United States Patent [19]

Bloom et al.

[11] **3,856,520**

[45] **Dec. 24, 1974**

[54] **COLOR DIFFUSION TRANSFER PHOTOGRAPHIC ELEMENTS COMPRISING A SULFUR-SUBSTITUTED TETRAHYDROPYRIMIDINE DEVELOPMENT INHIBITOR PRECURSOR AND PROCESS FOR THEIR USE**

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[73] Assignee: **Polaroid Corporation,** Cambridge, Mass.

[22] Filed: **Apr. 9, 1973**

[21] Appl. No.: **349,063**

Related U.S. Application Data

[63] Continuation of Ser. No. 210,650, Dec. 22, 1971, abandoned, which is a continuation-in-part of Ser. No. 60,272, Aug. 3, 1970, abandoned.

[52] **U.S. Cl.** ..... **96/3,** 96/29 D, 96/66.3 UX, 96/76 R, 96/77, 96/95 UX

[51] **Int. Cl.** **G03c 7/00,** G03c 5/54, G03c 5/30, G03c 1/48, G03c 1/40, G03c 1/06

[58] **Field of Search** ..... 96/3, 29 D, 77, 76 R, 95, 96/66, 109, 101, 62

[56] **References Cited**

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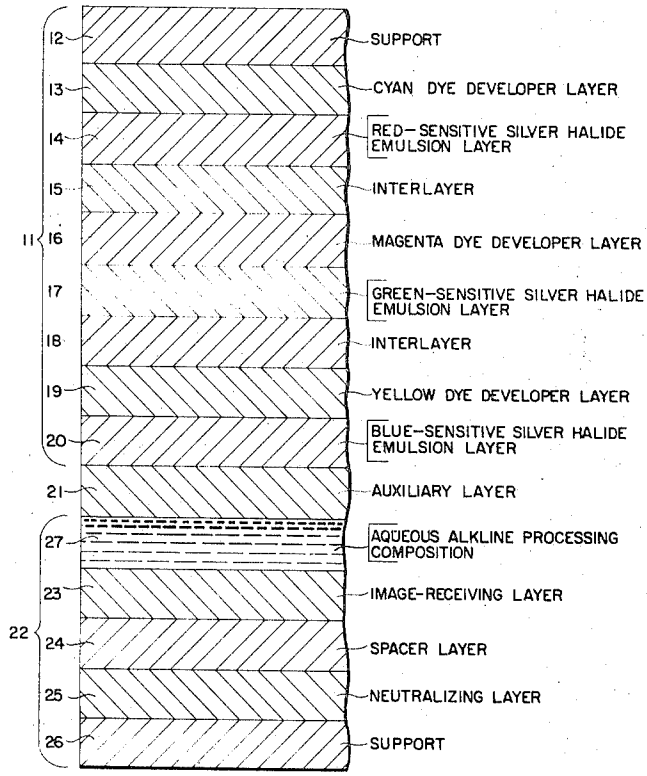
3,260,597	7/1966	Weyerts et al.	96/3
3,265,498	8/1966	Rogers et al.	96/3
3,674,478	7/1972	Grasshoff et al.	96/3
3,723,125	3/1973	Hayashi et al.	96/22
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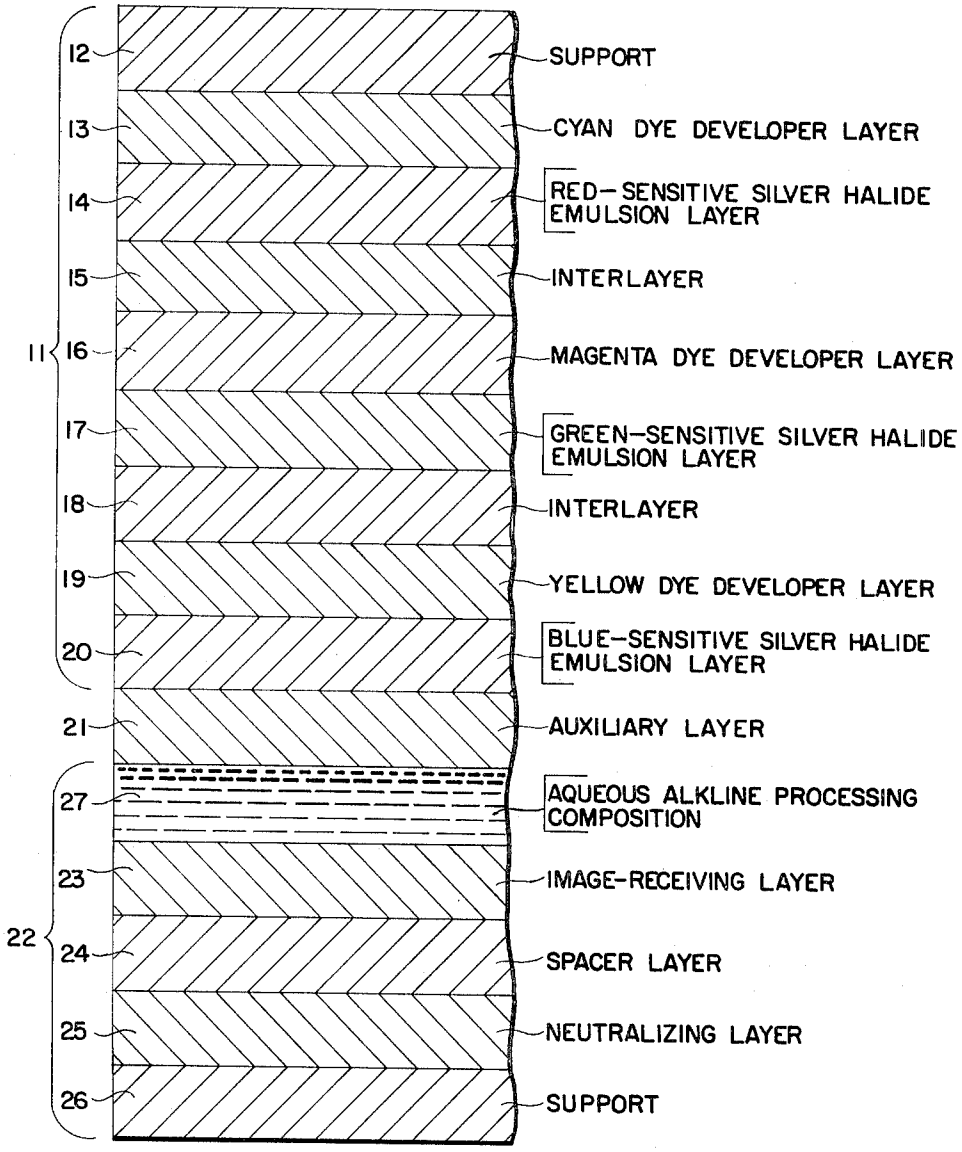
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[57] **ABSTRACT**

