

United States Patent

Stewart et al.

[15] 3,653,896
[45] Apr. 4, 1972

[54] DIFFUSION TRANSFER FILM UNIT

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[22] Filed: **Nov. 3, 1970**
[21] Appl. No.: **86,593**

[52]	U.S. Cl.....	96/3, 96/29 D, 96/66 R, 96/74, 96/76 C
[51]	Int. Cl.....	G03c 5/54, G03c 1/58, G03c 1/48
[58]	Field of Search.....	96/3, 29 D, 96, 21, 73, 66 R, 96/73, 74

[56] **References Cited**

UNITED STATES PATENTS

3,087,817 4/1963 Rogers..... 96/29 D

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[57]

ABSTRACT

Photographic elements and film units are disclosed comprising a silver halide emulsion having associated therewith a quinone-coupling dye capable of forming a diffusible methylene base in alkaline processing composition. A diffusible dye is produced imagewise which diffuses to a dye image-receiving layer to provide a positive dye image. The diffusible dye is immobilized in the developed areas of the negative by reacting with an oxidized hydroquinone or catechol developing agent. The dye image-receiving layer may be located integral with the photo-sensitive element or may be located on a separate support adapted to be superposed on the photosensitive element after exposure thereof.

27 Claims, No Drawings

DIFFUSION TRANSFER FILM UNIT

This invention relates to photography, and more particularly to quinone-coupling dyes and to their use in diffusion transfer systems to react with oxidized hydroquinone or catechol developing agents.

U.S. Pat. No. 3,087,817, issued Apr. 30, 1963, of Rogers, discloses that complete dye molecules having a coupling function such as (1) a phenolic hydroxyl group in a nucleus having the para positions free or occupied by radicals which split off during coupling, (2) a reactive methylene group, free or substituted by a radical which splits off during coupling such as an azo-linked group, or (3) an amino group on a ring in para position to an open position on the ring, are immobilized by coupling with an oxidized color developer, such as a phenylenediamine or aminophenol derivative, in the exposed regions of a photosensitive element. In the unexposed areas, the preformed dye which is soluble in alkaline solution diffuses to the image-receiving element, thereby providing a positive dye image. Due to the well-known propensity of color developers to stain the receivers, however, these dye images suffer in quality. In addition, it is also well-known that p-phenylenediamine derivatives can cause dermatitis.

It is an object of our invention to provide novel photographic elements and film units which can be processed with greatly decreased stain in comparison with elements and units processed with usual color developing agents.

It is another object of our invention to provide a novel process for obtaining a positive dye transfer image wherein developer stain is reduced to a minimum through the use of a hydroquinone or catechol silver halide developing agent.

These and other objects are obtained by a photographic film unit according to our invention which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members, such as would be found in a camera designed for in-camera processing, which comprises:

a. a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith a quinone-coupling dye capable of forming a diffusible methylene base in alkaline processing composition;

b. a dye image-receiving layer; and

C. a rupturable container containing an alkaline processing composition and which is adapted to be positioned during processing of c. a film unit so that a compressive force applied to the container by the pressure-applying members will effect a discharge of the container's contents within the film unit;

the film unit containing a hydroquinone or catechol silver halide developing agent.

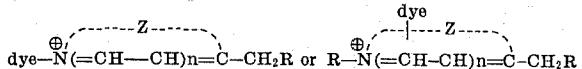
We have found that hydroquinone or catechol silver halide developing agents react more readily with methylene bases containing a dye moiety in alkaline processing compositions, are more stable, and cause less developer stain in the image-receiving layer. The developing agent can be incorporated into a layer of the photosensitive element or it can be located in the rupturable container, if desired.

A photosensitive element according to our invention comprises a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith (1) a quinone-coupling dye capable of forming a diffusible methylene base in alkaline processing composition and (2) a hydroquinone or catechol silver halide developing agent.

The dye image-receiving layer in the above-described film unit can be located on a separate support adapted to be superposed on the photosensitive element after exposure thereof. Such image-receiving elements are disclosed, for example, in U.S. Pat. No. 3,362,819. A rupturable container is usually employed and is positioned during processing of the described film unit so that a compressive force applied to the container by pressure-applying members in a camera will effect a discharge of the container's contents between the image-receiving element and the outermost layer of the photosensitive element.

