3,276,869.

On the other hand, as the support for the image-receiving element which comprises a mordant layer on a transparent support, a dimensionally stable transparent support is used. For instance, there are illustrated as such supports, a cellulose acetate film (cellulose triacetate film, cellulose diacetate film, etc.), a cellulose acetate butyrate film, a polyvinyl acetal film, a polystyrene film, a polyethylene terephthalate film, a polycarbonate film, a glass sheet etc.

As the mordant material for the mordant layer there can be used any material having the function of mordanting or fixing the dye formed by the coupling of the coupler developer and the oxidation product of an aromatic primary amino compound.

As an image-receiving material, it is necessary to use a material which has a layer which is hydrophilic and which is capable of mordanting a diffusible dye. So, it is preferred to use a hydrophilic, basic and film-forming polymer or a hydrophilic and film-forming polymer containing a basic polymer. As specific examples of the image-receiving layer in this invention, a mixture of polyvinyl alcohol and poly-4-vinyl pyridine as described in U.S. Pat. No. 3,148,061 is preferably used, but other materials such as a partially acetalated product of polyvinyl alcohol (degree of acetylation is no more than 20%), and trialkyl-ammonium benzaldehyde quaternary salt, a copolymer of vinyl alcohol and N-vinylpyrrolidone (any copolymerization ratio can be used), a condensed acetalation product (from about 4 : 1 to about 2 : 1 molar condensate) of polyvinyl alcohol and poly-N-vinylpyrrolidone, and a condensed acetalation product (from about 4 : 1 to about 2 : 1 molar condensate) of polyvinyl alcohol and 4-pyridine carboxaldehyde can also be used for the image-receiving layer. This listing is merely exemplary of materials which meet the above general criteria.

As further examples of such materials, there are the basic polymers such as polymers of the aminoguanidine derivatives of vinylmethyl ketone as disclosed in U.S. Pat. No. 2,882,156. Other examples of useful compounds for the mordant layer in this invention are poly-4-vinylpyridine and poly-2-vinylpyridine and such polymers as are described in U.S. Pat. No. 2,484,430. Those compounds may be used together with an alkali-permeable polymer such as N-methoxymethyl polyhexyl-methylene adipic acid, partially hydrolyzed polyvinyl acetate, polyvinyl alcohol, cellulose acetate, gelatin, etc.

The mordant layer may contain an ultraviolet absorbent to prevent fading of the dyes formed thereon and, further, a stilbene, triazine, or oxazole derivative, etc., to make the color image bright. Moreover, to control the gradation of the development of the silver halide in the photosensitive element after permeation of an alkaline processing solution, the mordant layer may contain a development inhibitor such as a mercaptotetrazole, benzotriazole, an iodine compound, etc., which can be dissolved in the alkaline processing solution.

Preferred of the aromatic primary amino compounds as are used in this invention are the p-phenylenediamine derivatives which are well known in the field of color photography. Examples of such derivatives are 4-amino-N,N-diethyl-3-methylaniline, N,N-diethyl-p-phenylenediamine, N-ethyl-N-(β-methanesulfonamido)-ethyl-3-methyl-4-aminoaniline, 4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)-aniline, 4-amino-N-ethyl-3-methoxy-N-(β-sulfoethyl)-aniline, 4-amino-N-ethyl-N-(β-hydroxyethyl)aniline, 4-amino-N,N-diethyl-3-hydroxymethylaniline, 4-amino-N-methyl-N-(β-carboxyethyl) aniline, 4-amino-N,N-bis(β-hydroxyethyl)aniline, 4-amino-N,N-bis(β-hydroxyethyl)aniline, 4-amino-N,N-bis(β-hydroxyethyl)-3-methylaniline, 3-acetamido-4-amino-N,N-bis(β-hydroxyethyl)-aniline, 4-amino-N-ethyl-N-(2,3-dihydroxypropyl)-3-methyl-aniline sulfate, 4-amino-N,N-diethyl-3-(3-hydroxypropoxy)aniline, etc. Usually these amines are used in an amount of 0.1–5 wt % of the processing solution.