A multicolor image is formed by a diffusion transfer process which includes exposing at least a first photosensitive silver halide layer having associated therewith a color-providing material, that is, a dye image-forming material, e.g., a dye which is a silver halide developing agent, which is diffusible in alkaline processing composition as a function of the photoexposure of the silver halide layer, applying an aqueous alkaline processing composition to effect development of said exposed silver halide layer and to provide thereby a diffusible distribution of said color-providing material as a function of the point-to-point degree of emulsion exposure, whereby at least a portion of the imagewise distribution of diffusible color-providing material is transferred to a superposed dyeable polymeric layer. A development restrainer is made available during processing after a predetermined period by incorporating in the photographic film unit, an S-substituted pyrimidine compound of the formula [Y—S—X wherein Y is a tetrahydropyrimidine group and X is hydrogen in its active or unblocked form or a group hydrolyzable by said alkaline processing composition as a function of temperature to provide thereby controlled release of development restrainer during said development process.

19 Claims, 1 Drawing Figure




12
SUPPORT
13
CYAN DYE DEVELOPER LAYER
14
RED-SENSITIVE SILVER HALIDE EMULSION LAYER
15
INTERLAYER
11
16
MAGENTA DYE DEVELOPER LAYER
17
GREEN-SENSITIVE SILVER HALIDE EMULSION LAYER
18
INTERLAYER
19
YELLOW DYE DEVELOPER LAYER
20
BLUE-SENSITIVE SILVER HALIDE EMULSION LAYER
21
AUXILIARY LAYER
27
AQUEOUS ALKLINE PROCESSING COMPOSITION
23
IMAGE-RECEIVING LAYER
22
24
SPACER LAYER
25
NEUTRALIZING LAYER
26
SUPPORT

COLOR DIFFUSION TRANSFER PHOTOGRAPHIC ELEMENTS COMPRISING A SULFUR-SUBSTITUTED TETRAHYDROPYRIMIDINE DEVELOPMENT INHIBITOR PRECURSOR AND PROCESS FOR THEIR USE

CROSS REFERENCE TO OTHER APPLICATIONS

This application is a continuation of U.S. application Ser. No. 210,650 filed Dec. 22, 1971, now abandoned which, in turn, is a continuation-in-part of U.S. application Ser. No. 60,272 filed Aug. 3, 1970, now abandoned.

BACKGROUND OF THE INVENTION

U.S. Pat. Nos. 2,647,049, issued July 28, 1953; 2,661,293, issued Dec. 1, 1953; 2,698,244, issued Dec. 28, 1954; 2,698,798, issued Jan. 4, 1955; 2,802,735, issued Aug. 13, 1957, disclose subtractive color diffusion transfer processes wherein color coupling techniques are utilized which comprise, at least in part, reacting one or more developing agents and one or more color formers to provide a positive color image on a superposed image-receiving layer. U.S. Pat. No. 3,019,124, issued Jan. 30, 1962, discloses the manufacture of photographic color screen elements; and U.S. Pat. Nos. 2,968,554, issued Jan. 17, 1961, and 2,983,606, issued May 9, 1961, disclose diffusion transfer processes wherein a color screen element is utilized to provide a multicolor positive image to a superposed image-receiving layer. U.S. Pat. Nos. 2,774,668, issued Dec. 18, 1956; 3,345,163, issued Oct. 3, 1967; and 3,087,817, issued Apr. 30, 1963 and the previously cited U.S. Pat. No. 2,983,606 disclose diffusion transfer processes wherein complete dyes are utilized to provide a positive color image to a superposed image-receiving layer.

In processes of the type set forth in U.S. Pat. No. 2,983,606, a photosensitive element containing a dye developer and a silver halide emulsion is exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheet-like support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides in imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

The dye developers, as noted above, are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include orthodihydroxyphenyl and ortho and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic development group which forms quinonoid or quinone substances when oxidized.

Multicolor images may be obtained using color image-forming components such as, for example, the previously mentioned dye developers, in diffusion transfer proceses by several techniques. One such technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in the previously noted U.S. Pat. Nos. 2,968,554 and 2,983,606. In such an embodiment, each of the minute photosensitive elements has associated therewith an appropriate dye developer in or behind the silver halide emulsion portion. In general, a suitable photosensitive screen, prepared in accordance with the disclosures of said patents, comprises minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern, and having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multilayer photosensitive element, such as is disclosed in the aforementioned U.S. Pat. No. 3,345,163, wherein at least two selectively sensitized photosensitive strata are superposed in a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, by a layer of gelatin

or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

U.S. Pat. No. 3,362,819, filed Jan. 9, 1968, discloses image-receiving elements, particularly adapted for employment in the preceding diffusion transfer processes, which comprise a support layer possessing on one surface thereof, in sequence, a polymeric acid layer, an inert timing or spacer layer, and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance.

