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3,698,898

PHOTOGRAPHIC PRODUCTS AND PROCESSES EMPLOYING A COMPOUND WHICH IN THE PRESENCE OF ALKALI RELEASES A DIFFUSIBLE PHOTOGRAPHIC REAGENT

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U.S. Cl. 96—3 31 Claims

ABSTRACT OF THE DISCLOSURE

Novel compounds which release a photographic reagent in the presence of alkali, which compounds may be defined as quinone- or naphthoquinone-methide precursors containing the photographic reagent moiety; and photographic products and processes employing the same.

BACKGROUND OF THE INVENTION

In various photographic systems for forming images, whether in black-and-white or in color, it is often desirable to include in the photographic film unit one or more of the various photographic reagents required for development and/or to enhance image quality. This practice extends to both conventional systems for forming negative images and to the various systems such as diffusion transfer, wherein a positive image in silver or in color is obtained.

In many instances, the photographic reagent may be contained initially in either the processing composition applied for development and image formation or in the film unit, the latter being preferred to reduce and hence simplify the number of ingredients required in the processing composition.

In other instances, the particular photographic reagent desired is not sufficiently stable in alkali to provide the requisite shelf life for the processing composition or the reagent is incompatible and/or reactable with another reagent of the composition and hence must be contained initially in the film unit.

In still other instances, the reagent must be provided at some particular time in the development process, which requires that it be contained in a specified layer or in specified proximity to another layer in the film unit.

In all of the foregoing instances it is desirable that the reagent be contained in the desired layer or layers of the particular film unit in such a manner that it is stable, non-migratory or non-diffusible, and yet available when required in the development process.

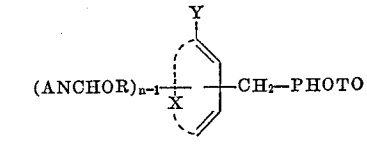
It is to this problem that the present invention is directed.

SUMMARY OF THE INVENTION

The objectives of this invention are accomplished by providing novel compounds which release a photographic reagent in the presence of alkali. These novel compounds may be defined as quinone-methide or naphthoquinone-methide precursors containing the photographic reagent moiety. They may also be defined as phenols or naphthols (including protected derivatives thereof) having the desired photographic reagent bonded to a nuclear carbon atom through a methylene (—CH_2—) substituent in a position ortho or para to the hydroxyl group.

These novel compounds, one or more of which may be disposed in the particular film unit contemplated for preparing the desired image, may be represented by the formula:

(A)



wherein:

X represents the atoms necessary to complete a benzene or a naphthalene nucleus, including substituted derivatives thereof;

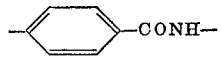
Y is hydroxyl or a protected hydroxyl, i.e., a substituent which upon hydrolysis provides a hydroxyl radical, e.g., an acyloxy such as acetoxy, carbethoxy, etc., cathyloxy; etc.;

PHOTO represents the photographic reagent, the —CH_2—PHOTO substituent being ortho or para to the Y substituent;

ANCHOR represents an anchoring or ballasting substituent such as is described, for example, in U.S. Pat. No. 3,443,940, e.g., an alkyl containing at least ten carbon atoms, such as decyl, dodecyl, stearyl, oleyl, etc., linked directly to the aromatic nucleus or indirectly through an appropriate linking group such as a

—CONH—

-alkylene-CONH- or



substituent, an aromatic ring, e.g., of the benzene or naphthalene series, or a heterocyclic ring, which rings may be either bonded to a single carbon atom of the aromatic nucleus formed by the X atoms or fused thereto by being bonded to a pair of adjacent carbon atoms; a polymeric substituent, e.g., a high polymer backbone; or ANCHOR may be a plurality of short chain radicals which together provide the anchoring moiety; and

n is 1 or 2.

If desired, the benzene or naphthalene nucleus of the novel compounds of this invention may contain other substituents providing particular desired functions, e.g., a substituent which will retard or slow down the hydrolysis rate and hence control the rate or time of release of the photographic reagent, as will be described hereinafter.

The invention may be applied to a wide list of photographic reagents including silver halide solvents, antifoggants, development arresters and restrainers, toning agents, etc. It is particularly adaptable from the standpoint of ease of preparation to photographic reagents containing a reactable sulfur- or nitrogen-containing substituent.

As was mentioned previously, this invention relates to photography and more particularly to the employment of photographic film units containing at least one compound which upon application of a photographic processing composition provides a photographic reagent performing a specific desired function in the particular photographic system selected for image formation.

A primary object of this invention, therefore, is to provide novel compounds of the foregoing description for providing the photographic reagent.

Another object is to provide novel photographic products including at least one of the aforementioned compounds.

Yet another object is to provide a novel means for incorporating a photographic reagent in a film unit in such a way that it is stable and non-diffusible but will be readily available upon application of an aqueous alkaline processing composition.

Still another object is to provide novel compounds which upon hydrolysis by contact with an aqueous alkaline medium provide a soluble photographic reagent for use

in systems wherein an image in black-and-white or in color is obtained by development of an exposed photosensitive element containing a developable image.

Other objects of this invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

The present invention is directed to the aforementioned novel means for including a photographic reagent in a film unit, e.g., by incorporating a compound of the foregoing description in a layer in the film unit. While the invention is applicable to photographic systems in general, of particular importance are those employing a photosensitive element having at least one light-sensitive silver halide layer and the invention will accordingly be described hereinafter for purposes of illustration by reference thereto.

Photosensitive elements comprising a support carrying a light-sensitive silver halide layer, typically a gelatino silver halide emulsion, are commonly employed to prepare images in silver. Negative images are obtained in known manner by developing the exposed element with an aqueous alkaline solution containing a silver halide developing agent and fixing by application of a silver halide solvent-fixer. The fixing step may be employed subsequent to development or in the same step by employing a so-called monobath composition including an alkaline material, a silver halide developing agent and a silver halide solvent.

By use of direct positive silver halide layers in such film units, positive rather than negative silver images are formed in the photosensitive element upon development.

Positive silver images are also obtainable from this type of film unit by the known silver diffusion transfer techniques wherein the exposed element containing the developable image is contacted with an aqueous alkaline solution containing a silver halide developing agent and a silver halide solvent to develop the image by reducing exposed and developable silver halide to image silver while forming an imagewise distribution of a soluble silver complex in terms of unexposed or undeveloped silver halide, and transferring this imagewise distribution, at least in part, by diffusion, to a silver-receptive stratum where it is reduced to impart thereto a positive silver image. The silver-receptive stratum may be contained initially on a separate element or in lieu thereof it may be contained on the same support as the silver halide layer. In any event, in the more typical systems, the stratum carrying the silver transfer image is separated following transfer image formation to provide the desired positive image. However, systems are also known where the stratum containing the positive silver image is retained in superposition with the negative image and either because of the low covering power of the negative image or because of the presence of an appropriate reflecting agent, e.g., a white pigment such as titanium dioxide, masking the negative image, the resulting composite print is viewable, without separation, as a positive reflection print.

In any of the aforementioned systems for forming positive and/or negative silver images, it is usually desirable to employ other photographic reagents performing specific desired functions, e.g., toning agents to achieve a silver image having more of a blue-black tonal quality, antifoggants and the like to prevent chemical and/or physical fog, etc.

In accordance with the present invention, any of the foregoing ingredients may be contained initially in a layer in the photosensitive element and/or in the image-receiving element in diffusion transfer processes employing a separate receiving element including the silver-receptive stratum.

As examples of such reagents which may be employed as the PHOTO moiety in the novel compounds of this invention, mention may be made of silver halide solvents such as sodium or potassium thiosulfate; inorganic silver halide developing agents such as sodium dithionite; organic silver halide developing agents of the dihydroxybenzene, diaminobenzene or aminophenol series; toning agents, particularly those containing a mercapto substituent, such as

2-thio-6-amino-uracil,
4-hydroxy-2-mercapto-6-methyl pyrimidine,
5,6-dimethyl-4-hydroxy-2-mercapto-pyrimidine,
4-hydroxy-2-mercapto-6-phenyl pyrimidine,
2-mercaptoorotic acid,
2-mercapto-4-methyl-pyrimidine,
4,6-dimethyl-2-mercapto pyrimidine,
2,5-dimercapto-1,3,4-thiadiazole,
5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium salt,
2-thiouracil-5-carboxylic acid,
5-ethyl-2-thiobarbituric acid,
2-mercapto-1-methylimidazole,
2-mercapto-3-phenyl-4,6,6-trimethyl dihydro pyrimidine,
α-mercaptoacetanilide,
o-mercapto benzoic acid,
cysteine,
2-mercapto-benzoxazole,
2-mercapto-6-nitrobenzothiazole,
2,3-quinoxaline dithiol,
mercaptopropionic acid,
sodium salt,
thiobarbituric acid,
thiouracil,
mercaptosuccinic acid,
toluene 3,4-dithiol,
4-amino-2-thiouracil,
2-aminothiophenol,
2-(mercaptomethyl)pyridine,
2-acetamido-5-mercapto-1,3,4-thiodiazole,
4-aza-2-mercaptobenzimidazole,
6-amino-8-mercaptopurine,
2-amino-6-hydroxy-8-mercaptopurine,
2-(furfurylamino)ethanethiol,
2-(α,α-methylphenethylamino)ethanethiol,
rhodanine,
2-(3-diethylaminopropylamino)ethanethiol,
2-cyclohexylamino-ethanethiol,
dodecanethiol, etc.;

antifoggants including many of the above-mentioned toning agents as well as other such as mercaptoimidazoles, e.g.,

1-methyl-2-mercapto-4,5-diphenylimidazole,
1,4,5-triphenyl-2-mercaptoimidazole,
1-phenyl-2-mercapto-4,5-difurylimidazole,
1-ethyl-2-mercapto-4,5,-diphenylimidazole,
1-methyl-2-mercapto-4,5-difurylimidazole,
1-phenyl-2-mercapto-4,5-di(p-methylphenyl)-imidazole,
1-phenyl-2-mercapto-4,5-di-(p-chlorophenyl)-imidazole,
1,5-diphenyl-2-mercapto-4-furyl-imidazole, etc.;

a mercaptotetrazaindene such as 5-ethoxycarbonyl-2-thio-6-oxo-1,3,3α,7-tetrazaindene; oxadiazoles such as 2-mercapto - 5-phenyl-1,3,4-oxadiazole, 2-mercapto-5-(m-nitrophenyl) - 1,3μ,oxadiazole, 2 - mercapto-5-(p-nitrophenyl) - 1,3,4 - oxadiazole, 2-mercapto-5-(p-methoxyphenyl) - 1,3,4 - oxadiazole, etc.; mercaptothiazoles such as 5 - amino - 4 - carbethoxy - 2 - mercaptothiazole, 5-methylamine - 4 - carbethoxy - 2 - mercaptothiazole, 5-amino - 4 - carbamyl - 2 - mercaptothiazole, and various other known antifoggants such as the thiazoles, pyrimidines, benzimidazoles, triazoles, tetrazoles, thioanilides, too numerous to mention.