Such an aromatic primary amino compound can be incorporated in the image-receiving element and, in the case of using, for instance, the mordant layer, the aromatic primary amino compound can be used by dispersing it in the aforesaid alkali-permeable polymer as a solution thereof in an organic solvent. For example, the primary amino compound can be dissolved in an oil (high boiling point solvent as heretofore discussed) and then dispersed in the coating solution of the mordant layer. Or the primary amino compound is dissolved in aqueous weakly acidic solution, and then this is mixed with the aqueous solution of the polymer. It can also be used by mixing a solution thereof with an alkaline aqueous solution. The aromatic primary amino compound may also be incorporated in either rupturable container of the film unit together with an alkali or may be incorporated in a layer adjacent the mordant layer, and moreover it may be incorporated in a layer of the photosensitive element or a layer of the water impermeable sheet (which can be in multi-layer form) of the film unit of this invention.

The aromatic primary amino compound would thus be incorporated in one or more of the following:

a. the mordant layer;

b. in either of the rupturable containers;

c. in a layer adjacent the mordant layer (in this case it would be a layer especially to hold the aromatic primary amino compound for example, by dissolving it in a high boiling point solvent as earlier defined and the emulsifying it in aqueous gelatin;

d. in any layer of the photosensitive elements;

e. in the water impermeable sheet.

In the present invention an oxidizing agent for oxidizing the above-indicated aromatic primary amino compound is used, preferably, at a 1 : 1 molar ratio. Examples of the oxidizing agent are potassium ferricyanide, hydrogen peroxide, potassium bichromate, ammonium persulfate, copper sulfate, exposed silver halide, quinone, etc., which are well known in the art. Such an oxidizing agent can be incorporated in a layer of the im-

age-receiving element or it may be incorporated in a member other than the image-receiving element. For instance, the oxidizing agent can be added to the rupturable container or in a layer of the photosensitive element.

The aromatic primary amino compound and the oxidizing agent can be present together or separately. Any assembly where the aromatic primary amino compound and oxidizing agent are mixed for the first time at the time of developing is preferred.

In the film unit of this invention, the use of a pH decreasing layer is effective to increase the stability of the transferred image and to improve the color reproducibility.

The pH decreasing layer generally has the effect of reducing the pH of the image-receiving layer which will have a pH of 11–14 by the permeation of the alkaline processing solution to a pH lower than 11, preferably 5–8 in a short length of time. It preferably has a dry thickness of 5–20 μ. The polymer acids as described in U.S. Pat. No. 3,362,819 can be used as the pH decreasing layer, for example. The polymer acid lowers the pH of the film assembly after development, stops the further transfer of the coupler developer, and further stabilizes the transferred color image. The polymer acid contains an acid group such as a carboxylic acid group or a sulfonic acid group and the acid group usually forms a sodium salt or a potassium salt or is combined with a quaternary ammonium salt such as ammonium 4-methylperoxide. The polymer may have been partially anhydrated (acid anhydride form) or may form a lactone, or may be combined with a base.

Examples of such a compound are cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, cellulose acetate succinate hydrogen phthalate, the ether and ester derivatives of cellulose treated with sulfo anhydide, polystyrene sulfonic acid, carboxymethyl cellulose, polyvinylhydrogen phthalate, polyvinyl acetate hydrogen phthalate, polyacrylic acid, and the acetal of polyvinyl alcohol treated with a carboxy- or sulfo-substituted aldehyde. Other compounds as described in U.S. Pat. Nos. 3,422,075 and 2,635,048 can also be used.

The pH decreasing layer is ordinary disposed between the mordant layer and the support of the image receiving layer of the film unit, but if the desired function is obtained the layer may be disposed at any position of the film unit or further, as described in U.S. Pat. No. 3,361,821, the polymer acid may be encapsulated by a polymer material and added to the photosensitive element or may be dispersed in an alkali permeable binder and added to the photosensitive element. In this case the alkaline processing solution permeates through the wall covering the dispersed particles of the polymer acid and hence the pH of the processing solution is reduced, which results in stabilizing the color image formed on the mordant layer of the film unit.

A photographically inactive timing layer or a spacer layer may be formed adjacent the pH decreasing layer. The timing layer is used to control the pH of the film unit so that it decreases as a function of the speed of the permeation of the alkaline processing solution through the inactive spacer layer. It is preferred that after the coupler developer is imagewise diffused and the coupling of the diffused coupler developer with the oxidation product of the aromatic primary amino compound is completed, the pH of the film unit decrease rapidly and then remain at about 5–8. It preferably has a 2–20 μ thickness (dry thickness). As such a timing layer, gelatin and polyvinyl alcohol can be used, and, further, the polymers described in U.S. Pat. No. 3,455,686 can also be used. Furthermore, the imagewise diffusion of the coupler developer and the coupling of the coupler developer and the oxidation product of the aromatic primary amino compound are a function of temperature, and hence the neutralization of the alkali is also a function of temperature. Therefore, it is useful to utilize the following compounds, individually or as a mixture thereof, for the timing layer or the spacer layer, that is, the hydratable polymers such as polyvinyl acetate, polyamide, polyvinyl ether, and the partial acetate of polyvinyl alcohol.