As set forth in the last-mentioned patent, the polymeric acid layer may comprise 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 or materials, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting component is, of course, nondiffusible 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 example 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 of 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 methylvinyl ether/maleic anhydrice copolymers; etc.

The acid layer is disclosed to contain at least sufficient acid 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 inbibition. As previously noted, the pH of the processing composition preferably is of the order of at lest 12 to 14.

It is, of course, necessary that the action of the acid be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the positive dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about pH 9 to 10, before the positive transfer image is separated and exposed to air. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

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 copending application, by (a) 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 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 butyrate, 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 may be employed to help the various polymeric layer adhere to each other during storage and use.

The inert spacer layer of the aforementioned copending application, for example, an inert spacer layer comprises 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 was 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 extend by the mere diffusion into the interlayer, but the pH drops

quite rapidly once the alkali diffuses through the spacer layer.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylons, as for example, 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, and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061.

Integral photographic film units are particularly adapted for the production of a dye transfer image by a color diffusion transfer process may constructed, for example, in accordance with the teachings specifically set forth in U.S. Pat. Nos. 3,415,644; 3,415,645; and 3,415,646 wherein said permanent composition or laminates include, in sequence, as essential layers, a dimensionally stable opaque layer, a photosensitive silver halide emulsion layer having associated therewith, dye image-providing material which is soluble and diffusible in alkali at a first pH as a function of silver halide layer photo-exposure, an alkaline solution permeable polymeric layer dyeable by the dye image-providing material, a polymeric layer containing sufficient acid to effect reduction subsequent to substantial dye transfer image formation of a processing composition having the first to a second pH at which said dye image-providing material is insoluble and nondiffusible, and a dimensionally stable transparent layer. In combination with the laminate, a means for obtaining an aqueous alkaline processing composition having the first pH and preferably containing an opacifying agent in a quantity sufficient to mask dye image-providing material associated with the silver halide layer is fixedly positioned at a leading edge of the laminate to effect unidirectional discharge of the container's contents between the alkaline solution permeable and dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto upon application of compressive force to the container.

In the preferred embodiments of the above-mentioned processes employing integral multilayer negatives processed with an aqueous alkaline processing composition, unoxidized dye developer diffusion from an underlying emulsion to the superposed image-receiving layer must pass through at least one other overlying photosensitive silver halide emulsion. If the unoxidized dye developer diffusion from the underlying layer enters an area of the overlying emulsion containing developable silver halide, there is as much likelihood that the duffusing dye developer from the underlying emulsion will react as dye developer associated with said overlying emulsion will react. This reaction in the "wrong" silver halide emulsion may be referred to as "cross-talk" and manifests itself by producing transfer images having reduced color separation.

U.S. Pat. No. 3,265,498, issued Aug. 9, 1966, is directed to means for causing the developable silver halide remaining undeveloped after a predetermined time to be rendered undevelopable so that unoxidized dye developer diffusion through said emulsion layer will not be immobilized by development of the developable silver halide contained therein. This object is achieved by incorporating in a layer of either the photosensitive element or the image-receiving element or, in some instances, in the processing composition, a reagent which is made available to the developable silver halide of a given emulsion layer only after a predetermined period during which development is affected without interference by said reagent. Since the added reagent effectively restrains, i.e., minimizes, further development of a developable silver halide after this predetermined period, such reagents employed for this purpose are referred to as development restrainers.

U.S. Pat. No. 3,265,498 also teaches the employment of hydrolyzable development restrainers, i.e., development restrainer precursors which are substantially nondiffusible or at least substantially less diffusible in its unhydrolyzed form than in its hydrolyzed form and wherein the development restrainer function is substantially unavailable in said unhydrolyzed form. Thus, development restrainers are made available at a predetermined period by hydrolysis of a suitable derivative of the development restrainer. Such hydrolysis of the hydrolyzable development restrainer after predetermined induction period will thus be an effective way of controlling the availability of the development restrainer and insuring the development is carried out unimpeded by a development restrainer for at least a time sufficient to develop the exposed and developable silver halide to the minimum extent necessary to properly modulate the appropriate dye developer.

SUMMARY OF THE INVENTION

A novel hydrolyzable, releasable development restrainer precursor has how been found which is made available to the system at a rate dependent upon the ambient temperature. Such temperature dependent release is believed to be effected by the rate of hydrolysis which is a direct function of temperature. The novel hydrolyzable development restrainer precursor of the present invention is an S-substituted pyrimidine compound wherein said compound is further substituted by a hydrolyzable group, i.e., a compound of the formula [Y—S+X wherein Y is a tetrahydropyrimidine and X is hydrogen in its active or unblocked form or a hydrolyzable blocking group wherein the mercapto function is blocked, i.e., the compound does not function as a development restrainer to any discernable extent. The group designated X may be bonded to the sulfur atom or to one of the ring nitrogens.

Thus, X may refer to a second substituent which controls the rate of diffusion or mobility of the compound, said substituent being hydrolyzable in an alkaline medium as a function of temperature to regenerate the mercapto function, thus providing the development restrainer activity. The hydrolysis is provided by the alkaline processing composition.