The dye-image receiving layer in the above-described film unit can also be located integral with the photosensitive element between the support and the lowermost photosensitive silver halide emulsion layer. Such integral receiver-negative 5 photosensitive elements are disclosed, for example, in U.S. Pat. No. 3,415,644 and are useful in camera apparatus of the type disclosed in Belgian Pat. Nos. 718,553 and 718,554. The processing composition for such integral elements wherein the receiver is permanently laminated to the negative contains opacifying agents such as titanium dioxide or carbon black. Barrier layers such as those described in Becker, U.S. Pat. No. 3,384,483 may be used to advantage in such integral elements between the various emulsion, quinone-coupling dye and/or developer layers.

15 The quinone-coupling dyes which can be employed in the practice of the invention can be, for example, ketomethylene-containing compounds such as 3-methyl-5-pyrazolones having a dye molecule attached to a nitrogen in the ring system, thereby leaving the reactive methylene moiety free for quinone coupling. Preferably, however, the quinone-coupling dyes employed in my invention are dye-quaternary ammonium compounds capable of forming a diffusible methylene base in alkaline processing composition. If desired, the dye chromophore could be part of the heterocyclic nucleus of the 20 quaternary ammonium compound or could be separated by an insulating group. The dye-quaternary ammonium compounds 25 preferably have the following general formulae:

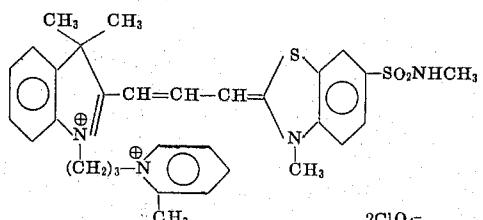


wherein Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus of a quaternary ammonium compound such as quaternary salts of the pyridine, quinoline, benzoquinoline, benzoxazole, benzoselenazole, thiazole, 40 benothiazole, naphthothiazole, benzimidazole, isoquinoline series, etc.; n is 0 or 1; R is hydrogen, alkyl, preferably lower alkyl containing one to four carbon atoms, aryl such as phenyl and including substituted alkyl or aryl such as hydroxyalkyl, 45 alkoxyalkyl, carboxyalkyl, sulfoalkyl, arylalkyl, tolyl, xylyl, etc.; X is an anion, e.g., bromide, chloride, iodide, perchlorate, p-toluenesulfonate, etc.; and dye can be any dye group such as, e.g., a cyanine, an azo, a bis-azo, an xanthane, a thiazine, a triphenylmethane, an anthraquinone dye, etc.

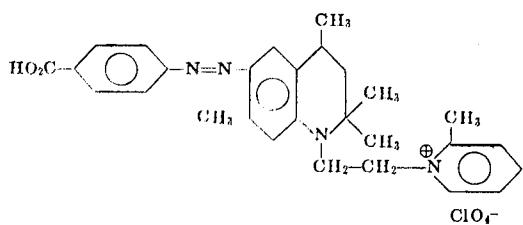
The dye-quaternary ammonium compounds comprising a preferred embodiment of the invention are dye-pyridinium salts which form diffusible methylene bases in alkaline processing composition and which have the above formulae in which Z represents the nonmetallic atoms necessary to complete a pyridinium nucleus. The dye-pyridinium salt is 55 preferably substituted in the pyridinium nucleus with from one to three active methyl groups, $-\text{CH}_2\text{R}$, present in at least one of the 2, 4, or 6 positions. The 3 and 5 position of the pyridinium nucleus may also be substituted with e.g. halogen, lower alkyl and haloalkyl groups such as chlorine, methyl, ethyl, 60 propyl, chloroethyl groups or the above-mentioned dye groups.

Typical dye-quaternary ammonium compounds having the above general formula A are as follows:

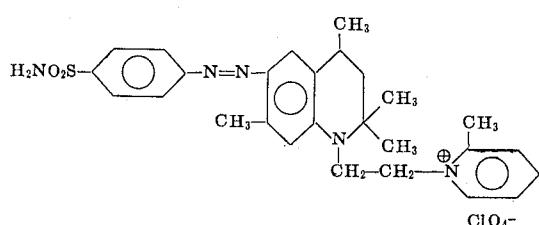
I. 3,3,3'-trimethyl-1-[3-(2-methyl-1-pyridino)propyl-6-N-methyl]-sulfamoylindothiacarbocyanine perchlorate



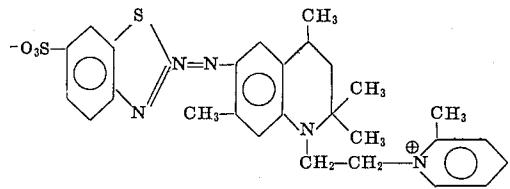
II. 1-[2-(6-{p-carboxyphenylazo}-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinolin-1-yl)ethyl]-2-methylpyridinium perchlorate