In the present invention an alkaline processing solution is placed in a rupturable container. As the alkaline processing solution, there can be illustrated aqueous alkaline solutions of sodium hydroxide, potassium hydroxide, sodium carbonate, lithium hydroxide, and diethylamine. The pH of the solution is preferably over 11. It is also preferable that the processing solution contain a high molecular weight polymer to increase the viscosity of the solution, e.g., hydroxyethyl cellulose and carboxymethyl cellulose. The amount of the viscosity increasing agent is about 1–5% of the total amount of the processing solution or it is added to the processing solution to adjust the viscosity thereof to 100–200,000 c. p. s.

In order to accelerate the development of silver halide, increase the maximum density of the mordanted color image on the posi layer, decrease the minimum density and to improve the color separation in color reproduction, an onium compound such as quaternary ammonium compound quaternary sulfonium compound or quaternary phosphonium compound can be added to the processing solution. Specific examples of such onium compounds include 1-ethylpyridinium bromide, lauryldimethylsulfonium cetyltrimethylammonium bromide, p-toluene-sulfonic acid and 1benzyl-α-picolinium tosylate tetraethyl phosphonium bromide. Usually 0.1–2 wt % based on processing solution of omium compound is used.

As the shading agent used in this invention, there are illustrated carbon black, barium sulfate, zinc oxide, barium stearate, silver powder, silica powder, alumina powder, zirconium oxide, zirconium acetylacetate, sodium zirconium sulfate, kaolin, mica, titanium dioxide, and organic dyes such as nigrosin. If necessary, two or more compounds as mentioned above may be used together to obtain a desired shading effect.

The shading agent is used to make the development of the film unit possible in a light place after exposing and withdrawing the film unit from the camera, and hence the shading agent can be incorporated in any part of the film unit so long as the photosensitive silver halide emulsion layers of the photosensitive element are prevented from being exposed to radiation which exposes the emulsions. That is, (i) the shading agent is incorporated in at one or more layers disposed between the mordant layer of the image-receiving element and the photosensitive silver halide emulsion layer of the photosensitive element most adjacent the image-receiving element and the rupturable container which will spread its contents between the photosensitive element and the image-receiving element or (ii) the shad-

ing agent is incorporated in at least one of the water impermeable sheet and the rupturable container which will spread its contents between the water impermeable sheet and the photosensitive element.

When the shading agent is added to the alkaline processing solution in the rupturable container, good results are obtained using the shading agent, e.g., carbon black or titanium dioxide, in an amount of 5–40% by weight of the processing solution.

In the case of adding the shading agent to the alkaline processing solution, it can be dissolved or suspended in the solution. In the case of incorporating the shading agent in the coating of the film unit, the shading agent is finely dispersed in an alkali-permeable binder such as polyvinyl alcohol and gelatin, followed by coating, e.g., 10% of carbon black by weight based on gelatin can be used at a dry thickness of 4 μ.

The shading agent is a material that shades light by absorbing or reflecting light, and in the film unit of this invention it is preferred, when the mordant layer is formed on a transparent support, to provide the shading agent reflecting light between the mordant layer and the photosensitive element. By employing such a configuration, the transferred color image can be clearly seen with high density due to the presence of the layer of the shading agent reflecting light at the back side of the mordant layer when observing the color image formed on the mordant layer through the transparent support.

Generally, density is above 4, preferably about 10, for the shading agent.

Specific examples of the processing solution are shown below, although the processing solution used in this invention is not limited to be taken as limited thereto to them only (I, II are for shading, III and IV are for developing):

I:	Water	100 ml
	Hydroxyethyl cellulose	3.2 g
	Titanium dioxide	6.0 g
II:	Water	100 ml
	Sodium hydroxide	3.0 g
	Hydroxyethyl cellulose	3.2 g
	Carbon black	0.6 g
III:	Water	100 ml
	Potassium hydroxide	3.5 g
	Hydroxyethyl celluose	5.5 g
	1-Benzyl-α-picolinium bromide	0.8 g
	Brium sulfate	10.0 g
IV:	Water	100 ml
	Sodium hydroxide	3.0 g
	3-Methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline	3.0 g
	1-Ethyl-pyridinium bromide	0.8 g
	Benzotriazole	0.5 g
	Titanium dioxide	7.0 g
	Hydroxyethyl cellulose	3.0 g

The water impermeable sheet can be selected from the transparent supports of the image-receiving elements used in this invention.