The photographic unit employing the novel hydrolyzable development restrainer precursors of the present invention comprises a photosensitive silver halide emulsion layer having associated therewith a dye image-forming material, preferably a dye developer, which is soluble and diffusible in alkali as a function of the exposure and development of the silver halide emulsion layer and a polymeric layer dyeable by said dye image-providing material, wherein said dyeable polymeric layer is at least in superposed relationship with said photosensitive element after exposure of said element and during processing of the exposed photosensitive silver halide emulsion, that is, during contact

of said emulsion with the aqueous alkaline processing composition. The novel hydrolyzable development restrainer precursor is incorporated in a layer of either the photosensitive element or in the image-receiving element. The hydrolyzed compound is preferably incorporated into the image-receiving element.

It should be understood that the term "tetrahydropyrimidine" as used herein is intended to refer to the substituted and unsubstituted tetrahydropyrimidine radical including tetrahydropyrimidine having fused ring systems associated therewith such as those disclosed and claimed in U.S. application Ser. No. 214,665, filed Jan. 3, 1973, now U.S. Pat. No. 3,785,813 issued Jan. 15, 1974.

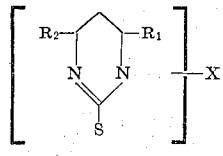
BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a diagrammatic enlarged cross-sectional view illustrating the association of elements during one stage of the performance of a diffusion transfer process for the production of a multicolor transfer image according to the present invention, the thickness of the various materials being exaggerated.

DETAILED DESCRIPTION OF THE INVENTION

The novel compounds of the present invention which may be characterized as development restrainer precursors may be represented by the formula:

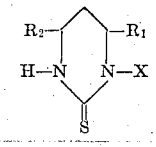
(A)



wherein R_1 and R_2 are hydrogen or alkyl groups, preferably a lower alkyl group, more preferably methyl, and X is an alkaline processing composition hydrolyzable group directly bonded to a ring nitrogen or the sulfur, or hydrogen. Thus, when X is hydrogen, the compound is in its hydrolyzed form and will function as a development restrainer.

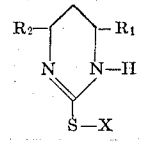
The compounds employed in the present invention are represented by the formula:

(B)



and

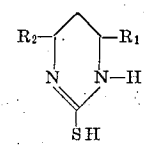
(C)



Thus, in each configuration indicated, the development restrainer function is substantially inactivated when X is a hydrolyzable group.

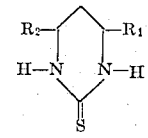
X may be moiety which, upon hydrolysis by the aqueous alkaline processing composition, will provide, from a compound which is substantially inactive as a development restrainer, a hydrolysis product which will so function, i.e., a compound of the formula:

(D)



It should also be understood that the above-indicated compound (D) is believed to exist in its tautomeric form

(E)

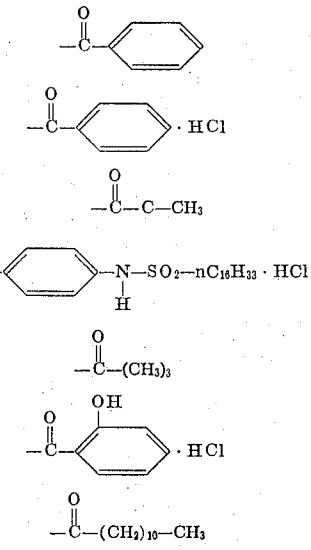


As stated above, the alkaline processing composition hydrolyzable group represented by X may comprise any group which would be removed by the action of said alkaline processing composition as a function of temperature. For example, X may comprise a group of the formula:



wherein R is aryl or alkyl, preferably an alkyl group of 1 to 20 carbon atoms. The length of the alkyl group is selected by the operator to provide the desired rate of solubility in alkaline processing composition and thus provide the desired rate of diffusion or mobility of the compound from its initial location in the film unit to other locations in the film unit where it can then be hydrolyzed at a temperature dependent rate to provide the development restrainer function. Alternatively, depending upon the selection of the specific substituents, the sequence and degree of diffusion and hydrolysis can be controlled and the locus of hydrolysis determined. Thus, the compounds of the present invention can diffuse in the inactive form to the desired locus in the film unit to help minimize a concentration gradient and avoid excess concentration of restrainer in various locations.

As examples of suitable alkaline hydrolyzable groups contemplated by X, mention may be made of the following:



At low temperatures, development and migration of the dye developers is retarded and providing prior art development restrainers under such conditions would impose further restraints on the development process resulting in decreased control of the image-forming process. Similarly, at higher temperatures, development proceeds at such a relatively rapid rate that levels of development restrainers available to be optionally effective would have to be so high that such levels would be wholly unsuitable for lower temperature processing. Thus, in order to satisfy one set of conditions, the employment of prior art restrainers would be detrimental to another set of conditions.

The novel hydrolyzable development restrainer precursors of the present invention, however, are not susceptible to the above-mentioned deficiencies which occur with prior art restrainers. The novel development restrainer precursors of the present invention are not immediately available to restrain or minimize further development of developable silver halide since such compounds are, in effect, blocked in their development restraining function by the presence of the aforementioned hydrolyzable group which serves two functions: (1) substantially prevents the compound from functioning as a development restrainer until the desired conditions are attained and (2) determines the rate of diffusion or availability of the compound within the film unit.

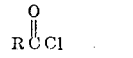
The above-mentioned group X, therefore, is hydrolyzable as a function of ambient temperature.

By means of the present invention, an effective method of controlling the availability of a development restrainer in a given photographic system is achieved as a function of temperature, that is, at the relatively low ambient temperature where the rate of diffusion of the dye developers would be relatively slow, and, as the ambient temperature rises, the relative amount of development restrainer available to the system increases proportionately as required.