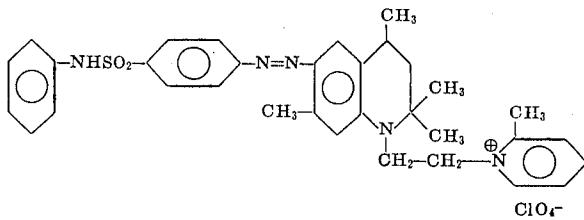
III. 1-[2-(6-{p-sulfamoylphenylazo}-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinolin-1-yl)ethyl]-2-methylpyridinium perchlorate



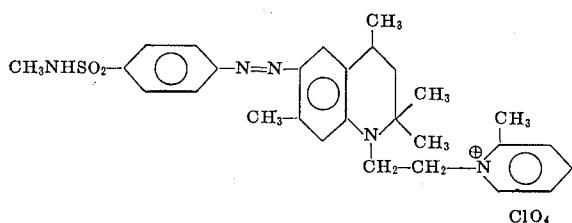
IV. Anhydro-1-[2-(6-{6-sulfobenzothiazol-2-ylazo}-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinolin-1-yl)ethyl]-2-methylpyridinium hydroxide



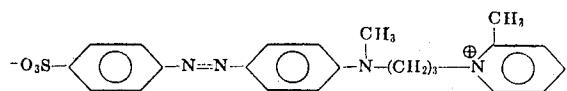
V. 1-[2-(6-{p-N-phenylsulfamoylphenylazo}-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinolin-1-yl)ethyl]-2-methylpyridinium perchlorate



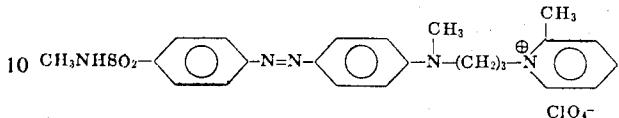
VI. 1-[2-(6-{p-N-methylsulfamoylphenylazo}-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinolin-1-yl)ethyl]-2-methylpyridinium perchlorate



VII. Anhydro-1-[3-{4-(p-sulfophenylazo)N-methylanilino}-propyl]-2-methylpyridinium hydroxide

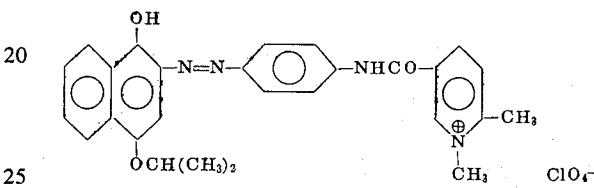


VIII. 2-methyl-1-[3-{4-(methylaminosulfonylphenylazo)N-methylanilino}-propyl]pyridinium perchlorate

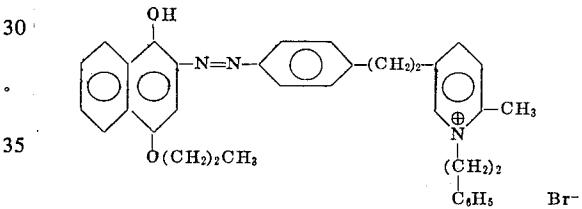


Typical dye-quaternary ammonium compounds having the above general formula B are as follows:

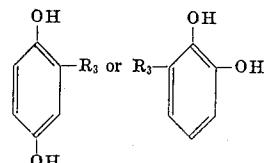
15 IX. 5-{N-[3-(1-hydroxy-4-isopropoxy-2-naphthylazo)-phenyl]carbamoyl}-1,2-dimethylpyridinium perchlorate



X. 1-Phenethyl-2-methyl-5-[p-(1-hydroxy-4-propoxy-2-naphthylazo)phenethyl]-pyridinium bromide



The silver halide developing agents employed in our invention preferably have the foulage



wherein R₃ can be hydrogen; alkyl, typically having four to 20 carbon atoms such as butyl, t-butyl, sec. butyl, pentyl, heptyl, 50 octyl, nonyl, decyl, dodecyl, octadecyl, eicosyl, etc; alkoxy typically having from four to 20 carbon atoms such as butoxy, pentoxy, etc; halogen, such as fluorine, chlorine, bromine, iodine; and aryl such as phenyl, 4'-methylphenyl, etc. Combinations of developing agents can also be employed if desired. The developing agents can be located in a rupturable container if one is employed or can be located in a silver halide emulsion and/or any other suitable location in the photographic element. The amount of developing agent employed can be varied over a wide range depending upon the quantity 60 of silver halide to be developed. The developing agents can be added from suitable solvents or in the form of dispersions as described in Yackel U.S. Pat. No. 2,592,368 and Dunn et al. French Pat. No. 1,505,778.