In the aforementioned discussion, reference has been made to the applicability of the present invention to film units and systems for preparing black-and-white images in silver. The invention is also well suitable for

use in the various known systems for preparing color images. In such systems, broadly speaking, an exposed photosensitive element comprising at least one light-sensitive layer having associated therewith a dye image-providing material is contacted with an appropriate developing composition to provide the desired reversed or positive color image. Multicolor images are obtained by employing a photosensitive element containing at least two selectively sensitized silver halide layers each having associated therewith a dye image-providing material exhibiting desired spectral absorption characteristics. The most commonly employed elements of this type are the so-called tripack structures employing a blue-, a green- and a red-sensitive silver halide layer having associated therewith, respectively, a yellow, a magenta and a cyan dye image-providing material. The dye image-providing materials commonly employed in the prior systems for forming color images are either complete dyes or dye intermediates, e.g., color couplers. Selective dye image formation is obtained by such techniques as selective coupling or dye formation, dye bleach, diffusion transfer, etc. Since the present invention is not predicated upon any particular imaging system, but is instead applicable to the known imaging systems in general, a detailed discussion of these systems for forming color images is accordingly unnecessary. However, for purposes of illustration, the adaptability of this invention to color photography will be illustrated in further detail by reference to diffusion transfer systems for forming images in color.

Diffusion transfer color systems in general rely upon a differential in solubility or diffusibility of a dye image-providing material obtained as a function of development of an exposed photosensitive element including at least one silver halide layer and dye image-providing material which, as noted above, may be a complete dye or a dye intermediate. The image-providing material may be initially soluble and diffusible in the processing composition, in which event it is selectively rendered non-diffusible as a function of development, leaving remaining an imagewise distribution of diffusible material available for transfer; or the material may be initially non-diffusible, in which event an imagewise distribution of diffusible image-providing material is obtained as a function of development. As examples of the former types of color transfer systems, mention may be made of those described, for example, in U.S. Pats. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 2,774,668; and 2,983,606. As examples of the latter type of diffusion transfer systems, mention may be made of those described, for example, in U.S. Pats. Nos. 3,443,939; 3,443,940; 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294; and 3,445,228.

A particularly useful ssytem for forming color images by diffusion transfer is that described in U.S. Pat. No. 2,983,606, employing dye developers (dyes which are also silver halide developing agents) as the dye image-providing materials. In such ssytems, a photosensitive element comprising at least one silver halide layer having a dye developer associated therewith (in the same or in an adjacent layer) is developed by applying an aqueous alkaline processing composition. Exposed and developable silver halide is developed by the dye developer which in turn becomes oxidized to provide an oxidation product which is appreciably less diffusible than the unreacted dye developer, thereby providing an imagewise distribution of diffusible dye developer in terms of unexposed areas of the silver halide layer, which imagewise distribution is then transferred, at least in part, by diffusion, to a dyeable stratum to impart thereto a positive dye transfer image. Multicolor images may be obtained with a photosensitive element having two or more selectively sensitized silver halide layers and associated dye developers, a tripack structure of the type described above and in various patents including the aforementioned U.S. Pat. No. 2,983,606 being especially suitable for accurate color recordation of the original subject matter. In either monochrome or multicolor systems, the dyeable stratum may be contained in a separate element or it may be contained in the film unit containing the photosensitive strata, e.g., in integral negative-positive structures of the type described, for example, in U.S. Pats. Nos. 3,415,644; 3,415,645 and 3,415,646. The dye developer process is preferably carried out in the presence of an onium compound, e.g., a heterocyclic quaternary ammonium compound such as

1-benzyl-2-picolinium bromide,
1-(3-bromopropyl)-2-picolinium-p-toluenesulfonate,
1-phenethyl-2-picolinium bromide,
1-γ-phenylpropyl-2-picolinium bromide,
2,4-dimethyl-1-phenethylpyridinium bromide,
2,6-dimethyl-1-phenethylpyridinium bromide,
5-ethyl-2-methyl-1-phenethylpyridinium bromide,
2-ethyl-1-phenethylpyridinium bromide,
1-[3-(N-pyridinium bromide)propyl]-2-picolinium-p-toluenesulfonate,
anhydro-1-(4-sulfobutyl)-2-picolinium hydroxide,
α-picoline-β-naphthoylmethylbromide,
1-β-phenylcarbamoyloxyethyl-2-picolinium bromide,
1-methyl-2-picolinium pts,
1-phenethyl-2,4,6-trimethylpyridinium bromide,
4-γ-hydroxypropyl-1-phenethylpyridinium bromide, and
1-n-heptyl-2-picolinium bromide;

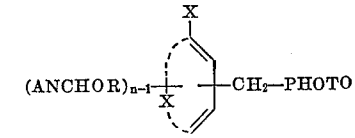
as well as the various onium compounds disclosed, for example, in U.S. Pats. Nos. 3,173,786; 3,253,915 and others, to obtain improvements in density and highlights.

Various other photographic reagents are also advantageously employed in the dye developer systems for forming color transfer images. For example, an auxiliary or accelerating silver halide developing agent, e.g., a benzenoid developing agent such as 4'-methylphenylhydroquinone, triptyene diol, etc., or a 3-pyrazolidone developing agent, e.g., 1-phenyl-3-pyrazolidone, is commonly employed in a layer of the film unit in accordance with the invention described and claimed in U.S. Pat. No. 3,192,044. A developer arrester or restrainer may also be employed, as is disclosed in U.S. Pat. No. 3,265,498. As examples of suitable development restrainers, mention may be made of thiobarbituric acids such as dodecyl thiobarbituric acid, phenyl-mercaptotetrazoles such as 1-phenyl-5-mercaptotetrazole, as well as various other heterocyclic mercaptans such as the mercaptobenzothiazoles. One may also employ an antifoggant of the type heretofore described. While silver halide solvents are usually thought of in terms of the previously described black-and-white processes, it has also been heretofore suggested that a small amount of a silver halide solvent such as an alkali metal or ammonium thiosulfate or thiocyanate may be employed in the dye developer process to increase photographic speed.

The present invention is also applicable to the various types of photographic reagents disclosed above, as well as others which could be mentioned, and provides a simple and efficient method for incorporating such reagents in a photographic film unit.

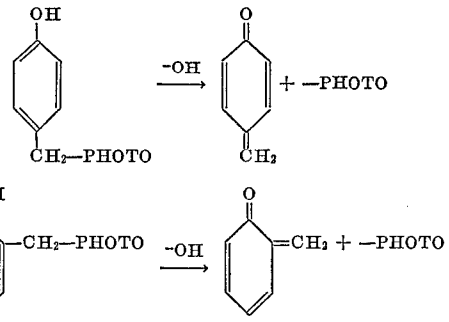
As was mentioned in the "Summary of the Invention," the desired photographic reagent is incorporated, in accordance with this invention, as a moiety of a compound of the formula:

(A)

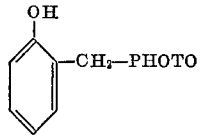


wherein X, Y, PHOTO, ANCHOR and *n* have the meanings heretofore noted. Compounds of the above formula may be defined as quinone-methide or naphthoquinone-methide precursors containing the photographic reagent moiety, since they split off the photographic reagent and form the quinone-methide or naphthoquinone-methide upon contact with alkali, e.g., upon application of an aqueous alkaline processing reagent.

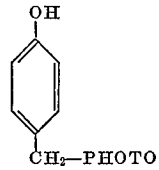
This reaction may be illustrated as follows:



One class of preferred compounds of this invention are phenols of the formulae:



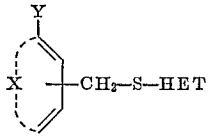
or



Of particular interest in the practice of this invention are those compounds containing an antifoggant or development restrainer moiety, e.g., those compounds of Formula A wherein PHOTO is an antifoggant or development restrainer moiety such as one of those derived from the aforementioned illustrative reagents.

A particularly preferred class of compounds including such a moiety are the mercapto derivatives of heterocyclic compounds heretofore employed as development restrainers, e.g., the mercaptotetrazoles, mercaptobenzothiazoles, etc. Such compounds may be represented by the formula:

(B)



wherein:

X and Y have the meanings heretofore noted;

The —CH_2—S—HET substituent is bonded to a nuclear carbon atom ortho or para to the Y substituent; and

HET represents a heterocyclic ring, particularly a heterocyclic 5-membered ring containing at least one nitrogen atom, e.g., a tetrazole, benzothiazole, etc., including nuclear substituted derivatives thereof, the —S—HET moiety being the monovalent radical of a development restrainer of the formula:

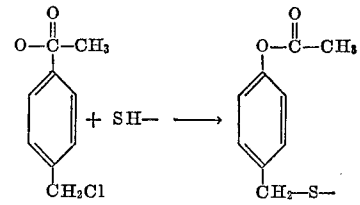
HS—HET

Where found desirable or expedient to do so, the compounds of this invention may be employed in the film units in their protected form which upon contact with an aqueous alkaline medium hydrolyze to form the corresponding phenol recited above. Incorporation in this manner may provide a means of retarding release of the photographic reagent where such retardation is desired, particularly where the protected group is not rapidly removable by hydrolysis.

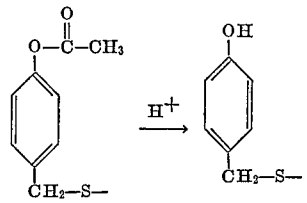
In instances wherein it is desired further to immobilize the compound or the benzyl alcohol ultimately obtained from the quinone-methide formed upon release of the photographic reagent, the above-noted anchoring moiety may be included in the compound.

In general, the novel compounds of this invention are readily obtainable by appropriate replacement or substitution reactions. In such reactions it may be, and usually is desirable to protect the phenolic hydroxyl group during the reaction step by which the photographic reagent moiety is incorporated.

By way of illustration, photographic reagents containing a mercapto group are readily incorporated by reaction with a protected chloromethyl phenol or naphthol, e.g., ortho- or para-acetoxy-benzyl chloride:

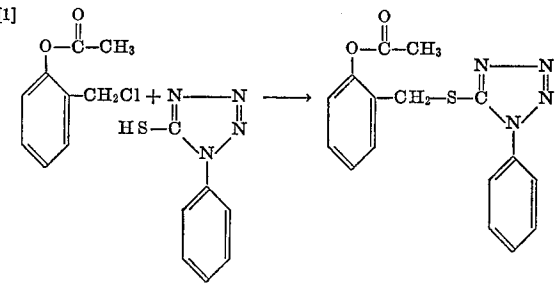


followed by hydrolysis in acid:

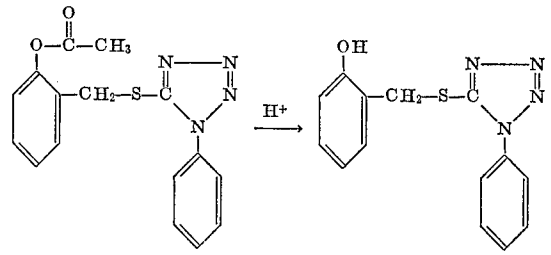


Further by way of illustration, the following reactions illustrate the preparation of a compound of this invention containing a developer restrainer, 1-phenyl-5-mercaptotetrazole, as the PHOTO moiety.

[1]

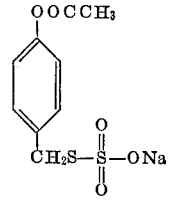


[2]



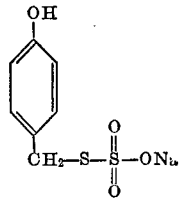
As examples of compounds contemplated by this invention, mention may be made of the following:

1.



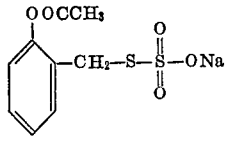
sodium S-(p-acetoxybenzyl)thiosulfate

2.



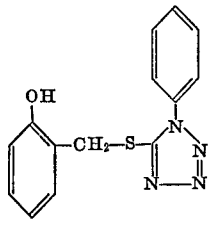
sodium S-(p-hydroxybenzyl)thiosulfate

3.