In a particularly preferred embodiment, R_1 is a methyl group and R_2 is hydrogen. In an alternative embodiment, R_1 and R_2 are both methyl groups. As stated above, the hydrolyzable group designated X is not critical and is selected at the option of the operator with respect to the particular alkaline processing solution solubility desired, which may vary in each system. In a particularly preferred embodiment, R is an 11 carbon alkyl group.

It is unexpected that the novel compounds of the present invention would function as development restrainers in the hydrolyzed form since what would be considered related compounds, that is, compounds which bear some structural resemblance to the compounds of the present invention, do not indicate such properties. Thus, the compounds of the present invention which contain alternative substituents or which contain a greater degree of unsaturation than is indicated in the above formulae are not satisfactory for use as hydrolyzable development restrainers.

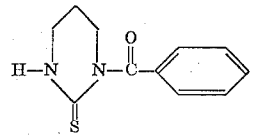
The novel compounds of the present invention are prepared by methods known to the art. A particularly preferred method of preparation comprises reacting 4-alkyl-3,4,5,6-tetrahydropyrimidine-2-thiol and a compound of the formula:



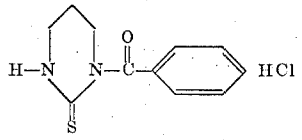
in the presence of triethylamine at room temperature. Other methods of synthesis known to the art will be obvious.

As examples of compounds within the scope of the present invention, mention may be made of the following:

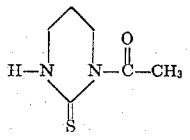
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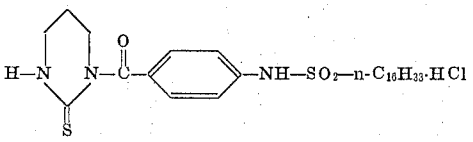
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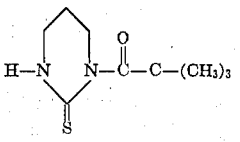
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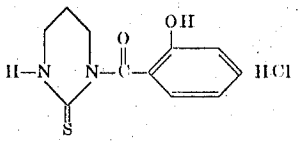
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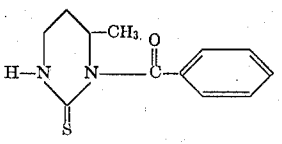
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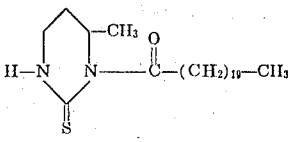
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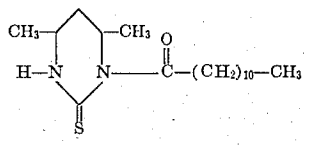
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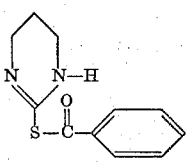
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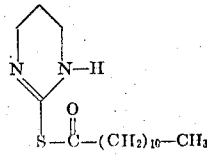
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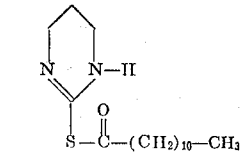
(X)



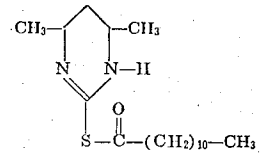
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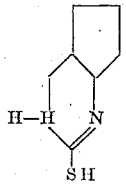
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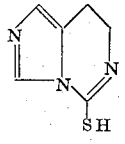
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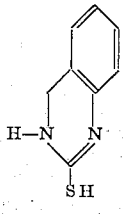
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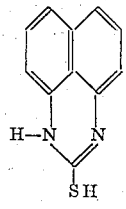
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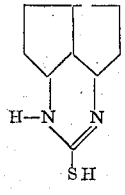
(XVI)



(XVII)



(XVIII)



As stated above, the novel hydrolyzable development restrainers of the present invention may be advantageously employed in the image-receiving layer which is composed of the dyeable polymeric material, in a separate layer adjacent to said image-receiving layer, for example, dispersed in a suitable binder polymer such as gelatin, or in the photosensitive element, for example, in one or more of the silver halide emulsion layers or in a separate layer adjacent thereto. It should be further understood that a combination of the above sites may be employed in disposing the hydrolyzable development restrainers of the present invention in a photographic film unit.

Further, a combination of the blocked form and hydrolyzed form may be employed in the photosensitive element and the image-receiving layer, respectively.

In a preferred embodiment of the present invention, a photosensitive element is employed which is specifically adapted to provide for the production of a multicolor dye transfer image and comprises a dimensionally stable support layer carrying at least two selectively sensitized silver halide emulsion strata each having a dye image-providing material adapted to provide a dye predetermined color associated therewith which is soluble and diffusible, in alkali as a function of the exposure of the associated silver halide strata. The preferred photoinsensitive image-receiving element comprises an alkaline solution permeable polymeric layer dyeable by the dye image-providing material; a polymeric spacer layer comprising a polymer possessing decreasing alkaline solution permeability with increasing temperature; an alkaline solution permeable polymeric layer containing sufficient acid to effect reduction, subsequent to substantial multicolor transfer dye image formation, of the image-receiving element from the first pH to a second pH, at which the dye image-providing material is insoluble and nondiffusible; and the dimensionally stable support layer.

The silver halide emulsions comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye, which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at a predetermined first pH, possessing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion.

In the preferred embodiment, each of the emulsion strata, and its associated dye, is separated from the remaining emulsion strata, and their associated dye, by separate alkaline solution permeable polymeric interlayers and the dyeable polymeric layer is separated from the polymeric acid layer by an alkaline solution permeable polymeric spacer layer having decreasing permeability to alkaline solution with increasing temperature.