A color film assembly according to our invention can contain various silver halide emulsion layers disposed in the usual order, i.e., the blue-sensitive silver halide emulsion layer first with respect to the exposure side, followed by the green-sensitive and red-sensitive silver halide emulsion layers. If desired, the selectively sensitized silver halide emulsion layers can be 70 disposed in a different order, e.g., the red-sensitive layer first with respect to the exposure side, followed by the green-sensitive and blue-sensitive layers.

An alkaline processing or activating composition is conveniently employed in a rupturable container or pod of the 75 film assembly of the present invention. After exposure of the

element, the alkaline processing or activating composition is released from the pod to permeate the emulsion layers and initiate development of the latent images contained therein. The quinone-coupling dyes are immobilized as a consequence of the development of these latent images. This immobilization is due to a change in the solubility characteristics of the dyes after coupling at the reactive methylene site with the quinone derivatives, formed as a result of the development of the latent images by the hydroquinone or catechol developing agent. In undeveloped areas of the emulsion layers, the remaining dye molecules, which have not undergone a coupling reaction with oxidized hydroquinone or catechol, remain diffusible in the alkaline processing or activating composition and thus provide imagewise distributions of unreacted quinone-coupling dye dissolved in the liquid processing composition as a function of the point-to-point degree of exposure of the silver halide emulsion layers. At least part of these imagewise distributions of unreacted quinone-coupling dye are transferred, by diffusion, to the image-receiving layer. The image-receiving layer contains materials adapted to mordant or otherwise fix the diffused, quinone-coupling dyes to provide a dye image.

Good results are obtained when the quinone-coupling dyes are employed in separate layers contiguous and below with respect to exposure direction to each silver halide emulsion layer. Such layers can be applied by using coating solutions containing about 0.5 to about 8%, by weight, of the quinone-coupling dye distributed in a hydrophilic film-forming natural material or synthetic polymer such as gelatin, polyvinyl alcohol, etc., which is adapted to be permeated by aqueous alkaline activating or processing composition.

In addition to conventional techniques for the direct dispersion of a particulate solid material in a polymeric or colloidal matrix such as ball-milling and the like techniques, the preparation of a quinone-coupling dye dispersion can also be obtained by dissolving the quinone-coupling dye in an appropriate solvent or mixture of solvents, dispersing the resultant solution in the polymeric binder, with optional subsequent removal of the solvent or solvents employed. Further details concerning these dispersing techniques and the solvents employed are found, for example, in U.S. Pat. Nos. 2,269,158; 2,322,027; 2,304,939; 2,304,940; 2,801,171 and the like.

Generally speaking, the silver halide emulsion layers in the invention comprise photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 microns in thickness while the quinone-coupling dyes are dispersed in an aqueous alkaline solution-permeable polymeric binder, such as gelatin, as a separate layer about 1 to 7 microns in thickness. Of course, these thicknesses are approximate only and can be modified according to the product desired.

Use of a polymeric acid layer, as disclosed in U.S. Pat. No. 3,362,819, in the film unit of the present invention will enhance the results obtained. Generally, the polymeric acid layer will effect a reduction in the pH of the image layer from about 13 or 14 to at least 11 and preferably 5-8 within a short time after imbibition. Such polymeric acids reduce the pH of the film unit after development to terminate further dye transfer and thus stabilize the dye image. Such polymeric acids comprise polymers containing acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium or potassium, or with organic bases particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide. The polymers can also contain potentially acid-yielding groups such as anhydrides or lactones or other groups which are capable of reacting with bases to capture and retain them. Generally, the most useful polymeric acids contain free carboxyl groups, are insoluble in water in the free acid form and which form water-soluble sodium and/or potassium salts.

An inert timing or spacer layer coated over the polymeric acid layer can also be used to "time" or control the pH reduction of the film unit as a function of the rate at which the alkali diffuses through the inert spacer layer. Examples of such tim-

ing layers include gelatin, polyvinyl alcohol or any of those disclosed in U.S. Pat. No. 3,455,686. The timing layer is also effective in evening out the various reaction rates over a wide range of temperatures, e.g., premature pH reduction is prevented when imbibition is effected at temperatures above room temperature; for example, at 95° to 100° F. The timing layer is usually about 0.1 to about 0.7 mil in thickness.