Preferred film units of this invention are illustrated in the accompanying drawings wherein like numbers refer to like components, and each element is shown in a diagrammatic enlarged cross-sectional view.

FIG. **1** is a perspective view showing an embodiment of the film unit of this invention. In the embodiment of FIG. **1**, a shade layer **2** and a photosensitive element are formed, in sequence, on an image-receiving element **3** and a shading water impermeable sheet **41** is connected thereto along the leading edge thereof. A rupturable container **5** containing the alkaline processing solution is position at the leading edge of the photosensitive element **1**. Numberal **6** represents pressure-applying rollers.

The shading water impermeable sheet **41** of the film unit of this type is so constructed that it does not obstruct the exposure of the photosensitive element **1** in the camera and then it is laminated on the photosensitive element by passing the film assembly, after exposure in the camera, through the rollers **6**. In this case the container **5** is ruptured and its contents spread between the photosensitive element and the shading water impermeable sheet.

Thus, the photosensitive element **1** of the film assembly withdrawn from the cameral is protected from unnecessary exposure by the shading water impermeable sheet **41** and the shade layer **2**.

FIG. **2** is a perspective view showing another embodiment of the film assembly of this invention, in which a photosensitive element **1** faces an image-receiving element **3** with a space therebetween and a rupturable container **5** containing an alkaline processing solution is so positioned that the processing solution will spread between the two elements when ruptured.

FIG. **3** is an enlarged cross-sectional view of the film unit shown in FIG. **2**. The photosensitive element comprises an alkali-permeable support **171** containing an oxidizing agent having coated thereon a red-sensitive emulsion layer **162**, a layer **161** containing cyan coupler developer, an intermediate layer **15**, a green-sensitive emulsion layer **142**, a layer **141** containing a magenta coupler developer, a yellow filter layer **13**, a blue-sensitive emulsion layer **122**, a layer **121** containing a yellow coupler developer, and a protective layer **11**. The image-receiving element comprises a transparent support **34** having coated thereon an alkali neutralizing layer **33**, spacer layer **32**, a mordant layer **31**. The rupturable container **5** retains an alkaline processing solution containing the aromatic primary amino compound and the shading agent.

In this embodiment, the film unit is exposed from the side of the protective layer in camera. When the film unit is exposed, the protective layer is not covered with shading sheet. After exposure, the film unit is passed through the pressure-applying rollers **6** in the case withdrawing the film unit from the camera, whereby the container **5** is ruptured and the processing solution is spread between the oxidizing agent-containing alkali-permeable support **171** of the photosensitive element and the mordant layer **31** of the image-receiving element and at the same time the shading water non-permeable sheet **41** is laminated onto the protective layer **11**. The processing solution thus spread permeates into the photosensitive element and thus the silver halide in each silver halide emulsion layer exposed in the aforesaid exposure step is developed by the coupler developer associated with the emulsion layer. The coupler developer thus used for the development of the silver halide becomes non-diffusible. On the other hand, the coupler developer which was not used for the development of the silver halide diffuses at least partially to the mordant layer and causes a coupling therein with the aromatic primary amino compound in the processing solution oxidized by the oxidizing agent contained in the alkali-permeable support **171**. The dye formed by the coupling dyes the mordant layer **31** to provide a positive image. The alkaline processing solution permeated in the image-receiving element is neutralized at

a proper rate by the space layer **32** adjacent the mordant layer **31** and the alkali neutralizing layer **33**, and hence does not have a harmful influence on the dye image in the mordant layer due to high pH, whereby a positive image of good stability and the desired image density is obtained. The positive image thus formed can be observed from the side of the transparent support **34** without stiripping the photosensitive element.

FIG. **4** is a perspective view showing still other embodiment of the film unit of this invention, in which a transparent water impermeable sheet **4** is used and the film unit has two rupturable containers **51** and **52**. In this embodiment, the transparent water impermeable sheet **4**, the photosensitive element **1**, and the image-receiving element **3** are disposed with a space between them and the rupturable containers **51** and **52** are so positioned that they spread their contents between the sheet **4** and the photosensitive element **1** and between the photosensitive element **1** and the image-receiving element **3**, respectively.