In such preferred embodiment of the invention, the silver halide emulsion comprises photosensitive silver halide dispersed in a gelatin and is about 0.6 to 6 microns in thickness; the dye itself is dispersed in an aqueous alkaline solution polymeric binder, preferably gelatin, as a separate layer about 1 to 7 microns in thickness; the alkaline solution permeable polymeric interlayers, preferably gelatin, are about 1 to 5 microns in thickness; the alkaline solution permeable and dyeable polymeric layer is about 0.25 to 0.4 mil. in thickness; the polymeric spacer layer intermediate the dyeable polymeric layer and the polymeric acid layer is about 0.1 to 0.7 mil. in thickness; the alkaline solution permeable polymeric acid layer is about 0.3 to 1.5 mils. in thickness; and each of the dimensionally stable support layers are alkaline solution impermeable and about 2 to 6 mils. in thickness. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

In the preferred embodiment of the present invention's film unit for the production of a multicolor transfer image, the respective silver halide/dye developer units of the photosensitive element will be in the form of a tripack configuration which will ordinarily com-

prise a cyan dye developer/red-sensitive emulsion unit contiguous the dimensionally stable support layer, the yellow dye developer/blue-sensitive emulsion unit most distant from the support layer and the magenta dye developer/green-sensitive emulsion unit intermediate those units, recognizing that the relative order of such units may be varied in accordance with the desires of the operator.

DETAILED DESCRIPTION OF THE DRAWINGS

Reference is now made to the drawing wherein there is illustrated a preferred film unit of the present invention.

As illustrated in the FIGURE, the film unit comprises a photosensitive laminate **11** including, in order, dimensionally stable support layer **12**, preferably a flexible sheet material; cyan dye developer layer **13**; red-sensitive silver halide emulsion layer **14**; interlayer **15**; magenta dye developer layer **16**; green-sensitive silver halide emulsion layer **17**; interlayer **18**; yellow dye developer layer **19**; blue-sensitive silver halide emulsion layer **20**; auxiliary layer **21**, which may contain an auxiliary silver halide developing agent; and an image-receiving element **22** including image-receiving layer **23**; spacer layer **24**; neutralizing layer **25**; and dimensionally stable support layer **26**, preferably a flexible sheet material.

As shown in the drawing, the multilayer exposed photosensitive element **11** is shown in processing relationship with an image-receiving element **22** and a layer **27** of processing solution distributed intermediate elements **11** and **22**.

As indicated above, the hydrolyzable development restrainer precursors of the present invention may be disposed in one or more of the layers shown. Preferably, they are disposed in image-receiving layer **22**.

In the performance of a diffusion transfer multicolor process employing the film unit, the unit is exposed to radiation, actinic to photsensitive laminate **11**.

Subsequent to exposure, the film unit may be processed by being passed through opposed suitably gapped rolls in order to apply compressive pressure to a frangible container in order and to effect rupture of the container and distribution of alkaline processing composition **27**, having a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate dyeable polymeric layer **23** and auxiliary layer **21**.

Alkaline processing solution **27** permeates emulsion layers **14**, **17** and **20** to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers **14**, **17** and **20**, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distribution of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to aqueous alkaline solution permeable polymeric layer **23** to provide a multicolor dye transfer image to that layer. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline solution **27** transfers, by diffusion, through permeable polymeric layer **23**, permeable spacer layer **24** and to permeable polymeric acid layer **25** whereby alkaline solution **27** decreases in pH, as a function of neutralization, to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are insoluble and nondiffusible, to provide thereby a stable multicolor dye transfer image.

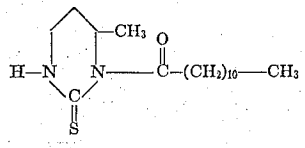
Subsequent to substantial transfer image formation, print-receiving element **22** may be manually dissociated from the remainder of the film unit, for example, by stripping. In a particularly preferred embodiment, however, the film unit is composed of a permanent laminate and print-receiving element **22** is not detached from photosensitive laminate **11**.

Assuming in the above-indicated photographic unit in a given unit area of the negative, exposure is effected only of the green-sensitive emulsion, unoxidized cyan dye developer will eventually diffuse into and through such exposed areas of the green-sensitive emulsion on route to the image-receiving layer superposed over the outermost or blue-sensitive emulsion layer. If the magenta dye developer has not substantially completed the development of the developable green-sensitive silver halide prior to the arrival of unoxidized cyan dye developer, said cyan dye developer could react since it will not distinguish between developable silver halides of different color sensitivity. However, employing the hydrolyzable development restrainers of the present invention would provide for the diffusion of said development restrainer precursor to the undeveloped developable green-sensitive silver halide indicated above, and may act as a development restrainer, thereby restraining or minimizing further development of developable silver halide prior to the arrival of the migrating dye developer into the given layer. Thus, by employing the novel hydrolyzable development restrainers of the present invention, the developable silver halide remaining undeveloped in the film unit after a predetermined period of time is rendered undevelopable, so that unoxidized dye developer diffusing through any given emulsion layer will not be immobilized by development of developable silver halide contained therein.

The present invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative photographic products and processes which, however, are also intended to be illustrative and not of limiting effect.