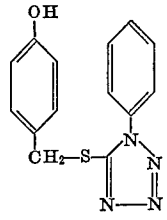
sodium S-(o-acetoxybenzyl)thiosulfate

4.



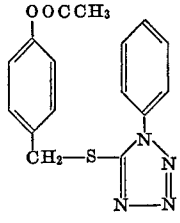
1-phenyl-5-(o-hydroxybenzylthio)-tetrazole

5.



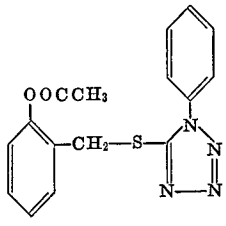
1-phenyl-5-(p-hydroxybenzylthio)-tetrazole

6.



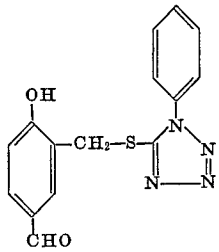
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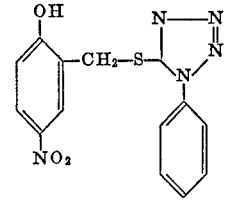
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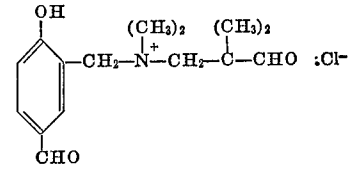
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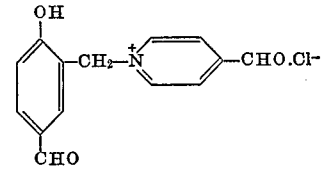
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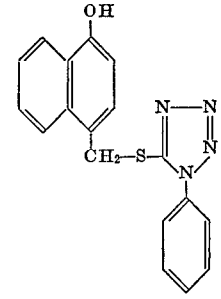
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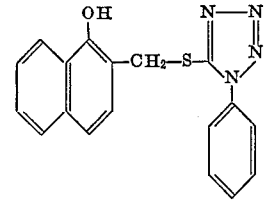
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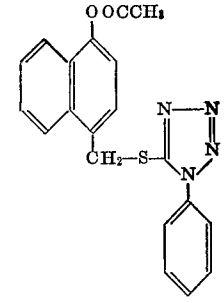
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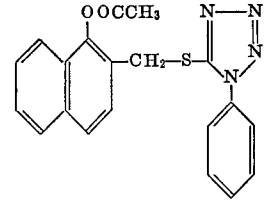
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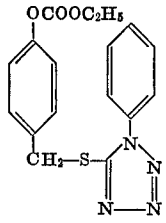
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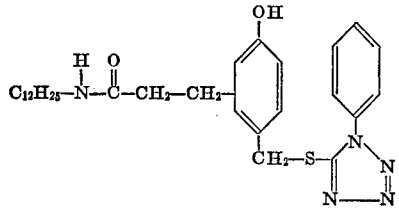
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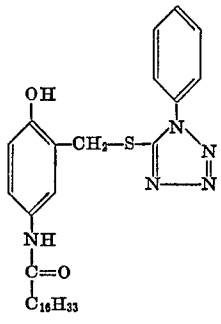
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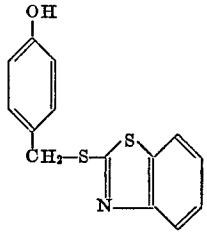
1-phenyl-5-(4'-hydroxy-3'-dodecylamidoethyl-benzylthio)-tetrazole

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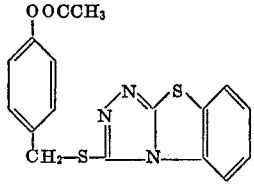


1-phenyl-5-(2'-hydroxy-5'-hexadecylamido-benzylthio)-tetrazole

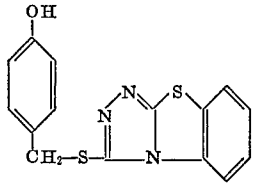
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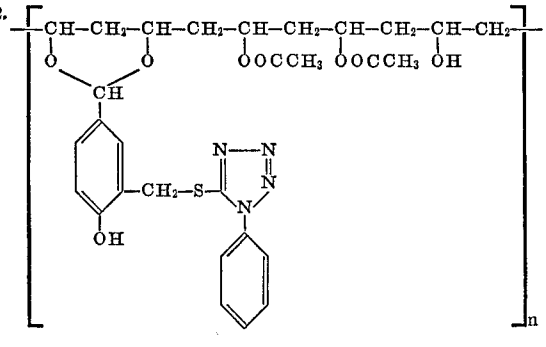
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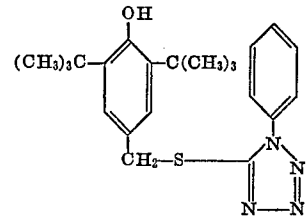
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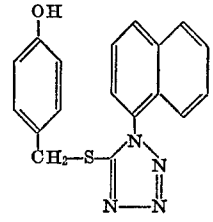
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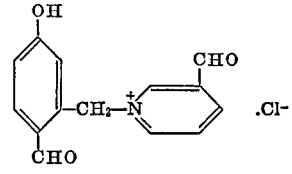
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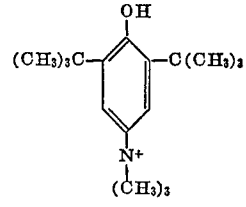
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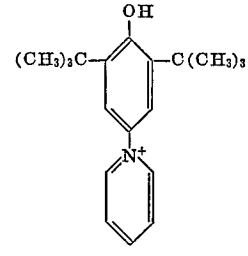
25.



26.



27.



Of the foregoing illustrative compounds, those of Formulae 1–3 contain a silver halide solvent moiety, i.e., release a silver halide solvent, sodium thiosulfate, upon hydrolysis; those of Formulae 4–9 and 12–24 release a development restrainer; those of Formulae 10, 11 and 25 are gelatin hardeners; and those of Formulae 26 and 27 release an amine dye mordant. The aforementioned gelatin hardeners are of interest in that they do not function in quite the same manner as do the other illustrative compounds. Generally speaking, the novel reagents of this invention do not perform their desired function until they are released by the aforementioned hydrolysis reaction. However, these gelatin hardeners function only prior to hydrolysis. Upon hydrolysis, e.g., upon contact with alkali, the compound decomposes and then is no longer capable of this function. Accordingly, these compounds may in a sense be regarded as temporary gelatin hardeners or cross-linking agents whose ability to function as such is terminated upon hydrolysis. The gelatin hardened by such compounds is also affected by alkali, swelling and breaking apart so that the gelatin so treated may also be regarded as temporarily hardened. Gelatin hardened in this manner, i.e., hardened by cross-linking obtained by use of these novel compounds, may be employed photographically as temporary barrier layers, e.g., layers which preclude or inhibit diffusion or permeation of solution of reagents until a desired stage in the photographic development process, in colloid transfer systems, etc.

The following examples show by way of illustration and not by way of limitation the preparation of the novel compounds of this invention.

EXAMPLE 1

15 g. of o-hydroxybenzyl alcohol were gradually added while stirring to 45 g. of ice-cooled acetyl chloride. About 30 minutes after the addition had been completed, unchanged acetyl chloride was evaporated using a thin film evaporator. 50 ml. of water were then added to the residue followed by neutralization by adding solid sodium bicarbonate. This mixture was extracted three times with 50 ml. of ethyl ether (each extraction) and the ether phase was then dried. Vacuum distillation yielded 17 g. of o-acetoxybenzyl chloride, a colorless liquid, B.P. (1.5 mm.) 98–102° C.

EXAMPLE 2

100 g. of p-hydroxybenzyl alcohol were added in small portions, while stirring, to 300 ml. of ice-cooled acetyl chloride. Upon standing at room temperature overnight, the major portion of excessive acetyl chloride had evaporated and the remainder was removed using a thin film evaporator. The residue was then neutralized by shaking with concentrated aqueous sodium bicarbonate solution. The aqueous phase was extracted twice with 100 ml. of ethyl ether and the combined organic layers were filtered and then dried. Vacuum distillation yielded 81 g. of pure p-acetoxybenzyl chloride, a colorless liquid, B.P. (1.5 mm.) 104–106° C.

EXAMPLE 3

45 g. of the sodium salt of phenylmercaptotetrazole were dissolved in 500 ml. of acetone. This solution was then filtered and heated to boiling, after which a solution of 41.5 g. of o-acetoxybenzyl chloride (as prepared in Example 1) in 100 ml. of acetone were added. The resulting solution was refluxed for two hours and filtered. The filtrate was evaporated to yield a solid residue which was extracted with warm 3% aqueous sodium bicarbonate solution. After filtration the solid material was washed with water and then dried to yield 64.5 g. of 1-phenyl-5-(o-acetoxybenzylthio)-tetrazole (Formula 7), white crystals melting at 103–105° C.

Elemental analysis.—Calculated (percent): C, 59.0; H, 4.3; N, 17.2; S, 9.8. Found (percent): C, 58.8; H, 4.6; N, 16.9; S, 9.7.

64.5 g. of the compound of Formula 7 (as prepared above) was dissolved in 1.6 l. of methanol, 15 ml. of 10% aqueous hydrochloric acid were added and the solution was then heated while stirring to 55–57° C. in the presence of nitrogen. After two hours 100 ml. of methanol were slowly added to replace methanol which had evaporated. After two more hours the methanol was flushed off using a thin film evaporator. The solid residue was pulverized, extracted with warm dilute aqueous sodium bicarbonate solution, washed with water and then dried. Recrystallization from benzene/hexane yielded 46 g. of 1-phenyl-5-(o-hydroxybenzylthio)-tetrazole (the compound of Formula 4), white crystals melting at about 102° C., soluble in methanol and benzene and slightly soluble in water.

Elemental analysis.—Calculated (percent): C, 59.2; H, 4.2; N, 19.7; S, 11.8. Found (percent): C, 59.3; H, 4.3; N, 19.5; S, 11.6.

EXAMPLE 4

45 g. of the sodium salt of phenylmercaptotetrazole were dissolved in 500 ml. of acetone. This solution was filtered and heated to boiling, after which 41.5 g. of p-acetoxybenzyl chloride (as prepared in Example 2) in 100 ml. of acetone were added. The resulting solution was refluxed for two hours and filtered. The filtrate was evaporated to yield a solid residue which was extracted with warm 3% aqueous sodium bicarbonate solution. It was then filtered and the solid material recovered was washed with water and dried in a vacuum oven to yield 72 g. of 1-phenyl-5-(p-acetoxybenzylthio)-tetrazole (the compound of Formula 6), white crystals melting at 71–72° C.

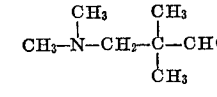
Elemental analysis.—Calculated (percent): C, 59.0; H, 4.3; N, 17.2. Found (percent): C, 58.9; H, 4.3; N, 17.3.

57 g. of the last-mentioned compound were dissolved in 1.3 l. of methanol. 10 ml. of 10% aqueous hydrochloric acid were added and the solution was heated to 55–57° C. while stirring and in the presence of nitrogen. After two hours 100 ml. of methanol were added slowly to replenish evaporated methanol. About one hour later the methanol was flashed off using a thin film evaporator. The resulting solid residue was pulverized, extracted with warm dilute sodium bicarbonate solution, washed with water and dried. Recrystallization from benzene/hexane yielded 35 g. of 1-phenyl-5-(p-hydroxybenzylthio)-tetrazole, white crystals melting at 130–131° C., soluble in methanol and benzene and slightly soluble in water.

Elemental analysis.—Calculated (percent): C, 59.2; H, 4.2; N, 19.7; S, 11.8. Found (percent): C, 59.2; H, 4.4; N, 19.7; S, 11.3.