The liquid processing composition that may be employed in this invention is, for example, the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12. The composition also preferably contains a viscosity-increasing compound such as a high molecular weight polymer, e.g., a water-soluble ether inert to alkaline solutions such as hydroxyethyl cellulose or alkali metal salts of carboxymethyl cellulose such as sodium carboxymethyl cellulose. A concentration of viscosity-increasing compound of about 1 to about 5% by weight of the processing composition is preferred which will impart thereto a viscosity of about 100 c.p.s. to about 200,000 c.p.s.

The silver halide emulsions used with this invention can comprise silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The emulsions can be coarse or fine grain and can be prepared by any of the well-known procedures, e.g., single jet emulsions, double jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264; Illingsworth U.S. Pat. No. 3,320,069; and McBride U.S. Pat. No. 3,271,157. Surface image emulsions can be used or internal image emulsions can be used such as those described in Davey et al. U.S. Pat. No. 2,592,250; Porter et al. U.S. Pat. No. 3,206,313 and Bacon et al. U.S. Pat. No. 3,447,927. The emulsions may be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, Vol. 12, No. 5, Sept./Oct., 1964 pp. 242-251. If desired mixtures of surface and internal image emulsions can be used as described in Luckey et al. U.S. Pat. No. 2,996,382.

40 Negative type emulsions can be used or direct positive emulsions can be used such as those described in Leermakers U.S. Pat. No. 2,184,013; Kendall et al. U.S. Pat. No. 2,541,472; Berriman U.S. Pat. No. 3,367,778; Schouwenaars British Pat. No. 723,019; Illingsworth et al. French Pat. No. 1,520,821; Ives U.S. Pat. No. 2,563,785; Knott et al. U.S. Pat. No. 2,456,953 and Land U.S. Pat. No. 2,861,885.

50 Spectral sensitizing dyes can be used conveniently to confer addition sensitivity to the light sensitive silver halide emulsion of the photographic elements of the invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion as described in Owens et al. British Pat. No. 1,154,781. For optimum results, the dye can either be added to the emulsion as a final step or at some earlier stage.

55 Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. No. 2,526,632, issued Oct. 24, 1950; Sprague U.S. Pat. No. 2,503,776, issued Apr. 11, 1950; Brooker et al. U.S. Pat. No. 2,493,748; and Taber et al. U.S. Pat. No. 3,384,486. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri or tetrานuclear) merocyanines, complex (tri or tetrานuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e. enamine hemicyanines), oxonols and hemionoxols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine

chain. The merocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition, supersensitizing addenda which do not absorb visible light can be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Pat. No. 2,933,390 and Jones et al. U.S. Pat. No. 2,937,089.

The silver halide emulsions can be unwashed or washed to remove soluble salts. In the latter case the soluble salts may be removed by chill-setting and leaching or the emulsion may be coagulation washed, e.g. by the procedures described in Hewitson et al U.S. Pat. No. 2,618,556; Yutzy et al. U.S. Pat. No. 2,614,928; Yackel et al. U.S. Pat. No. 2,565,418; Hart et al. U.S. Pat. No. 3,241,969; and Waller et al. U.S. Pat. No. 2,489,341.

Also, the silver halide emulsions may contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. No. 2,886,437; Dann et al. U.S. Pat. No. 3,046,134; Carroll et al. U.S. Pat. No. 2,944,900; and Goffe U.S. Pat. No. 3,294,540.

Likewise, the silver halide emulsions can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include the thiazolium salts described in Brooker et al. U.S. Pat. No. 2,131,038 and Allen et al. U.S. Pat. No. 2,694,716; the azaindenes described in Piper U.S. Pat. No. 2,886,437 and Heimbach et al. U.S. Pat. No. 2,444,605; the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663; the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652; the oximes described in Carroll et al. British Pat. No. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927; Kennard et al. U.S. Pat. No. 3,266,897 and Luckey et al. U.S. Pat. No. 3,397,987; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405; the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 and Yutzy et al. U.S. Pat. No. 2,597,915.

Any suitable material can be employed as the image-receiving layer in this invention as long as the desired function of mordanting or otherwise fixing the quinone-coupling dye images will be obtained.

Suitable image-receiving materials for the dye-containing moiety include N-methoxymethyl polyhexylmethylen adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate; gelatin; and other materials of a similar nature. Polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine as disclosed in U.S. Pat. No. 3,148,061 can also be employed in the invention with good results. Generally, the image-receiving layer is from about 0.25 to about 0.04 mil in thickness. This thickness, of course, may be modified depending upon the result desired. The image-receiving layer may also contain ultraviolet absorbing materials to protect the mordanted dye images from fading due to ultraviolet light.