FIG. **5** to FIG. **10** are perspective views of various specific embodiments of the film unit shown in FIG. **4**.

In the embodiment shown in FIG. **5**, numeral **4** represents the transparent water impermeable sheet. The photosensitive element comprises an alkali-permeable support **17** having coated thereon a red-sensitive emulsion layer containing a cyan coupler developer, an intermediate layer **15**, a green-sensitive emulsion layer **14** containing a magenta coupler developer, a yellow filter layer **13**, a blue-sensitive emulsion layer **12** containing a yellow coupler developer, and a protective layer **11**. The image-receiving element comprises a transparent support **34** having coated thereon an alkali neutralizing layer **33**, a spacer layer **32**, a mordant layer **311** containing an oxidizing agent, and a layer **211** containing an aromatic primary amino compound and a shading agent. The container **51** contains processing solution II heretofore identified and is so positioned that its contents are spread, on rupturing, between the transparent water impermeable sheet **4** and the protective layer **11**, and the container **52** contains processing solution II heretofore identified and is so positioned that its contents are spread, on rupturing, between the lakali-permeable support **17** of the photosensitive element and the layer **211** of the image-receiving element containing an alkaline processing solution containing the shading agent.

The film unit is exposed in the camera from the side of the transparent impermeable sheet **4** and then the film unit is passed through the pressure-applying rollers **6** by withdrawing it from the camera, whereby the contents of the rupturable containers **51** and **52** are spread between the elements, respectively. Since the processing solution in the container contains the shading agent, the photosensitive element is protected from light exposure after the film unit is withdrawn from the camera. Thus, a positive image is formed on the mordant layer and the image can be observed from the side of the transparent support of the image-receiving element.

In the embodiment shown in FIG. **6**, the positions of the green-sensitive emulsion layer **14** containing the magenta coupler developer and the red-sensitive emulsion layer **16** containing the cyan coupler developer in the embodiment shown by FIG. **5** are reversed and a layer **21** containing an aromatic primary amino compound is formed on the alkali-permeable support **17**. The layer **212** of the image-receiving element contains the oxidizing agent and the shading agent. The rupturable container **51** contains a solution containing the shading agent and the rupturable contaner **52** contains the alkaline processing solution containing the shading agent.

In the embodiment shown in FIG. **7**, the alkali-permeable support **171** of the photosensitive element contains a shading agent and also a layer **212** containing an oxidizing agent and a shading agent is formed on the image-receiving element. The rupturable container **51** contains a shading agent and the rupturable container **52** contains an alkaline processing solution containing an aromatic primary amino compound.

In the embodiment shown in FIG. **8**, an alkali neutralizing layer **33** and a spacer layer **32** are formed, in sequence, on a transparent water impermeable sheet **4**. The rupturable container **51** contains an alkaline processing solution containing a shading agent and the rupturable container **52** contains an alkaline processing solution and an aromatic primary amino compound.

In the embodiment shown in FIG. **9**, a shade layer **2** is formed on the mordant layer **31** of the image-receiving element. The rupturable container **51** contains an alkaline processing solution containing an aromatic primary amino compound and a shading agent and the rupturable container **52** contains an alkaline processing solution containing an oxidizing agent and a shading agent.

In the embodiment shown in FIG. **10**, the photosensitive element comprises an alkali-permeable support **17** having coated thereon a layer **18** having dispersed in a hydrophilic colloid binder microcapsules containing therein a magenta coupler developer and a green-sensitive emulsion and microcapsules containing therein a cyan coupler developer and a red-sensitive emulsion, a yellow filter layer **13**, a blue-sensitive emulsion layer **12** containing a yellow coupler developer, and a protective layer **111** containing an aromatic primary amino compound. The rupturable containers **51** and **52** contain each an alkaline processing solution containing a shading agent.

FIG. **11** is a perspective view showing a further embodiment of the film unit of this invention. In this embodiment a shade layer **2** and a photographic element **1** are formed, in sequence, on an image-receiving element **3**.

FIG. **12** is an enlarged cross-sectional view of the film unit shown in FIG. **11**. As shown in FIG. **12**, a shade layer **211** containing an aromatic primary amino compound is disposed between a mordant layer **311** containing an oxidizing agent and a red-sensitive emulsion layer **16**. The rupturable container **5** retains an alkaline processing solution containing a shading agent.