EXAMPLE 5

A solution of 0.02 mole of 4-hydroxy-3-chloromethylbenzaldehyde in 130 ml. of ethyl ether was added dropwise at room temperature to a stirred solution of 0.02 mole of a tertiary amine of the formula:



in 70 ml. of ethyl ether. The resulting mixture was stirred overnight and then filtered. The residue was washed with ethyl ether and then dried to yield the monohydrate of N-(3-formyl - 6 - hydroxy-benzyl)-N-(2'-formyl-2',2'-dimethylethyl)-N,N-dimethylammonium chloride, the hydrolyzable gelatin hardener of Formula 10, a white powder, M.P. 130° C.

Elemental analysis.—Calculated (percent): C, 56.8; H, 7.6; Cl, 11.1. Found (percent): C, 57.1; H, 7.5; Cl, 10.8.

EXAMPLE 6

Substitution of 4-formylpyridine for the tertiary amine in the reaction of Example 5 yielded another hydrolyzable gelatin hardener, N-(3'-formyl-6'-hydroxybenzyl)-4-formylpyridinium chloride, the compound of Formula 11, a yellow powder.

EXAMPLE 7

Substitution of 3-formylpyridine in Example 5 yielded the hydrolyzable gelatin hardener of Formula 25, N-(3'-formyl-6'-hydroxybenzyl)-3-formylpyridinium chloride, a yellow powder.

EXAMPLE 8

9.92 g. of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) were dissolved in 20 ml. of water and the resulting solution was heated to 70° C. while stirring. A solution of 7.38 g. of p-acetoxybenzyl chloride in 20 ml. of 2B ethanol was then added dropwise. The resulting clear solution was then gently refluxed for 40 minutes. After cooling, the solvent was evaporated using a thin film evaporator to yield a crystalline residue which was then extracted with about 150 ml. of boiling ethanol, followed by filtration. Refrigeration and filtration of the resulting precipitate yielded about 7 g. of sodium S-(p-acetoxybenzyl) thiosulfate, the compound of Formula 1, white platelets, M.P. 220° C. (decomp.), soluble in water, alkali, warm ethanol.

Elemental analysis.—Calculated (percent): C, 38.1; H, 3.2; Cl, 22.5. Found (percent): C, 37.9; H, 3.2; Cl, 22.4.

The S-(o-acetoxybenzyl) thiosulfate isomer of Formula 3 may be prepared by substituting o-acetoxybenzyl chloride in the above example.

EXAMPLE 9

To a solution of 8.7 g. of the sodium salt of 1-phenyl-5-mercaptotetrazole in 200 ml. of acetone was added a solution of 6.4 g. of 2-hydroxy-5-formyl-benzyl chloride in 50 ml. of acetone. After stirring for 30 minutes at room temperature, the resulting mixture was filtered and the filtrate was refluxed for 30 minutes, filtered again and the solvent was then evaporated with a thin film evaporator. The solid residue was washed with warm aqueous sodium bicarbonate solution for 15 minutes, filtered, dried and washed with ether to yield 5.5 g. of 1-phenyl-5-(2'-hydroxy-5'-formyl-benzylthio)-tetrazole, the compound of Formula 8, white crystals soluble in acetone and methanol, M.P. 168° C. 1.5 g. of "Elvanol 70-05" (trademark of E. I. du Pont de Nemours & Co. for a low viscosity polyvinyl alcohol) was suspended in a solution of 3.5 g. of the compound of Formula 8 (prepared as described above) and 0.5 ml. of H_3PO_4 in 30 ml. of glacial acetic acid for 3 hours at 80° C. under nitrogen and with stirring. The temperature was then lowered to 55° C. for 3 days with stirring. The resulting clear yellow solution was then cooled to room temperature, decanted and precipitated into dilute aqueous sodium bicarbonate. It was then washed and dried to yield 2.3 g. of the polymer of Formula 22, soluble in methyl Cellosolve.

Elemental analysis.—Calculated (percent): C, 57.7; H, 6.1; N, 7.7; S, 4.4. Found (percent): C, 57.1; H, 6.1; N, 8.1; S, 4.1.

The compounds of this invention, e.g., the aforementioned illustrative compound, are advantageously incorporated in photographic products including a layer in which a visible image is formed. These photographic products include the known photosensitive elements, image-receiving elements and unitary film units containing both, and apart from the incorporation of such compounds, the specific structures of such photographic products are per se known and therefore comprise no part of the present invention.

While the photographic products to which this invention is applicable have been heretofore known, the following description will illustrate the types of photographic products contemplated by this invention.

Photosensitive elements or films for preparing silver images generally comprise a support carrying a light-sensitive silver halide layer, e.g., a gelatin mixed silver halide emulsion. This layer may, and usually does contain additional reagents performing specific desired functions. Development and fixing of such an element in known manner provides a negative silver image in the silver halide layer from which one or more positive images may then be prepared. The fixing step may follow the development step or the two may be carried out concurrently by employing a so-called monobath consisting of an alkaline solution of a silver halide developing agent, e.g., an ortho- or paradihydroxybenzene, aminophenol or diaminobenzene, and a silver halide solvent-fixer, e.g., sodium or potassium thiosulfate.

The aforementioned element may also be employed to obtain positive silver images by diffusion transfer techniques wherein the exposed element is developed with an aqueous alkaline composition including a silver halide developing agent and a silver halide solvent (such as described above) to develop exposed and developable silver halide and to form from unexposed and undeveloped silver halide an imagewise distribution of a soluble silver complex which is transferred, at least in part, by diffusion, to a superposed silver-receptive stratum of known description to impart thereto a positive silver transfer image. The silver-receptive stratum may be contained as a separate element, generally referred to as an image-receiving element, comprising at least a support, which may be opaque or transparent, depending upon whether reflection prints or transparencies are contemplated, carrying the silver-receptive stratum. Alternatively, the silver-receptive stratum and silver halide layer may be contained on the same support as a unitary film unit. As examples of such unitary film units, mention may be made of those described and claimed in U.S. Pat. No. 2,861,885 and in the copending application of Edwin H. Land, Ser. No. 519,995, filed Jan. 11, 1966, now abandoned, and the copending application of Edwin H. Land and Leonard C. Farney, Ser. No. 519,884, filed Jan. 11, 1966 and now abandoned.

While mention has been made of development compositions containing the essential ingredients for development and silver image formation, e.g., a silver halide developing agent and a silver halide solvent, it has heretofore been suggested that such reagents be contained initially in the photographic product, in which case the desired processing composition is obtained by contacting the product with an aqueous medium. In addition to the named reagents, it is known to include various other ingredients such as antifoggants, toning agents, etc. in the processing composition and/or initially in the photographic product.

The present invention provides a novel system for incorporating such reagents in the photographic product, e.g., photosensitive elements and/or receiving elements of the foregoing description, in such a manner that they are non-diffusible from the layer or layers in which incorporated during the shelf life of the product and yet are available when needed in the development process upon application of the aqueous alkaline developing medium.

The present invention is also useful in photographic products intended for the production of images in color, regardless of the particular system employed in the preparation of the color images.

Generally speaking, photosensitive elements intended for the production of color images include at least one light-sensitive silver halide layer and an associated dye image-providing material, e.g., a dye or dye intermediate such as those mentioned earlier and disclosed in the illustrative patents. The associated dye image-providing material may be contained in the same layer as the silver halide or in an adjacent layer. Multicolor images are obtained by employing a photosensitive element containing at least two selectively sensitized silver halide layers each having associated therewith a dye image-providing material exhibiting desired spectral absorption characteristics. As was mentioned previously, the most common photosensitive elements for forming multicolor images are of the tripack structure comprising a plurality of essential layers including a red-sensitive silver halide layer and associated cyan dye image-providing material, a green-sensitive silver halide layer and associated magenta dye image-providing material, and a blue-sensitive silver halide layer and associated yellow dye image-providing material. While the layers denoted above have been referred to as the "essential layers," a photosensitive element containing these layers may also contain additional layers providing specific desired functions. For example, interlayers or spacer layers may be provided between the respective silver halide layers and associated dye image-providing materials; a layer or layers providing a pH-reducing function may be included in the photosensitive element; and/or an auxiliary layer or overlayer may also be provided on the outer surface, e.g., over the blue-sensitive silver halide layer. Various photographic reagents, e.g., developing agents, antifoggants, development restrainers, desensitizers, etc., may be included in such additional layers and/or in the aforementioned essential layers.

Color images may be obtained from such elements by known color techniques as dye bleach, selective dye formation, diffusion transfer, etc. In diffusion transfer systems, an imagewise distribution of soluble and diffusible

dye image-providing material is formed as a function of development and this imagewise distribution is then transferred, at least in part, by diffusion, to a superposed dyeable stratum to impart thereto a color transfer image. The dyeable stratum may be contained on a separate support member as a separate image-receiving element, which may additionally contain other layers, e.g., a layer or layers providing a pH-reducing function, as is known in the art. Alternatively, the dyeable stratum along with any associated layers may be contained together with the photosensitive strata as a unitary film unit which may be termed an integral negative-positive film unit comprising a negative component including the aforementioned essential layers and a positive component including at least the dyeable stratum in which the color transfer image is to be formed. These integral negative-positive film units may be adapted for use in systems wherein the transfer image formed in the dyeable stratum is to be separated from the negative component following image formation or they may be employed in film units and systems wherein the transfer image need not be separated following image formation, e.g., in systems wherein the transfer image is viewable, without separation, as a reflection print.

In addition to the essential layers comprising the negative and positive components, integral negative-positive film systems wherein the transfer image need not be separated generally further include means for providing a reflecting layer between the dyeable stratum and the negative component in order to mask effectively the silver image or images formed as a function of development of the silver halide layer or layers and any remaining associated dye image-providing material and to provide a background for viewing the color image formed in the dyeable stratum, without separation, by reflected light. This reflecting layer may comprise a preformed layer of a reflecting agent included in the essential layers of the film unit or the reflecting agent may be provided after photoexposure, e.g., by including the reflecting agent in the processing composition. These essential layers are preferably contained on a transparent dimensionally stable layer or support member positioned closest to the dyeable stratum so that the resulting transfer image is viewable through this transparent layer. Most preferably another dimensionally stable layer which may be transparent or opaque is positioned on the opposed surface of the essential layers so that the aforementioned essential layers are sandwiched or confined between a pair of dimensionally stable layers or support members, at least one of each is transparent to permit viewing therethrough of a color transfer image obtained as a function of development of the exposed film unit in accordance with the known color diffusion transfer system such as will be detailed hereinafter. In a particularly preferred form such film units are employed in conjunction with a rupturable container of known description containing the requisite processing composition and adapted upon application of pressure of applying its contents to develop the exposed film unit, e.g., by applying the processing composition in a substantially uniform layer between the dyeable stratum and the negative component. It will be appreciated that the film unit may optionally contain other layers performing specific desired functions, e.g., spacer layers, pH-reducing layers, etc.

Opacifying means may be provided on either side of the negative component so that the film unit may be processed in the light to provide the desired color transfer image. In a particularly useful embodiment such opacifying means comprise an opaque dimensionally stable layer or support member positioned on the free or outer surface of the negative component, i.e., on the surface of the film unit opposed from the positive component containing the dyeable stratum to prevent photoexposure by actinic light incident thereon from this side of the film unit and an opacifying agent applied during development between the dyeable stratum and the negative component, e.g., by including the opacifying agent in a developing composition so applied, in order to prevent further exposure (fogging) by actinic light incident thereon from the other side of the film unit when the thus exposed film unit is developed in the light. The last-mentioned opacifying agent may comprise the aforementioned reflecting agent which masks the negative component and provides the requisite background for viewing the transfer image formed thereover. Where this reflecting agent does not by itself provide the requisite opacity it may be employed in combination with an additional opacifying agent in order to prevent further exposure of the light-sensitive silver halide layer or layers by actinic light incident thereon.