The layers of the photographic element employed and described herein may be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing two to 10 carbon atoms such as 75

polyethylene, polypropylene, ethylenebutene copolymers and the like.

The photographic emulsions and elements described in the practice of the present invention can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinyl-pyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of the present photographic elements of this invention 15 can also contain alone or in combination with hydrophilic, water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. No. 3,142,568, issued July 28, 1964; White U.S. Pat. No. 3,193,386, issued July 6, 1965; Houck et al. U.S. Pat. No. 3,062,674, issued Nov. 6, 1962; Houck et al. U.S. Pat. No. 3,220,844, issued Nov. 30, 1965; Ream et al. U.S. Pat. No. 3,287,289, issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 3,411,911, issued Nov. 9, 1968. Particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate 20 hardening or curing and those having recurring sulfobetaine units as described in Dykstra Canadian Pat. No. 774,054.

The various photographic layers can contain plasticizers and lubricants such as polyalcohols, e.g. glycerin and diols of the type described in Milton et al. U.S. Pat. No. 2,960,404; 25 fatty acids or esters such as those described in Robijns U.S. Pat. No. 2,588,765 and Duane U.S. Pat. No. 3,121,060; and silicone resins such as those described in DuPont British Pat. No. 955,061.

The photographic layers used in the practice of this invention 30 can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. No. 2,681,294. If desired, two or more layers may be 35 coated simultaneously by the procedures described in Russell U.S. Pat. No. 2,761,791 and Wynn British Pat. No. 837,095. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. No. 968,453 and LuValle et al. U.S. Pat. No. 3,219,451.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the 40 aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

60 The following examples further illustrate the invention.

EXAMPLE 1

A photosensitive element comprising a silver halide emulsion, a quinone-coupling dye and a hydroquinone silver halide 65 developing agent is prepared by coating the following liquid composition on a cellulose acetate film support at 10.0g. melt/ft.² or 130 mg. silver/ft.².

1-methyl-2-pyrrolidinone-methanol solvent mixture (1:3)	
containing 1% by weight of 2-methyl-1-[3-[4-(4-	
(methylaminosulfonyl)-phenylazo]-N-methylanilino]-	
propyl]pyridinium perchlorate (Dye VIII)	2.0 ml
Gelatin-silver chloride emulsion (3.4 kg of	6.0 g
emulsion/Ag mole which contains 100g gel/Ag	
mole)	
Water containing 10% by weight formaldehyde	0.15 ml

Water containing 15% by weight saponin	0.15 ml
Methanol-water (1:1) containing 1.4% by weight t-butylhydroquinone	2.0 cc

The air-dried coating is exposed to tungsten light and laminated to a receiver sheet of the type described in U.S. Pat. No. 3,362,819, which has been soaked for 15 seconds in 1N sodium hydroxide. After 2 minutes, the negative photosensitive element is separated from the receiver sheet and a well-defined yellow positive dye image free from developer stain is observed on the image-receiving element.

EXAMPLE 2 - COMPARATIVE EXAMPLE

In order to illustrate the results obtained when a dye is employed which does not form a diffusible methylene base in alkaline processing composition, the procedure of Example 1 is repeated with the exception that an equimolar amount of 1-[3-[4-(methylaminosulfonyl)phenylazo]-N-methylanilino]propyl]pyridinium perchlorate (similar to the dye of Example 1 except for the 2-methyl group) is substituted for the quinone-coupling dye utilized in Example 1. After exposure and lamination with a soaked image-receiving element as described in Example 1, an indiscriminate transfer of yellow dye is observed. This indicates that the above dye is incapable of forming a diffusible methylene base in an alkaline activating composition, thereby preventing coupling with oxidized t-butylhydroquinone and subsequent immobilization in the exposed areas of the negative.

EXAMPLE 3

A photosensitive element is prepared by coating the following layers on a cellulose acetate film support:

1. Gelatin (250 mg./ft.²) and 1-[2-(6-{p-N-methylsulfamoylphenylazo}-2,2,4,7-tetramethyl-1,2,3-4-tetrahydroquinolin-1-yl)ethyl]-2-methyl-pyridinium perchlorate (Dye VI, 0.02 millimoles/ft.²)
2. Tricresyl phosphate (200 mg./ft.²), gelatin (200 mg./ft.²), silver bromoiodide (0.50 millimoles Ag/ft.²) and dodecyl hydroquinone (0.125 millimoles/ft.²)

A sample of the photosensitive element is imagewise exposed for 5 seconds to a 200 watt tungsten lamp at a distance of 12 inches and then laminated to a soaked image-receiving element as described in Example 1. After 1 minute, the negative photosensitive element is separated from the receiver sheet and a well-defined yellow positive dye image, free from developer stain, is observed on the image-receiving element.