An image-receiving element may be prepared by coating a cellulose nitrate subcoated baryta paper with the partial butyl ester of poly-ethylene/maleic anhydride copolymer prepared by refluxing, for 14 hours, 300 grams of DX–840-31 Resin [trade name of Monsanto Chemical Co., St. Louis, Mo., for high viscosity poly-(ethylene/maleic anhydride)], 140 grams of n-butyl alcohol and 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.3 mils. thick. The external surface of the acid layer may be coated with a 4% solution of partial acetaldehyde acetal of polyvinyl alcohol in water-methanol-isopropanol to provide a polymeric spacer layer approximately 0.15 mils. thick. The external surface of the spacer layer may then be coated with a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of approximately 600 mgs./ft.^{2}, to provide a polymeric image-receiving layer approximately 0.40 mils.

thick into which had been incorporated, e.g., 90–120 mgs./ft.^{2} of a compound of the formula:



in a solution of methyl cellusolve.

A multicolor, multilayer photosensitive element may then be prepared in a manner similar to that disclosed in the aforementioned U.S. Pat. No. 3,345,163 and detailed hereinbefore. In general, the photosensitive elements comprised a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum. In turn, the emulsions had dispersed behind them in water-immiscible organic solvents and contained in separate gelatin polymeric layers, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. A gelatin interlayer was positioned between the yellow dye developer layer and the green-sensitive emulsion stratum, and also between the magenta dye developer layer and the red-sensitive emulsion stratum. The particular dye developers employed in the photosensitive elements were 1,4-bis-(α-methyl-β-hydroquinonyl-ethylamino)-5,8-dihydroxyanthraquinone (a cyan dye developer); 2-(p-[2′,5′-dihydroxyphenethyl] -phenylazo)-4-isopropoxy-1-naphthol (a magenta dye developer); and 1-phenyl-3-n-hexyl-carbamyl-4-(p-[hydroquinonylethyl]-phenylazo)-5-pyrazolone (a yellow dye developer). The last-mentioned yellow and magenta dye developers are disclosed in U.S. Pat. No. 3,134,764 and the cyan dye developer is disclosed in U.S. Pat. No. 3,135,606.

The photosensitive element may then be exposed and processed at 35° to 40° F. by spreading an aqueous liquid processing composition comprising:

Water	100	cc.
Potassium hydroxide	11.2	g.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250]	4.03	g.
Potassium thiosulfate	0.5	g.
Benzotriazole	3.5	g.
N-benzyl-α-picolinium bromide	2.3	g.
Lithium hydroxide	0.3	g.

between said image-receiving element and said exposed multicolor element as they are brought into superposed relationship in a Polaroid Land Camera. After an imbibition period of 3 minutes, the picture door of the camera may be opened and the image-receiving element separated from the remainder of the film assembly.

The last-mentioned procedure may then be repeated at 75° F. employing an imbibition period of 1 minute.

For purposes of comparison, an image-receiving element may be fabricated in accordance with the last-mentioned procedure with the exception that phenyl mercaptotetrazole was employed as a development restrainer.

The thus-prepared image-receiving element may then be processed, as detailed above, at the temperatures designated.

The image-receiving elements containing development restrainers of the present invention show a greater degree of photographic activity at both processing temperatures illustrated by high toe saturation on the H & D curve and speed maintenance over the temperature ranges than does the image-receiving elements containing phenyl mercaptotetrazole.

Although the preferred image-receiving layer is a mixture of polyvinyl alcohol and poly-4-vinylpyridine, the invention is not limited thereto. Other image-receiving layers are known in the art and may be employed. Similarly, while the preferred embodiment effects development in the presence of a quaternary ammonium compound, as disclosed and claimed in U.S. Pat. No. 3,173,786, issued Mar. 16, 1965, and particulary a quaternary ammonium compound capable of forming an active methylene base in alkali, the invention is not so limited, even though the advantages are most dramatic when such an active methylene quaternary ammonium salt is used.

The symbol pH as used throughout the specification represents the logarithm of the reciprocal of the hydrogen ion concentration.

The support layers referred to may comprise any of the various types of conventional rigid or flexible supports, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include paper; aluminum; polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetal; polyamides such as nylon; polyesters such as polymeric films derived from ethylene glycol terephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate. Where desired, the support for the image-receiving layer may be transparent or opaque.

Processing preferably is effected in the presence of an auxiliary or accelerating silver halide developing agent which is substantially colorless, at least in the unoxidized form. Particularly useful are substituted hydroquinones, such as phenylhydroquinone, 4′-methylphenylhydroquinone, toluhydroquinone, tertiary-butylhydroquinone, and 2,5-triptycene diol. These hydroquinones may be employed as components of the processing composition or they may be incorporated in one or more layers of the negative. Particularly useful results are obtained when 4′-methylphenylhydroquinone is dispersed in one or more of the gelatin interlayers and/or in a gelatin layer coated over the blue-sensitive emulsion layer.

It is also contemplated to provide other adjuvants, e.g., ultraviolet absorbers, effective to improve the light stability or other properties of the positive image. Thus, an ultraviolet absorber may be included in the processing composition and deposited on the image-receiving layer during imbibition, or it may be present in a thin overcoat on the image-receiving layer prior to imbibition.

Although the invention has been discussed in detail throughout employing dye developers, the preferred image-providing materials, it will be readily recognized that other, less preferred, image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U.S. Pat. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,789; 2,802,735; 3,148,062; 3,227,550; 3,227,551; 3,227,552;

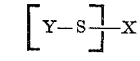
3,227,554; 3,243,294; 3,330,655;; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,443,940; 3,443,941; 3,443,943; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color or dye formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pat. Nos. 2,774,668 and 3,087,817, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials which, as disposed in the film unit, are initially diffusible or nondiffusible in the processing composition selected and are capable of providing an imagewise distribution of processing composition diffusible dye image-forming material as a direct or indirect function of exposure.