As examples of such integral negative-positive film units for preparing color transfer images viewable without separation as reflection prints, mention may be made of those described and claimed in U.S. Pats. Nos. 3,415,644, 3,415,645, 3,415,646 and 3,473,925; as well as those described in copending applications Ser. Nos. 782,056, now U.S. Pat. No. 3,573,043, and 782,075, now U.S. Pat. No. 3,573,044, filed Dec. 9, 1969, 65,084, filed Aug. 19, 1970, all in the name of Edwin H. Land; and Ser. Nos. 39,646 and 39,666 of Howard G. Rogers, filed May 22, 1970, now U.S. Pat. Nos. 3,594,165 and 3,594,164, respectively.

In general, the film units of the foregoing description, e.g., those described in the aforementioned patents and/or copending applications, are exposed to form a developable image and thereafter developed by applying the appropriate processing composition to develop exposed silver halide and to form, as a function of development, an imagewise distribution of diffusible dye image-providing material which is transferred, at least in part by diffusion, to the dyeable stratum to impart thereto the desired color transfer iamge, e.g., a positive color transfer image. Common to all of these systems is the provision of a reflecting layer between the dyeable stratum and the photosensitive strata to mask effectively the latter and to provide a background for viewing the color image contained in the dyeable stratum, whereby this image is viewable without separation, from the other layers or elements of the film unit. In certain of these systems, this reflecting layer is provided prior to photoexposure, e.g., as a preformed layer included in the essential layers of the laminar structure comprising the film unit, and in others it is proivded at some time thereafter, e.g., by including a suitable light-reflecting agent, for example, a white pigment such as titanium dioxide, in the processing composition which is applied between the dyeable stratum and the next adjacent layer to develop the latent image and to form the color transfer image.

An illustrative integral negative-positive film unit of this description may contain a negative (photosensitive) component comprising, as the essential layers, a layer of cyan dye developer, a red-sensitive silver halide emulsion layer, a first interlayer, a layer of magenta dye developer, a green-sensitive silver halide emulsion layer, a second interlayer, a yellow dye developer layer, a blue-sensitive silver halide emulsion layer, and an auxiliary layer or overlayer; and a positive (image-receiving) component comprising an image-receiving layer, a spacer layer, and a pH-reducing or neutralizing layer between a first dimensionally stable layer or support member which is positioned on the outer surface of the negative component and is preferably opaque so as to permit development in the light and a second dimensionally stable layer or support member which is positioned on the outer surface of the positive component and is effectively transparent to permit viewing of a color transfer image formed as a function of development in receiving layer or dyeable stratum.

These dimensionally stable layers may, for example, be liquid-impermeable layers which when taken together may possess a processing composition solvent vapor permeably sufficient to effect, subsequent to substantial trans-

fer image formation and prior to any substantial environmental image degradation to which the resulting image may be prone, osmotic transpiration of processing composition solvent in a quantity effective to decrease the solvent from a first concentration at which the color-providing material is diffusible to a second concentration at which it is not. Although these layers may possess a vapor transmission rate of 1 or less gms./24 hrs./100 in.²/mil., they preferably possess a vapor transmission rate for the processing composition solvent averaging not less than about 100 gms./24 hrs./100 in.²/mil., most preferably in terms of the preferred solvent, water, a vapor transmission rate averaging in excess of about 300 gms. of water/24 hrs./100 in.²/mil., and may advantageously comprise a microporous polymeric film possessing a pore distribution which does not unduly interfere with the dimensional stability of the layers or, where required, the optical characteristics of such layers. As examples of useful materials of this nature, mention may be made of those having the aforementioned characteristics and which are derived from ethylene glycol terephthalic acid; vinyl chloride polymers; polyvinyl acetate; cellulose derivatives, etc.

The silver halide layers preferably comprise photosensitive silver halide, e.g., silver chloride, bromide or iodide or mixed silver halides such as silver iodobromide or chloriodobromide dispersed in a suitable colloidal binder such as gelatin and such layers may typically be on the order of 0.6 to 6 microns in thickness. It will be appreciated that the silver halide layers may and in fact generally do contain other adjuncts, e.g., chemical sensitizers such as are disclosed in U.S. Pats. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; etc.; as well as other additives performing specific desired functions, e.g., coating aids, hardeners, viscosity-increasing agents, stabilizers, preservatives, ultraviolet absorbers and/or speed-increasing compounds. While the preferred binder for the silver halide is gelatin, others such as albumin, casein, zein, resins such as cellulose derivatives, polyacrylamides, vinyl polymers, etc., may replace the gelatin in whole or in part.

The respective dye developers, which may be any of those heretofore known in the art and disclosed for example in U.S. Pat. No. 2,983,606, etc., are preferably dispersed in an aqueous alkaline permeable polymeric binder, e.g., gelatin as a layer from about 1 to 7 microns in thickness.

The interlayers and auxiliary layer may comprise an alkaline permeable polymeric material such as gelatin and may be on the order of from about 1 to 5 microns in thickness. As examples of other materials for forming these interlayers, mention may be made of those disclosed in U.S. Pat. No. 3,421,892 and the copending applications of Richard J. Haberlin, Ser. No. 854,491, filed Sept. 2, 1969, now U.S. Pat. No. 3,615,422, and Lloyd D. Taylor, Ser. No. 790,648, filed Jan. 13, 1969, now U.S. Pat. No. 3,575,700, etc. These interlayers may also contain additional reagents performing specific functions and the various ingredients necessary for development may also be contained initially in such layers in lieu of being present initially in the processing composition, in which event the desired developing composition is obtained by contacting such layers with the solvent for forming the processing composition, which solvent may include the other necessary ingredients dissolved therein.

The image-receiving layer may comprise any of the dyeable strata heretofore known in the art for preparing color transfer images. It may be on the order of 0.25 to 0.4 mil in thickness and may, for example, comprise a dyeable polymer such as nylon, e.g., N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, etc. The receiving layers may, if desired, contain suitable mordants, e.g., any of the conventional mordant materials for acid dyes such as those disclosed, for example, in the aforementioned U.S. Pat. No. 3,227,550; as well as other additives such as ultraviolet absorbers, pH-reducing substances, etc.

While not necessary to the practice of this invention, with the film units employing color-providing materials such as dye developers wherein development is effected in the presence of a processing composition having a relatively high pH, say, for example, on the order of at least 12 to 14, it may be desirable or expedient to provide means for reducing the pH following development to a level wherein the resulting dye image is not adversely affected.

One such system as is disclosed in U.S. Pat. No. 3,362,-819 employs a polymeric acid layer in association with the image-receiving layer. An inert timing or spacer layer is preferably disposed between the polymeric acid layer and the image-receiving layer.

As is disclosed in this patent, the polymeric acid layer comprises polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium, potassium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, non-diffusible from the acid polymer layer. In the preferred embodiments disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose, which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives or cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methyl-vinyl ether/maleic anhydride copolymers; etc.

As previously noted, the pH of the processing composition may be of the order of at least 12 to 14. The acid polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition, thus requiring, of course, that the action of the polymeric acid be accurately so controlled as not to interfere with the either development of the negative of image transfer of the color-providing material. For this reason, the pH of the image layer must be kept at a functional transfer level until dye image has been formed. Where the color-providing material is not diffusible at the lower pH obtained by the polymeric acid layer, the subsequent

pH reduction, in addition to its desirable effect upon image light stability, also serves a highly valuble photographic function by substantially terminating further dye transfer.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the acid polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer, which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid groups in the acid polymer layer may be effected by mixing the acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited copending patent, by (a) mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also there disclosed that the layer containing the polymeric acid may contain a water-insoluble polymer, preferably a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the polymer acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrote, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats are employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer, for example, a layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It is there stated to have been found that the pH does not drop until the alkali has passed through the spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the interlayer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer.

As disclosed in aformentioned U.S. Pat. No. 3,362,819, the presence of an inert spacer layer was found to be effective in evening out the various reaction rates over a wide range of temperatures, for example, by preventing premature pH reduction when imbibition is effected at temperatures above room temperature, for example, at 95° to 100° F. By providing an inert spacer layer, that application discloses that the rate at which alkali is available for capture in the polymeric acid layer becomes a function of the alkali diffusion rate.

However, as disclosed in U.S. Pat. No. 3,455,686 preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer processing temperatures in order to provide diffusion transfer color processes relatively independent of positive transfer image variations over an extended rang eof ambient temperatures.

Specifically, it is there stated to have been found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with inncreased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperautres above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion to alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was stated to be especially true of alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective with the temperature range of optimum transfer processing. Conversely, at temperatures below the optimum transfer processing range, for example, temperatures below approximately 40° F., the last-mentioned inert spacer layer was disclosed to provide an effective diffusion barrier timewise preventing effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates and to result in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation formation of transfer image stain and its resultant degradation of the positive transfer images color definition.

It is further stated in the last-mentioned U.S. Pat. No. 3,455,686 to have been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintainance and/or premature pH reduction are obviated.

As examples of polymers which were disclosed to exhibit inverse temperature-dependent permeability to alkali, mention may be of: hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidone, hydroxypropyl methyl cellulose, isopropyl cellulose, partial acetals of polyvinyl alcohol such as partial polyvinyl butyral, partial polyvinyl formal, partial polyvinyl acetal, partial polyvinyl propional, and the like.

The last-mentioned specified acetals of polyvinyl were stated to generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1,000, preferably of about 1,000 to 50,000, possessing a degree of acetalation within about 10% to 30%, 10% to 30%, 20% to 80% and 10% to 40%, of the polyvinyl alcohol's theoretical polymeric hydroxy groups, respectively, and including mixed acetals where desired.

Where desired, a mixture of the polymers is to be employed, for example, a mixture of hydroxypropyl methyl cellulose and partial polyvinyl butyral.

While the acid-containing or neutralizing layer and spacer of timing layer have heretofore been described as being disposed between the receiving layer and the transparent layer as layers of the positive component of the integral negative-positive film unit, this pH-reducing means may be disposed elsewhere in the film unit and may, for example, be disposed in the negative component, as is disclosed in the copending application of Edwin H. Land, Ser. No. 782,056, filed Dec. 9, 1968, now U.S. Pat. 3,573,043.

The structural integrity of the film unit may be maintained by an adhesive capability installed between the various layers comprising the laminate. However, the adhesive capability installed between image-receiving layer and the negative component should be less than that between the opposed surfaces of the remainder of the layers forming the laminate so as to permit the processing fluid to be applied therebetween. The laminate's structural integrity may also be enhanced or provided by a binding member extending around the edges of the laminate, and maintaining the layers comprising the laminate intact, except at the interface between the receiving layer and the negative component during distribution of the processing fluid between those layers.

The processing fluid may be contained in a pod or rupturable container of the type shown and described in any of U.S. Pats. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,492; 3,056,491; 3,152,515; and the like. In general, such containers will comprise a rectangular blank of fluid- and air-impervious sheet material folded

longitudinally upon itself to form two walls which are sealed so as to form a cavity for containing the processing composition.