EXAMPLE 4 - COMPARATIVE EXAMPLE

In order to illustrate the results obtained with coupling dyes of the prior art, the procedure of Example 3 is repeated with the exception that an equimolar amount of the sodium salt of 1-phenyl-3-methyl-4-(4'-sulfophenylazo)-5-pyrazolone is substituted for the quinone-coupling dye of Example 3. This pyrazolone dye is described in U.S. Pat. No. 2,455,170 issued Nov. 30, 1968, and is cited in column 7, line 32 of U.S. Pat. No. 3,087,817 issued Apr. 30, 1963, as an example of a coupling dye employed in the practice of that invention. When the image-receiving sheet is separated from the photographic element, an indiscriminate transfer of dye is observed which indicates that the dye did not couple with oxidized dodecyl hydroquinone with subsequent immobilization in the exposed areas of the photographic element.

EXAMPLE 5

The procedure described in Example 3 is repeated with the exception that an equimolar amount of 1-phenethyl-2-methyl-5-[p-(1-hydroxy-4-propoxy-2-naphthylazo)-phenethyl]pyridinium bromide (Dye X) is substituted for the dye of Example 3 and 4'-methyl-phenyl hydroquinone is substituted for dodecyl hydroquinone in the negative photosensitive element. A sample of the photosensitive element is exposed, activated, laminated with an image-receiving sheet, and separated as described in Example 3. A well-defined magenta dye image is observed on the image-receiving sheet.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

I. a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith a quinone-coupling dye capable of forming a diffusible methylene base in alkaline processing composition;

II. a dye image-receiving layer; and

III. a rupturable container containing an alkaline processing composition, said container being adapted to be positioned during processing of said film unit so that a compressive force applied to said container by said pressure-applying members will effect a discharge of the container's contents within said film unit;

said film unit containing a hydroquinone or catechol silver halide developing agent.

2. The film unit of claim 1 wherein said dye image-receiving layer is located in said photosensitive element between said support and the lowermost photosensitive silver halide emulsion layer.

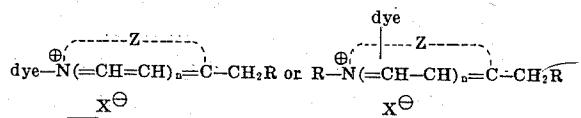
3. The film unit of claim 1 wherein said dye image-receiving layer is coated on a separate support and is adapted to be superposed on said photosensitive element after exposure thereof.

4. The film unit of claim 3 wherein said rupturable container is so positioned during processing of said film unit that a compressive force applied to said container by said pressure-applying members will effect a discharge of the container's contents between said dye image-receiving layer and the outermost layer of said photosensitive element.

5. The photographic film unit of claim 1 wherein said photosensitive element comprises a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a quinone-coupling cyan dye capable of forming a diffusible methylene base in alkaline processing composition, a green-sensitive silver halide emulsion layer having associated therewith a quinone-coupling magenta dye capable of forming a diffusible methylene base in alkaline processing composition, and a blue-sensitive silver halide emulsion layer having associated therewith a quinone-coupling yellow dye capable of forming a diffusible methylene base in alkaline processing composition.

6. The photographic film unit of claim 1 wherein said quinone-coupling dye is a dye-quaternary ammonium compound capable of forming a diffusible methylene base in alkaline processing composition.

7. The photographic film unit of claim 6 wherein said dye-quaternary ammonium compound has the formula:



wherein

dye is a dye group;

n is 0 or

Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus;

X is an anion; and

R is hydrogen, alkyl or aryl.

8. The photographic film unit of claim 7 wherein Z represents the non-metallic atoms necessary to complete a pyridinium nucleus.

9. The photographic film unit of claim 8 wherein said pyridinium compound is 2-methyl-1-[3-[4-(methylaminosulfonyl)-phenylazo]-N-methylanilino]propyl]pyridinium perchlorate.

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10. The photographic film unit of claim 8 wherein said pyridinium compound is 1-[2-(6-{p-N-methylsulfamoylphenylazo}-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinolin-1-yl)ethyl]-2-methylpyridinium perchlorate.

11. The photographic film unit of claim 8 wherein said pyridinium compound is 1-phenethyl-2-methyl-5-[p-(1-hydroxy-4-propoxy-2-naphthylazo)phenethyl]pyridinium bromide.