Examples of rupturable containers as can be used in this invention are described in U.S. Pat. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,492; 3,056,491; and 3,152,515. Such containers are formed by doubling a liquid and gas impermeable sheet so that two walls are formed and the longitudinal edges of the walls and also both ends are sealed to provide a space for retaining a processing solution. The longitudinal seal of the container is weaker than the seals at the ends thereof and thus when pressure is applied to the walls of the container retaining a processing solution, the longitudinal seal of the container is ruptured by the liquid pressure.

The elements of the film unit of this invention are fixed together by means of a binding member and the binding member may be a pressure-sensitive tape securing or maintaining the layers of each element together at the respective edges. The tape also acts to maintain the processing solution between the elements and also acts to prevent the leakage of the processing solution from the film unit.

In a film unit using a conventional dye developer in which the photosensitive element is not stripped from the image-receiving element, it is necessary to employ and optical system for reversing the image in the camera. Furthermore, in a film unit using a non-diffusible dye image providing a material capable of forming a diffusible dye by reaction with an (oxidized) developer as described in U.S. Pat. No. 3,635,707, it is necessary, to obtain a positive image, to provide an image reversion capability to the photosensitive element (for instance, to use a direct-positive silver halide emulsion).

On the other hand, in the film unit of this invention, the exposure side of the film unit is positioned opposite to the side of observing the positive image and hence the employment of the optical reversion system as mentioned above is unnecessary. And, in the present invention, a diffusible and substantially colorless compound which forms a dye by reaction with the oxidiation product of an aromatic primary amino compound and is a developing agent for silver halide is used, and it is unnecessary to provide an image reversion capability to the element such as by using a direct positive silver halide emulsion in the photosensitive element.

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.

What we claim is:

1. A photographic film unit for diffusion transfer color process which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members and which comprises the combination, in sequence, of

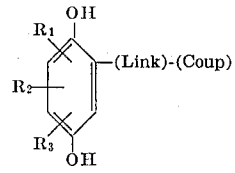
1. an image-receiving element having formed on a transparent support a mordant layer,
2. a photosensitive element having at least one photosensitive silver halide emulsion layer,
3. a water impermeable sheet, and
4. at least one of
   a. a rupturable container capable of releasing, upon rupturing, its contents between said image-receiving element (1) and said photosensitive element (2) and
   b. a rupturable container capable of releasing, upon rupturing, its content between said photosensitive element (2) and said water impermeable sheet (3), said photosensitive element (2) containing a substantially colorless and diffusible compound which develops silver halide and which is capable of forming a dye by reaction with the oxidation product of an aromatic primary amino compound, at least one of said rupturable containers retaining an alkaline processing solution,

A. said film unit containing an aromatic primary amino compound and an oxidizing agent together or separately in one or more members of said image-receiving element (1), said photosensitive element (2), said water impermeable sheet (3) or at least one of said rupturable containers (a) and (b), and

B. said film unit containing a shading agent in

i. at least one of a layer disposed between the photosensitive silver halide emulsion layer of the photosensitive element (2) most adjacent to the image-receiving element and the mordant layer of the image-receiving element and said rupturable container (a) or

ii. at least one of said impermeable sheet (3) or said rupturable container (b) wherein said substantially colorless and diffusible compound is represented by the general formula



wherein (Coup) stands for a coupler group, (Link) stands for a group connecting (Coup) and the hydroquinone nucleus, and R_1, R_2, and R_3 each stands for a hydrogen atom, a hydroxy group, a halogen atom, an alkoxyl group or an alkyl group.

2. The photographic film unit for diffusion transfer color process as set forth in claim **1** in which said coupler group of (Coup) is a phenol or a naphthol.

3. The photographic film unit for diffusion transfer color process as set forth in claim **1** in which said coupler group of (Coup) is a benzylacetanilide or a 1-phenyl-5-pyrazolone.

4. The photographic film unit for diffusion transfer color process as set forth in claim **1** in which said coupler group is a cyanoacetyl, a phenylacetonitrile, a pyrazolo compound, a pyrazolo-benzimidazole, or an indazoline-3-on.

5. The photographic film unit for diffusion transfer color process as set forth in claim **2** in which said group shown by (Link) is an alkylene group.

6. The photographic film unit of claim **1**, wherein said silver halide emulsion is chemically ripened with sulfur, gold, platinum, palladium, or tellurium compounds.

7. The photographic film unit of claim **1**, wherein said silver halide emulsion is color sensitized.

8. The photographic film unit of claim **7**, wherein said silver halide emulsion is color sensitized by the addition of a sensitizing dye.