The processing composition may comprise an aqueous alkaline solution having a pH at which the dye developers are soluble and diffusible and an opacifying agent in a quantity sufficient to mask the dye developers associated with the silver halide emulsions after processing and to provide the requisite background for viewing the color transfer image. As mentioned before, the concentration of opacifying agent is preferably sufficient to protect the film product's silver halide emulsion or emulsions from further exposure by actinic radiation traversing through the dimensionally stable transparent layer after the opacifying agent is applied to the emulsion(s). Accordingly, where the opposed dimensionally stable layer is opaque, the film product may be processed, after distribution of the composition, in the presence of actinic radiation, in view of the fact that the silver halide emulsion or emulsions of the laminate are appropriately protected at one major surface by the opaque processing composition and at the remaining major surface by the dimensionally stable opaque layer. Any edge leakage of actinic radiation incident on the emulsion or emulsions may also be prevented by the use of appropriate means such as opaque binder tapes.

A preferred opacification system to be contained in the processing composition is that described in the copending application of Edwin H. Land, Ser. No. 43,782, filed June 5, 1970, now abandoned, comprising an inorganic reflecting pigment dispersion containing at least one optical filter agent at a pH above the pKa of the optical filter agent in a concentration effective, when the processing composition is applied, to provide a layer exhibiting optical transmission density>than about 6.0 density units with respect to incident radiation actinic to the photosensitive silver halide layer and optical reflection density<than about 1.0 density with respect to incident visible radiation.

In lieu of having the reflecting pigment contained in the processing composition, e.g., as disclosed in the aforementioned copending application Ser. No. 43,782, the reflecting pigment needed to mask the photosensitive strata and to provide the requisite background for viewing the color transfer image formed in receiving layer **22** may be contained initially in whole or in part as a preformed layer in the film unit. As an example of such a preformed layer, mention may be made of that disclosed on the copending applications of Edwin H. Land, Ser. Nos. 846,441, filed July 31, 1969, now U.S. Pat. No. 3,615,421, and 3,645, filed Jan. 19, 1970, now U.S. Pat. No. 3,620,724. The reflecting pigment may be generated in situ as is disclosed in the copending applications of Edwin H. Land, Ser. Nos. 43,741 and 43,742, both filed June 5, 1970.

The following examples show by way of illustration and not by way of limitation the use of the novel compounds of this invention in photographic products and systems for preparing visible images.

EXAMPLE 10

On a gelatin subcoated triacetate film base was coated a layer containing a gelatino silver iodobromine emulsion at a coverage of 100 mgs./ft.^{2} of silver, 40 mgs./ft.^{2} of toluhydroquinone and 300 mgs./ft.^{2} of the compound of formula 1, sodium S-(p-acetoxybenzyl) thiosulfate. The resulting film unit was exposed and then developed by applying between the thus exposed element and an image-receiving element from a Polaroid Type 107 Land film comprising a siliceous silver-receptive stratum containing silver precipitating nuclei, at a gap of .0030", a developing composition containing the following proportions of ingredients:

Water	cc..	111.25
Sodium hydroxide	g..	6.25
Sodium carboxymethyl cellulose	g..	6.0

After about 60 seconds the respective elements were separated to reveal a positive silver transfer image.

A film unit prepared in Example 10 was subjected to a standard aging test for five days at 120° F. prior to use. Exposure and development in the foregoing manner produced a like positive silver image of substantially the same silver density, indicating no appreciable instability of the film unit under the test conditions. In contrast with the foregoing results, attempts to include a water-soluble silver halide solvent, e.g., sodium thiosulfate, in the silver halide layer produced no silver image.

EXAMPLE 11

Aqueous gelatin solutions containing 5–15% by weight of the compound of Formula 10 to dry gelatin were prepared. By the addition of triethyl amine, the pH of the solutions were adjusted within the range of pH 6 to pH 10. In each instance, after heating to 30° C., cross-linking of the gelatin was observed. Similar results were obtained with the gelatin hardeners of Formulae 11 and 25.

EXAMPLE 12

On a transparent polyethylene terephthalate film base was coated a 7:3 mixture, by weight, of polyethylene/maleic acid copolymer and polyvinyl alcohol at a coverage of about 1,000 mgs./ft.^{2} to provide a polymeric acid layer. Over this was coated a graft copolymer of acrylamide and diacetone acrylamide on a polyvinyl alcohol backbone in a molar ratio of 1:3.2:1 at a coverage of about 750 mgs./ft.^{2} to provide a polymeric spacer of timing layer. A layer was next applied comprising a mixture of the aforementioned graft copolymer and a compound of Formula 5 at a coverage of 750 mgs./ft.^{2} of graft copolymer and 72 mgs./ft.^{2} of the compound of Formula 5. Finally, a dyeable stratum comprising a 2:1 mixture by weight of polyvinyl alcohol and poly-4-vinylpyridine was coated at a coverage of about 500 mgs./ft.^{2} to provide the positive component of an integral negative-positive film unit.

EXAMPLE 13

On a transparent polyethylene terephthalate film base was coated the polymeric acid layer described in Example 12 at the same coverage. Over this was applied a mixture of the graft copolymer described in Example 12 and the compound of Formula 4 at a coverage of about 750 mgs./ft.^{2} of the graft copolymer and about 72 mgs./ft.^{2} of the compound of Formula 4. Finally, the dyeable stratum referred to in Example 12 was applied at a coverage of 500 mgs./ft.^{2} to provide another positive componnet of an integral negative-positive film unit.

To prepare an integral negative-positive film unit, the positive component prepared in Examples 11 or 12 is placed in superposition with the negative component and the respective components are then laminated or otherwise maintained together to provide the requisite film unit. If desired it may be taped together in laminate form, at their respective edges, by means of a pressure-sensitive binding tape extending around, in contact with, and over the edges of the resulting laminate.

The following example illustrates a typical negative component which may be employed in combination with the aforementioned positive component to provide a composite film unit of this invention.

EXAMPLE 14

The negative component may be prepared by coating, in succession, on an opaque film base the following layers:

(1) A layer of cyan dye developer dispersed in gelatin and coated at a coverage of about 80 mgs./ft.^{2} of dye and about 100 mgs./ft.^{2} of gelatin;

(2) A red-sensitive gelatino-silver iodobromine emulsion coated at a coverage of about 225 mgs./ft.^{2} of silver and about 50 mgs./ft.^{2} of gelatin;

(3) A layer of acrylic latex sold by Rohm and Haas Co. under the trade designation AC–61 and polyacryl-

amide coated with a coverage of about 100 mgs./ft.^{2} of AC–61 and about 5 mgs./ft.^{2} of polyacrylamide;

(4) A layer of magenta dye developer dispersed in gelatin and coated at a coverage of 70 mgs./f.^{2} of dye and about 120 mgs./ft.^{2} of gelatin;

(5) A green-sensitive gelatino-silver iodobromide emulsion coated in a coverage of about 120 mgs./ft.^{2} of silver and 60 mgs./ft.^{2} of gelatin.

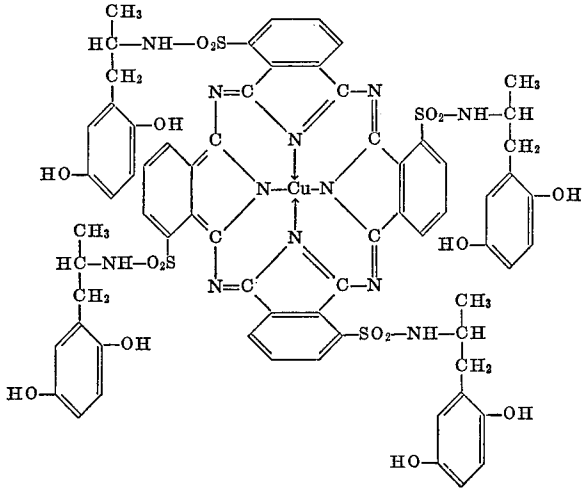
(6) A layer comprising the acrylic latex sold by Rohm and Haas Co. under the trade designation B–15 and polyacrylamide coated in a coverage of about 100 mgs./ft.^{2} of B–15 and about 10 mgs./ft.^{2} of polyacrylamide;

(7) A layer of a yellow dye developer and the auxiliary developer 4'-methylphenyl hydroquinone dispersed in gelatin and coated at a coverage of about 50 mgs./ft.^{2} of dye, about 15 mgs./ft.^{2} of auxiliary developer and 50 mgs./ft.^{2} of gelatin;

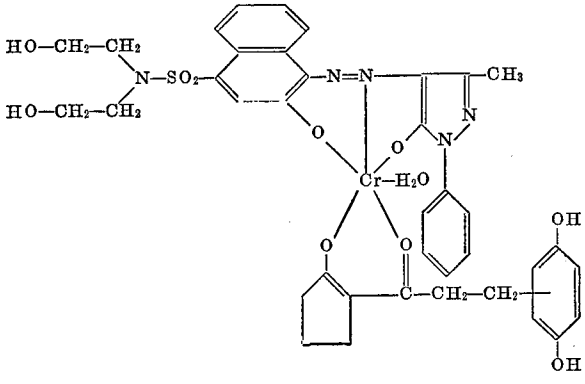
(8) A blue-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 75 mgs./ft.^{2} of gelatin; and

(9) A layer of gelatin coated at a coverage of about 50 mgs./ft.^{2} of gelatin.

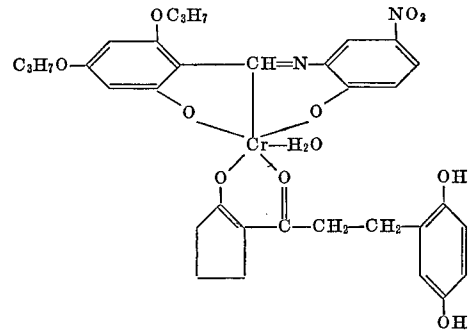
The three dye developers employed above may be the following:



a cyan dye developer;



a magenta dye developer; and



a yellow dye developer.

Film units containing the positive component of this invention were compared with control film units containing a conventional development restrainer, 1-phenyl-5-mercaptotetrazole (PMT) in the dyeable stratum or in an underlying layer, i.e., a structure analgous to that described in Example 12.

The following examples show the preparation of these control components.

EXAMPLE 15

On a transparent polyethylene terephthalate film base was coated the polymeric acid layer referred to in Example 12 at the same coverage i.e., 1,000 mgs./ft.^{2}. Over this was applied the graft copolymer referred to in Example 12 at the same coverage, i.e., 750 mgs./ft.^{2}. Finally, a mixture comprising a 2:1 mixture by weight of polyvinyl alcohol and poly-4-vinylpyridine was coated at a coverage of about 735 mgs./ft.^{2} of this mixture and 15 mgs./ft.^{2} of PMT to provide a positive component wherein the development restrainer (PMT) was contained in the dyeable stratum.

EXAMPLE 16

On a transparent polyethylene terephthalate film base was coated the polymeric acid layer referred to in Example 12 at the same coverage, i.e., 1,000 mgs./ft.^{2}. Over this was applied a layer of the graft copolymer referred to in Example 12 at a coverage of 750 mgs./ft.^{2}. A layer was next applied comprising a mixture of this graft copolymer and PMT at a coverage of about 750 mgs./ft.^{2} of the graft copolymer and 45 mgs./ft.^{2} of PMT. Finally, the dyeable stratum referred to in Example 12 was coated at a coverage of about 500 mgs./ft.^{2} to provide a positive component wherein the development restrainer is positioned in a layer beneath the dyeable stratum, i.e., a positive component analogous in structure to that prepared in Example 12.