12. A process of forming a transfer image comprising

I. imagewise exposing a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith a quinone-coupling dye capable of forming a diffusible methylene base in alkaline processing composition;

II. treating the layer outermost from the support of said photosensitive element with an alkaline processing composition to effect development of each of said exposed silver halide emulsion layers with a hydroquinone or catechol silver halide developing agent thereby oxidizing said developing agent to a quinone;

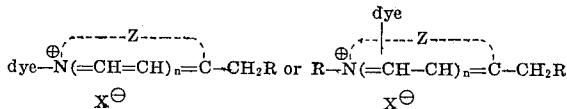
III. said quinone coupling with said quinone-coupling dye to produce an immobile product as a function of said imagewise exposure of each said silver halide emulsion layer; and

IV. at least a portion of said quinone-coupling dye corresponding to the undeveloped areas of each said silver halide emulsion layer diffusing to a dye image-receiving layer.

13. The process of claim 12 wherein said photo-sensitive element comprises a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a quinone-coupling cyan dye capable of forming a diffusible methylene base in alkaline processing composition, a green-sensitive silver halide emulsion layer having associated therewith a quinone-coupling magenta dye capable of forming a diffusible methylene base in alkaline processing composition, and a blue-sensitive silver halide emulsion layer having associated therewith a quinone-coupling yellow dye capable of forming a diffusible methylene base in alkaline processing composition.

14. The process of claim 12 wherein said quinone-coupling dye is a dye-quaternary ammonium compound capable of forming a diffusible methylene base in alkaline processing composition.

15. The process of claim 14 wherein said dye-quaternary ammonium compound has the formula:



wherein

dye is a dye group;

n is 0 or 1;

Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus;

X is an anion; and

R is hydrogen, alkyl or aryl.

16. The process of claim 15 wherein Z represents the nonmetallic atoms necessary to complete a pyridinium nucleus.

17. The process of claim 16 wherein said pyridinium compound is 2-methyl-1-[3-{4-[4-(methylaminosulfonyl)phenylazo]-N-methylanilino} propyl]pyridinium perchlorate.

18. The process of claim 16 wherein said pyridinium compound is 1-[2-(6-{p-N-methylsulfamoylphenylazo}-2,2,4,7-tetra-methyl-1,2,3,4-tetrahydroquinolin-1-yl)ethyl]-2-methyl-

pyridinium perchlorate.

19. The process of claim 16 wherein said pyridinium compound is 1-phenethyl-2-methyl-5-[p-(1-hydroxy-4-propoxy-2-naphthylazo)phenethyl]pyridinium bromide.

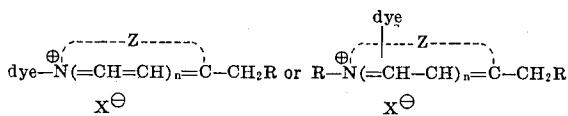
20. A photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith:

1. a quinone-coupling dye capable of forming a diffusible methylene base in alkaline processing composition, and
2. a hydroquinone or catechol silver halide developing agent.

21. A photosensitive element comprising a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a quinone-coupling cyan dye capable of forming a diffusible methylene base in alkaline processing composition, a green-sensitive silver halide emulsion layer having associated therewith a quinone-coupling magenta dye capable of forming a diffusible methylene base in alkaline processing composition, and a blue-sensitive silver halide emulsion layer having associated therewith a quinone-coupling yellow dye capable of forming a diffusible methylene base in alkaline processing composition, said element containing a hydroquinone or catechol silver halide developing agent.

22. The photosensitive element of claim 20 wherein said

23. The photosensitive element of claim 22 wherein said dye-quaternary ammonium compound has the formula:



wherein

dye is a dye group;

n is 0 or 1;

Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus;

X is an anion; and

R is hydrogen, alkyl or aryl.

24. The photosensitive element of claim 23 wherein Z represents the non-metallic atoms necessary to complete a pyridinium nucleus.

25. A photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith:

1. 2-methyl-1-[3-{4-[4-(methylaminosulfonyl)phenylazo]-N-methylanilino} propyl]pyridinium perchlorate, and
2. a hydroquinone or catechol silver halide developing agent.

26. A photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith:

1. 1-[2-(6-{p-N-methylsulfamoylphenylazo}-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinolin-1-yl)ethyl]-2-methylpyridinium perchlorate, and
2. a hydroquinone or catechol silver halide developing agent.

27. A photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer having associated therewith:

1. 1-phenethyl-2-methyl-5-[p-(1-hydroxy-4-propoxy-2-naphthylazo)phenethyl]pyridinium bromide, and
2. a hydroquinone or catechol silver halide developing agent.

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