9. The photographic film unit of claim **1**, wherein said silver halide emulsion contains a development accelerator.

10. The photographic film unit of claim **9**, wherein said development accelerator is a polyalkylene glycol, a cationic sulface active agent or a thioether.

11. The photographic film unit of claim **1**, wherein said silver halide emulsion contains a stabilizer.

12. The photographic film unit of claim **11**, wherein said stabilizer is one selected from thiazonium compounds, azaindenes, mercury salts, urazols, sulfocatechols, oximes, nitroindazole mercaptotetrazoles, polyvalent metal salts, palladium salts, platinum salts, and gold salts.

13. The photographic film unit of claim **1**, wherein said substantially colorless and diffusible compound is

diffusible in the presence of alkaline processing solution but non-diffusible in the photosensitive element before processing by an alkaline processing solution.

14. The photographic film unit of claim **1**, wherein said substantially colorless and diffusible compound is dispersed in the dissolved state in a hydrophilic collid in fine particles of a high boiling solvent having a boiling point above 120°C.

15. The photographic film unit of claim **14**, wherein said solvent is selected from alkyl phthalates, phosphoric acid esters, alkylamides, or acetanilides.

16. The photographic film unit of claim **15**, wherein said alkyl phthalate is methyl phthalate, ethyl phthalate, propyl phthalate, n-butyl phthalate, di-n-butyl phthalate, amyl phthalate, iso-amyl phthalate, or dioctyl phthalate.

17. The photographic film unit of claim **15**, wherein said phosphoric acid ester is triphenyl phosphate, tricresyl phosphate, or diphenyl-mono-p-tert-butylphenyl phssphate.

18. The photographic film unit of claim **15**, wherein said acetanilide is N-n-butylacetanilide. or n-methyl-p-methyl-acetanilide.

19. The photographic film unit of claim **14**, wherein said phydrophilic colloid is gelatin or polyvinyl alcohol.

20. The photographic film unit of claim **14**, wherein said hydrophilic colloid further contains a surface active agent.

21. The photographic film unit of claim **20**, wherein said surface active agent is saponin, an anionic compound, or an amphoteric compound.

22. The photographic film unit of claim **1**, wherein said unit further contains an auxiliary developing agent selected from benzenoid-type silver halide developing agents or 3-pyrazolidones.

23. The photographic film unit of claim **22**, wherein said auxiliary developing agent is hydroxyphenyl hydroquinone, phenyl hydroquinone, 4'-methyl-phenyl hydroquinone, p-(t)-butyl catechol, (t)-butyl-hydroquinone, 1-phenyl-3-pyrazolidone, or 1-(p-methyl) phenyl-3-pyrazolidone.

24. The photographic film unit of claim **22**, wherein said auxiliary developing agent is incorporated in at least one layer of said photosensitive element.

25. The photographic film unit of claim **22**, wherein said auxiliary developing agent is present in an amount of from 1/100 to 10 moles per mole of said substantially colorless and diffusible compound.

26. The photographic film unit of claim **1**, wherein the silver halide of a silver halide emulsion layer is present in an amount of from $0.1–10\times10^{-4}$ mole/100 cm^2, said substantially colorless and diffusible compound is present in an amount from 0.5 to 50×10^{-5} mole/100 cm^2 and the molar ratio of said silver halide/said substantially colorless and diffusible compound is from 1–10.

27. The photographic film unit of claim **1**, wherein said mordant layer comprises a hydrophilic, basic and firm forming polymer, or a hydrophilic and film forming polymer containing a basic polymer.

28. The photographic film unit of claim **27**, wherein said mordant layer comprises a mixture of polyvinyl alcohol and poly-4-vinyl pyridine, a partially acetalated product of polyvinyl alcohol and trialkyl-ammonium benzaldehyde quaternary salt, a copolymer of vinyl alcohol and N-vinylpyrrolidone, a condensed acetalation product of polyvinyl alcohol and polyvinylpyrrolidone, a condensed acetalation product of polyvinyl alcohol and 4-pyridine carboxyaldehyde, polymers of the aminoguanidine derivatives of vinylmethyl ketone, poly-4-vinylpyridine, or poly-2-vinylpyridine.