An integral negative-positive film unit prepared by laminating the positive component as prepared in Example 12 to a negative component of the type prepared in Example 14 was compared for contamination with similar control units similar in all respects except that the positive components of the controls were those prepared in Examples 15 and 16. In each instance, exposure times, development procedures, etc., were the same to establish established and accepted test procedures. One set of tests compared the D_{min} and D_{max} obtained on storage at room temperature for three days. Since the problem of contamination is greater at higher temperatures and/or humidities, another standard-type test compared the D_{min} and D_{max} obtained after storage for five days at 100° F. and 80% relative humidity.

In each instance, after storage, the film unit was exposed for the same time and then developed by applying between the dyeable stratum and the adjacent layer of the

negative component a processing composition comprising the following proportions of ingredients:

Water	cc--	100.0
Titanium dioxide	gms--	50.0
Carboxymethyl cellulose	gms--	3.4
Potassium hydroxide	gms--	11.2
Benzotriazole	gms--	1.7
5-hydroxy-4-azabenzimidazole	gm--	0.35
Phenethyl-α-picolinium bromide	gms--	1.37

The density readings for cyan, magenta and yellow dye transfer were then determined to be as follows:

	3 days at room temp.		5 days at 100° F. and 80% R.H.	
	D_{min}	D_{max}	D_{min}	D_{max}
Control with PMT in dyeable stratum:				
C	.17	1.95	.20	2.11
M	.33	1.86	.41	1.91
Y	.71	1.98	.95	1.75
Control with PMT in layer under dyeable stratum:				
C	.18	2.46	.19	2.13
M	.38	2.49	.42	2.27
Y	.58	2.48	.75	2.27
Film unit with Formula 5 under dyeable stratum:				
C	.16	2.50	.18	2.27
M	.34	2.50	.38	2.33
Y	.45	2.50	.67	2.37

Comparing first the room temperature test with the heat and humidity storage test for any of the film units, it will be seen that the D_{mins} (unwanted dye transfer) are higher in each instance, due to greater contamination whereby development is prematurely restrained, thus permitting dye which would normally be able to develop the respective silver halide emulsion layers and hence be immobilized to instead remain mobile and diffusible and hence transfer. As would be expected, this contamination is most pronounced in the blue-sensitive emulsion layer, the closest one in point of distance to the development restrainer, as is evidenced by the so-called "yellow flooding" resulting in comparatively high unwanted yellow dye transfer. Thus, for example, in the first control wherein the PMT was in the dyeable stratum, the yellow D_{mins} were .71 and .95, the latter being at the more extreme storage test, as expected. Placing the PMT more distant as in the second control unit wherein it was positioned in an underlying layer afforded some benefits of lower D_{min} with regard to the yellow dye, as noted by the D_{min} readings of .58 and .75. No lowering of the D_{mins} for the cyan and magenta were noted however, although the D_{max} for each dye was up. The film unit containing the compound of Formula 1 showed clearly superior results. The yellow D_{mins} of .45 and .67 were appreciably better. The respective D_{max} were also improved.

It should be noted, however, that some contamination was still observed with the compound of Formula 5, as observed, for example, by the higher D_{min} in the heat-humidity storage test. Accordingly, use of this compound in lieu of standard development restainers such as PMT does not at present appear to obviate fully the contamination problem. However, this compound is so markedly superior to such standard development restrainers that it is clear that the present invention provides a great improvement in this regard over the prior systems utilizing development restrainers.

In addition to the foregoing storage tests, a temperature latitude series of tests were conducted for the same three film units to determine performance upon development in the cold (10 minutes at 40° F.); at room temperature (3 minutes at 70° F.); and in the hot (2 minutes at 100° F.). The dye density (D_{max}) readings for each of the three dyes showed, quite unexpectedly, superior dye densities.

These readings were as follows:

	Cold	Room	Hot
Control with PMT in dyeable stratum:			
C	2.01	2.07	2.06
M	2.20	2.17	1.98
Y	2.07	2.13	1.97
Control with PMT in layer under dyeable stratum:			
C	2.23	2.38	2.14
M	2.19	2.36	1.97
Y	2.09	2.29	1.90
Film unit with Formula 5 under dyeable stratum:			
C	2.30	2.22	2.35
M	2.41	2.33	2.20
Y	2.24	2.23	2.08

The increased cyan and magenta dye transfer obtained with the film unit of this invention over that obtained, for example, with the control wherein the PMT is in the dyeable stratum, would appear to indicate that the compound of Formula 1 functions more effectively as a development restrainer in eliminating or minimizing the aforementioned problem of cross-talk wherein these dye developers develop the "wrong" silver halide layer and hence are immobilized where they should be free to transfer. However, it is not clearly understood why the present invention provides increased yellow dye density in the cold, at room temperature and in the hot. It may be due, at least in part, to a presently unexplained and unaccountable phenomenon whereby the compound of Formula 1 diffuses slower than PMT in the cold, where the restraining action should optimally be slower due to slower dye diffusion rates, and yet faster in the hot where more rapid restraining action is required.

In any event, the temperature latitude series indicates clearly that the film unit of this invention gives overall superior results in terms of desired dye transfer. Taken in conjunction with the previously described superior performance in terms of reduced contamination, it will therefore be apparent that the present invention provides a significant advance in the art to which it is directed.

In the foregoing illustrative examples, the reagent containing the development restrainer moiety was incorporated in the positive component of the film unit. In accordance with this invention, the reagent may also be contained in the negative component provided it is incorporated in such a manner that the development restrainer is not released for diffusion to the photosensitive strata too soon in the development process, i.e., before the desired development and imagewise dye distribution formation are substantially effected. Where the compound is employed in its free hydroxy form, e.g., where the phenolic hydroxy substituent is not protected, the development restrainer may be released too rapidly, unless some physical barrier means is provided to retard or delay contact of the reagent with alkali and/or diffusion of the released restrainer to the photosensitive strata. Thus, for example, in film units of the type described previously, it was determined that incorporation of 39.9 mgs./ft.^{2} of the free hydroxy compound of Formula 5 or Formula 4 in a silver halide emulsion layer contaianing about 150 mgs./ft.^{2} of silver and 150 mgs./ft.^{2} of gelatin desensitized too rapidly so that no silver image was noted and no transfer image was formed.

However, the necessary time delay in the development process may be obtained by employing a protected derivative in lieu of the free hydroxy compound, e.g., one of the illustrative compounds wherein the Y substituent is a radical which upon hydrolysis provides a hydroxy substituent.

Thus, whereas the free hydroxy compound releases the development restrainer in a single reaction step upon application of alkali, as in the reaction mechanism previously illustrated, the protected derivatives require two reaction steps: (1) hydrolysis to form the free hydroxy compound; and (2) the subsequent release reaction providing the development restrainer.

The following example illustrates the preparation of a monochromatic film unit wherein the reagent is included in the silver halide layer.

EXAMPLE 17

On a transparent polyester sheet was coated a layer containing 50 mgs./ft.^{2} of the magenta dye developer shown in Example 14 and 75 mgs./ft.^{2} of gelatin; a silver halide layer containing 150 mgs./ft.^{2} of silver, 150 mgs./ft.^{2} of gelatin and 45.8 mgs./ft.^{2} of the p-acetoxy compound of Formula 6 (equivalent by weight to 25 mgs./ft.^{2} of 1-phenyl-5-mercaptotetrazole); and a gelatin overcoat containing 150 mgs./ft.^{2} of gelatin to provide a negative component containing a reagent of this invention in the silver halide layer. A similar (control) negative was prepared which diffused only in that it did not contain the reagent. The control negative was developed in superposition with a positive component containing a development restrainer, 1-phenyl-5-mercaptotetrazole, in the dyeable stratum similar to that described in Example 15, whereas the test negative containing the compound of Formula 6 was developed in superposition with a similar positive component containing no development restrainer. The data comparing the two negative components with developments at 40°, 75°, and 100° F. is as follows:

	40	75	100
Control negative:			
D_{max}	1.46	.66	.64
D_{min}	.52	.36	.46
Negative with Formula 6 in silver halide layer:			
D_{max}	.83	1.68	1.55
D_{min}	.53	.77	.88

The above results indicate that in overall performance (exclusive of contamination) the control system wherein the development restrainer was in the positive component provided better results. The higher D_{mins} obtained with the test negative are believed to be caused by the fact that the compound of Formula 6 is releasing the development restrainer too rapidly in terms of the rate of development in the particular system tested. In other words, better results may be obtained if the release rate were slower, e.g., by employing a reagent which hydrolyzes to the free hydroxy compound at a slower rate, or, conversely, if the development rate were increased.

Accordingly, while at first blush it would appear from the foregoing data that no advantage over the prior art is obtained by including a reagent of this invention in the silver halide layer or layers, one skilled in the art will recognize that significant benefits can in fact be obtained. First, in integral negative-positive film units, the stable reagents, e.g., compounds such as that of Formula 6, can be included in the negative component without the problem of contamination found where a typical soluble restrainer is employed, for example, in the positive component. Secondly, when one contemplates that the addition of as little as 3 mgs./ft.^{2} of 1-phenyl-5-mercaptotetrazole in a silver halide layer will substantially totally desensitize so that no image can be obtained, it is significant to note that the addition of the reagent in an amount equivalent to 25 mgs./ft.^{2} of 1-phenyl-5-mercaptotetrazole provided a usable image. Thirdly, one skilled in the art will recognize from the foregoing discussion and illustrative data that by selection of the appropriate reagent in combination with the development rate of the particular system will in turn provide the appropriate release rate in the time-rate sequence to achieve optimum photographic results.

In Example 17, a monochromatic negative component was prepared. The following example illustrates the preparation of a multilayer negative component.

EXAMPLE 18

On a polyester film base was coated the following layers: (1) a layer containing 100 mgs./ft.^{2} of the cyan dye developer shown in Example 14, 150 mgs./ft.^{2} of gelatin and 22 mgs./ft.^{2} of the acetoxy compound of Formula 6; (2) a red-sensitive silver halide emulsion layer containing 19.5 mgs./ft.^{2} of gelatin and 140 mgs./ft.^{2} of silver; (3) a latex interlayer similar to Example 14; (4) a layer containing 65 mgs./ft.^{2} of the magenta dye developer shown in Example 14; 32 mgs./ft.^{2} of gelatin, 7.5 mgs./ft.^{2} of 4'-methylphenyl hydroquinone; and 12 mgs./ft.^{2} of the acetoxy compound of Formula 6; (5) a green-sensitive silver halide emulsion layer containing 56.4 mgs./ft.^{2} of gelatin and 50 mgs./ft.^{2} of silver; (6) a latex interlayer; (7) a layer containing 70 mgs./ft.^{2} of the yellow dye developer shown in Example 14; 31 mgs./ft.^{2} of gelatin, 7.5 mgs./ft.^{2} of 4'-methylphenyl hydroquinone and 11 mgs./ft.^{2} of the acetoxy compound of Formula 6; (8) a blue-sensitive silver halide emulsion layer containing 46.5 mgs./ft.^{2} of gelatin and 65 mgs./ft.^{2} of silver; and (9) a layer containing 30 mgs./ft.^{2} of gelatin. A control negative component was also prepared similar in all respects except layers 1, 4 and 7 contained none of the acetoxy compound. As in the comparative test of Example 17, the negative component of this invention was employed in conjunction with a positive component containing no development restrainer; whereas the control negative component was employed in conjunction with a positive component containing the development restrainer, 1-phenyl-5-mercaptotetrazole in the dyeable stratum. In the usual manner, the red, green and blue densities were determined from transfer images prepared at 40°, 75° and 100° F.

The results tabulated are as follows:

	40		75		100	
	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$
Control:						
R	.29	2.10	.21	2.46	.20	2.12
G	.44	2.12	.24	2.26	.24	1.82
B	.79	2.18	.36	2.42	.42	2.03
Test:						
R	.47	1.99	.27	2.23	.37	2.20
G	.63	1.85	.31	2.00	.33	2.06
B	1.04	1.91	.52	1.98	.52	2.33

The film units prepared in Example 18 were also subjected to accelerated aging (six days at 120° F.) and heat-humidity (5 days at 100° F. and 80% relative humidity) storage test conditions prior to use. The red, green and blue densities were determined from color images prepared at 75° F. The readings were as follows:

ACCELERATED AGING

	Control		Test	
	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$
R	.22	2.15	.34	2.08
G	.25	1.85	.31	1.80
B	.37	1.65	.63	1.88

HEAT HUMIDITY

	Control		Test	
	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$
R	.20	1.97	.26	2.00
G	.23	1.79	.32	1.82
B	.34	1.17	.42	1.75

EXAMPLE 19

A negative component was prepared similar to that shown in Example 14, except that the negative component was overcoated with a tenth layer containing 26 mgs./ft.^{2} of the acetoxy compound of Formula 6 and 26 mgs./ft.^{2} of gelatin. When a color transfer image prepared by using this negative component in conjunction with a positive component containing no development restrainer was component in conjunction with a positive component containing no development restrainer was compared with a color transfer image prepared by using a similar negative component containing none of the acetoxy compound in

conjunction with the positive component containing 1-phenyl-5-mercaptotetrazole in the dyeable stratum, the results were as follows:

	40		75		100	
	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$
Control:						
R	2.04	.38	1.84	.17	1.90	.14
G	2.10	.58	1.93	.24	1.81	.28
B	1.83	.53	1.87	.26	1.94	.46
Test:						
R	1.89	.34	1.66	.19	1.52	.15
G	1.95	.54	1.72	.25	1.32	.35
B	1.69	.55	1.71	.29	1.53	.59

The observations taken from the comparative tests of Examples 18 and 19 are generally similar to that derived from Example 17 and previously discussed. However, these three illustrative examples clearly show the adaptability of this invention to the employment of the novel reagents of this invention in the negative component.

It is to be noted that in the illustrative negative components prepared in Examples 17–19 and in the systems employing them, no substantial effort was made to achieve optimum results. The experiments conducted do however show clearly the efficacy of employing such negative components. One skilled in the art will understand that the function of the development restrainer is a time-rate phenomenon wherein the restrainer must be present to function in this capacity at the right time in the particular system employed. This in turn is a function of the development rate.

Accordingly, while in the preferred embodiments of this aspect of the invention, the reagent is incorporated in the positive component, it may also be incorporated in the negative component. Since incorporation in the negative component places the reagent in closer proximity to the photosensitive strata to which it is intended to function, when incorporated in the negative form it must be so disposed in such a manner that it will not be available to perform its development restraining action too early in the development process, e.g., it should not be able to perform its restraining function before substantially all of the exposed and developable silver halide has been developed. While various physical means in the form of temporary barriers to migration of the released restrainer may be suggested to those skilled in the art, particularly in the light of the foregoing description, it will be seen that the requisite delay in release of the restrainer may be accomplished chemically by employment of the compounds wherein the Y moiety is a substituent which must first hydrolyze to the corresponding hydroxy compound before the second stage wherein the restrainer is released. The rate of release may thus be controlled by selection of the appropriate Y substituent, e.g., esters which hydrolyze more or less rapidly, or by the inclusion in the nucleus of the reagent of a substituent which affects the rate of hydrolysis.

From the foregoing description and illustrative examples, it will be seen that the present invention provides an effective and practical means for incorporating various photographic reagents in photographic film units intended for the preparation of black-and-white or color images. The photographic reagents so incorporated are generally characterized as being stable and immobile or nondiffusible but yet available to perform their intended function at the requisite time in the development process, e.g., upon hydrolysis by application of an aqueous alkaline medium. The rate of hydrolysis desired may be regulated in accordance with the condition required in the particular photographic system employed by selection of the appropriate Y substituent of the reagent, which, as heretofore noted, may be a hydroxyl group, a substituent hydrolyzable relatively rapidly to a hydroxyl group, or a substituent hydrolyzable less rapidly to a hydroxyl group.

While the photographic moiety has been described as being bonded to the benzene or naphthalene nucleus of the novel compounds of this invention through a methylene (—CH_2—) substituent, it may be possible to so link the photographic moiety through a substituted methylene substituent, e.g., a substituted methylene radical wherein one or both of the hydrogen atoms are replaced by an alkyl radical such as methyl, ethyl, etc.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a photographic product including a layer in which a visible image is to be formed; the improvement which comprises including in a layer in said product a non-diffusible compound which in the presence of alkali forms a quinone-methide or a naphthoquinone-methide and releases a diffusible photographic reagent selected from the group consisting of silver halide solvents, silver halide developing agents, toning agents, antifoggants and development restrainers.

2. A product as defined in claim **1** wherein said compound is a phenol, a naphthol or a protected derivative thereof which in the presence of alkali forms a phenol or a naphthol, said compound further having a radical providing said photographic reagent bonded to a nuclear carbon atom of the aromatic nucleus through an alkylene substituent in a position ortho or para to the hydroxyl group or its protected derivative.

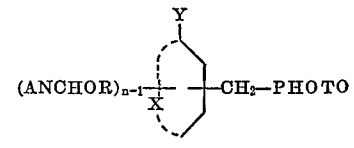
3. A product as defined in claim **2** wherein said radical is a substituent which, upon contacting said compound with alkali, provides a reagent selected from the group consisting of silver halide solvents, antifoggants and silver halide development restrainers.

4. In a photographic product comprising a support carrying a light-sensitive silver halide layer, the improvement which comprises including in a layer in said product a non-diffusible compound which in the presence of alkali forms a quinone-methide or a naphthoquinone-methide and releases a diffusible photographic reagent selected from the group consisting of silver halide solvents, silver halide developing agents, toning agents, antifoggants and development restrainers.

5. A product as defined in claim **4** wherein said compound is a phenol, a naphthol or a protected derivative thereof which in the presence of alkali forms a phenol or a naphthol, said compound further having said photographic reagent bonded to a nuclear carbon atom of the aromatic nucleus through a methylene substituent in a position ortho or para to the hydroxyl group or its protected derivative.

6. A product as defined in claim **4** wherein said compound is of the formula:

(A)



wherein:

X represents the atoms necessary to complete a benzene or a naphthalene nucleus;

Y is hydroxy or a substituent which upon hydrolysis provides hydroxy;

PHOTO is a photographic reagent selected from the group consisting of silver halide solvents, silver halide developing agents, toning agents, antifoggants and development restrainers, said —CH_2—PHOTO substituent being ortho or para to said Y substituent;

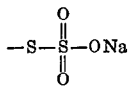
ANCHOR is an anchoring substituent rendering said

compound appreciably less diffusible than it would be without said ANCHOR substituent; and

n is 1 or 2.

7. A product as defined in claim 6 wherein —PHOTO is the monovalent radical of a silver halide solvent.

8. A product as defined in claim 7 wherein —PHOTO is



9. A product as defined in claim 6 wherein —PHOTO is the monovalent radical of a silver halide antifoggant or development restrainer.

10. A product as defined in claim 9 wherein said radical is of the formula:

—S—HET

wherein HET is a heterocyclic ring.

11. A product as defined in claim 4 wherein a dye image-providing material is disposed in a layer associated with said silver halide layer, said dye image-providing material being selected from dyes and dye intermediates which are soluble and diffusible in an aqueous alkaline medium and dyes and dye intermediates which are insoluble and non-diffusible in said medium.

12. A product as defined in claim 11 wherein said photographic reagent is a silver halide antifoggant or development restrainer.

13. A product as defined in claim 12 wherein said dye image-providing material is a dye developer and said photographic reagent is

HS—HET

wherein HET is a heterocyclic ring.

14. A product as defined in claim 11 including a dyeable stratum adapted for forming a color transfer image by dye diffusing thereto from said layer of dye image-providing material.

15. A product as defined in claim 14 wherein said compound is disposed in the same layer as said silver halide or in a layer adjacent to said silver halide layer.

16. In a photographic product including a plurality of essential layers comprising a red-sensitive silver halide layer and an associated cyan dye image-providing material, a green-sensitive silver halide layer and an associated magenta dye image-providing material and a blue-sensitive silver halide layer and a yellow dye image-providing material, said image-providing materials being adapted for providing imagewise distributions of diffusible dyes as a function of development of the respective silver halide layers;

the improvement which comprises including in a layer of said product a non-diffusible compound which in the presence of alkali forms a quinone-methide or a naphthoquinone-methide and releases a diffusible photographic reagent selected from the group consisting of silver halide solvents, silver halide developing agents, toning agents, antifoggants and development restrainers.

17. A product as defined in claim 16 wherein said compound is a phenol, a naphthol or a protected derivative thereof which in the presence of alkali forms a phenol or a naphthol, said compound further having a radical providing said photographic reagent bonded to a nuclear carbon atom of the aromatic nucleus through a methylene substituent in a position ortho or para to the hydroxyl group or its protected derivatives.

18. A product as defined in claim 16 wherein said radical is a substituent which, upon contacting said compound with alkali, provides a reagent selected from the group consisting of silver halide solvents, antifoggants and silver halide development restrainers.

19. A product as defined in claim 18 wherein said essential layers comprise the negative component of said product and wherein said product further includes a positive component containing a dyeable stratum adapted for receiving color image by diffusion transfer.

20. A product as defined in claim 19 wherein a transparent dimensionally stable layer is disposed on the outer surface of said positive component.

21. A product as defined in claim 20 wherein an opaque dimensionally stable layer is disposed on the outer surface of said negative component.

22. A product as defined in claim 20 including means for applying an aqueous alkaline processing composition to said product.

23. A product as defined in claim 22 wherein said means includes a rupturable container confining said composition positioned so as to be capable, upon rupturing, of spreading its contents in a substantially uniform layer.

24. A product as defined in claim 23 wherein said rupturable container is positioned so as to be capable of discharging its contents between said positive and negative components, said processing composition containing an opacifying agent sufficient effectively to prevent exposure of said silver halide layers by actinic light incident on said transparent layer.

25. In am image-receiving element adapted for forming visible images by diffusion transfer, said element including a support carrying an image-receiving layer;

the improvement which comprises including in a layer in said element a non-diffusible compound which in the presence of alkali forms a quinone-methide or a naphthoquinone - methide and releases a diffusible photographic reagent selected from the group consisting of silver halide solvents, silver halide developing agents, toning agents, antifoggants and development restrainers.

26. A product as defined in claim 25 wherein said compound is a phenol, a naphthol or a protected derivative thereof which in the presence of alkali forms a phenol or a naphthol, said compound further having a radical providing said photographic reagent bonded to a neuclear carbon atom of the aromatic nucleus through a methylene substituent in a position ortho or para to the hydroxyl group or its protected derivative.

27. A product as defined in claim 25 wherein said radical is a substituent which, upon contacting said compound with alkali, provides a reagent selected from the group consisting of silver halide solvents, antifoggants, silver halide development restrainers, and gelatin hardeners.

28. A product as defined in claim 6 wherein said compound is disposed in said silver halide layer.

29. A product as defined in claim 6 wherein —PHOTO is the monovalent radical of a gelatin hardener reagent.

30. A product as defined in claim 7 wherein said silver halide solvent is an alkali metal thiosulfate.

31. A product as defined in claim 7 wherein said compound is sodium S-(p-acetoxybenzyl) thiosulfate.

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