29. The photographic film unit of claim **1**, wherein said aromatic primary amino compound is selected from 4-amino-N,N-diethyl-3-methylaniline, N,N-diethyl-p-phenylenediamine, N-ethyl-N-(β-methanesulfonamido)-ethyl-3-methyl-4-aminoaniline, 4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)-aniline, 4-amino-N-ethyl-3-methoxy-N-(β-sulfoethyl)-aniline, 4-amino-N-ethyl-N-(β-hydroxyethyl)aniline, 4-amino-N,N-diethyl-3-hydroxymethylaniline, 4-amino-N-methyl-N-(β-carboxyethyl)aniline, 4-amino-N,N-bis(β-hydroxyethyl)aniline, 4-amino-N,N-bis(β-hydroxyethyl)aniline, 4-amino-N,N-bis(β-hydroxyethyl)-3-methyl-aniline,3-acetamido-4-amino-N,N-bis(β-hydroxyethyl)-aniline, 4-amino-N-ethyl-N-(2,3,-dihydroxypropyl)-3-methyl-aniline sulfate, or 4-amino-N,N-diethyl-3-(3-hydroxypropoxy)aniline.

30. The photographic film unit of claim **1**, wherein said aromatic primary amino compound is present in an amount of from 0.1 to 5 wt% of said processing solution.

31. The photographic film unit of claim **1**, wherein said oxidizing agent is potassium ferricyanide, hydrogen peroxide, potassium bichromate, ammonium persulfate, copper sulfate, exposed silver halide, or quinone.

32. The photographic film unit of claim **1**, wherein said oxidizing agent is contained in an equimolar proportion to said aromatic primary amino compound.

33. The photographic film unit of claim **1**, wherein said aromatic primary amino compound and said oxidizing agent are incorporated in an assembly whereby said aromatic primary amino compound and said oxidizing agent are first mixed at the time of developing.

34. The photographic film unit of claim **1**, wherein said unit further contains a pH decreasing layer which reduces the pH of said image-receiving layer, which initially has a pH of 11 to 14, by permeation of said alkaline processing solution to a pH lower than 11.

35. The photographic film unit of claim **34**, wherein said pH decreasing layer comprises a polymer acid.

36. The photographic film unit of claim **35**, wherein said polymer acid contains a carboxylic acid group or a sulfonic acid group.

37. The photographic film unit of claim **36**, wherein said polymer acid is cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, cellulose acetate succinate hydrogen phthalate, the ether or ester derivatives of cellulose treated with sulfo anhydride, polystrene sulfonic acid, carboxymethyl cellulose, polyvinyl hydrogen phthalate, polyvinyl acetate hydrogen phthalate, polyacrylic acid, or the acetal of polyvinyl alcohol treated with a carboxy-or sulfo-substituted aldehyde.

38. The photographic film unit of claim **34**, wherein said pH decreasing layer is disposed between the mordant layer and the support of said image-receiving element.

39. The photographic film unit of claim **34**, wherein said pH decreasing layer has a dry thickness from 5 to 20 μ.

40. The photographic film unit of claim 34, wherein said unit further contains a photographically inactive timing layer adjacent said pH decreasing layer.

41. The photographic film unit of claim 40, wherein said timing layer has a 2 to 20μ thickness.

42. The photographic film unit of claim 40, wherein said timing layer comprises gelatin, polyvinyl alcohol, polyvinyl acetate, polyamide, polyvinylether, or the partial acetate of polyvinyl alcohol.

43. The photographic film unit of claim 1, wherein said processing solution further contains an onium compound.

44. The photographic film unit of claim 43, wherein said onium compound is a quaternary ammonium compound, a quaternary sulfonium compound, or a quaternary phosphonium compound.

45. The photographic film unit of claim 44, wherein said onium compound is 1-ethylpyridinium bromide, lauryldimethylsulfonium, cetyl-trimethyl-ammonium bromide, p-toluene sulfonic acid, 1-benzyl-α-picolenium tosylate, or tetraethyl phosphonium bromide.

46. The photographic film unit of claim 1, wherein said shading agent is carbon black, barium sulfate, zinc oxide, barium stearate, silver powder, silica powder, alumina powder, zirconium oxide, zirconium acetylacetate, sodium zirconium sulfate, kaolin, mica, titanium dioxide or an organic dye.

47. The photographic film unit of claim 1, wherein said shading agent is contained in said processing solution.

48. The photographic film unit of claim 47, wherein said shading agent is carbon black or titanium dioxide.

49. The photographic film unit of claim 47, wherein said shading agent is present in an amount from 5 to 40 wt% of said processing solution.

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