In addition to the described essential layers, it will be recognized that the elements denoted may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of improving adhesion, etc.

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

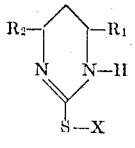
What is claimed is:

1. In a process for forming diffusion transfer images in color which comprises the steps of developing an exposed photosensitive element comprising a plurality of layers including a silver halide layer, at least one of said layers containing a dye image-providing material, by contacting said element with an aqueous alkaline solution, forming thereby an imagewise distribution of mobile dye image-providing material as a function of the point-to-point degree of exposure of said element, transferring by imbibition at least a portion of said imagewise distribution of mobile dye image-providing material to a superposed image-receiving element which comprises a dyeable polymeric layer, to provide to said dyeable polymeric layer a dye image; the improvement which comprises carrying out said process in the presence of a compound of the formula:

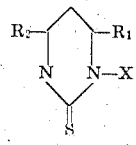


wherein Y is a tetrahydropyrimidine group and X is selected from the group consisting of hydrogen and a group hydrolyzable in said alkaline solution, said X being bonded to said compound through the sulfur or a ring nitrogen.

2. A process as defined in claim 1 wherein said compound is selected from the group consisting of compounds of the formula:



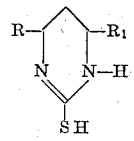
and



wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups, and X is selected from the group consisting of hydrogen and a group hydrolyzable by said alkaline solution.

3. A process as defined in claim 1 which comprises, in combination, the steps of exposing a photosensitive element which includes a support layer, carrying on one surface at least two selectively sensitized silver halide emulsion layers each having a dye, which dye is a silver halide developing agent, of a predetermined color associated therewith, each of said dyes being soluble and diffusible in alkali, contacting said exposed photosensitive element with an aqueous alkaline processing composition, effecting thereby development of latent images contained in each of said silver halide emulsions, immobilizing the dye associated with each of said emulsions as a result of said development, forming thereby an imagewise distribution of mobile dye as a function of the point-to-point degree of exposure thereof, transferring by imbibition at least a portion of each of said imagewise distributions of mobile dye to a superposed image-receiving element which comprises a dyeable polymeric layer to provide thereto a multicolored dye image.

4. A process as defined in claim 1 wherein said compound is represented by the formula:



5. A process as defined in claim 2 wherein R_1 is methyl and R_2 is hydrogen.

6. A process as defined in claim 2 wherein X is



wherein R is an alkyl group of 1 to 20 carbon atoms.

7. A process as defined in claim 1 wherein said compound is N-lauroyl 4-methyl-3,4,5,6-tetrahydropyrimidine 2-thiol.

8. A process of forming a multicolored image by diffusion transfer comprising:

a. exposing a photosensitive element comprising a support carrying in turn a layer including a red-sensitive silver halide emulsion, a layer including a green-sensitive silver halide emulsion, and a layer including a blue-sensitive silver halide emulsion; said silver halide emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer, and a yellow dye developer;

b. applying an aqueous alkaline processing solution to said photosensitive element to initiate development of exposed silver halide, said dye developers being oxidized and thereby immobilized where development occurs;

c. continuing said development of exposed silver halide for a predetermined period, said predetermined development period being sufficiently long to form

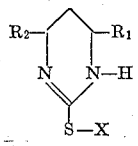
an imagewise distribution of diffusible unoxidized dye developer in undeveloped areas of each of said silver halide emulsion layers as a function of said development, said unoxidized dye developers being transferred by diffusion to an image-receiving layer in superposed relationship with said silver halide emulsion layers to form said multicolor image;

d. said process being carried out in the presence of a compound of the formula:

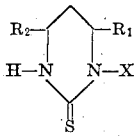
$$[Y—S—]—X$$

wherein Y is a tetrahydropyrimidine group and X is selected from the group consisting of hydrogen and a group hydrolyzable in said alkaline solution, said X being bonded to said compound through the sulfur or a ring nitrogen.

9. A process as defined in claim **8** wherein said compound is selected from the group consisting of compounds of the formula:



and



wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups, and X is selected from the group consisting of hydrogen and a group hydrolyzable by said aqueous alkaline processing composition at a temperature dependent rate to provide for the restraining of further development of exposed silver halide after said predetermined development period.

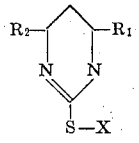
10. A photgraphic film unit comprising a support carrying a plurality of layers including a silver halide layer, at least one of said layers having a dye image-providing material associated therewith, said film unit including a compound of the formula:

$$[Y—S—]—X$$

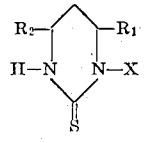
wherein Y is a tetrahydropyrimidine group and X is selected from the group consisting of hydrogen and a group hydrolyzable by alkali.

11. A product as defined in claim **10** wherein said film unit includes a support carrying on one surface at least two selectively sensitized silver halide layers, each having a dye which dye is a silver halide developing agent.

12. A product as defined in claim **10** wherein said compound is selected from the group consisting of compounds of the formula:



and



wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups and X is selected from the group consisting of hydrogen and a group hydrolyzable by alkali.

13. The product as defined in claim **10** which includes a diffusion transfer image-receiving element fixed to at least one edge of said photosensitive element.

14. The product as defined in claim **13** which includes a rupturable container retaining an aqueous alkaline processing composition fixed to one edge of said photosensitive and said image-receiving elements and adapted upon rupturing to distribute its contents intermediate said photosensitive element and said image-receiving element.

15. The product as defined in claim **13** wherein said photsensitive silver halide emulsion layers comprise, in sequence, a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a blue-sensitive silver halide emulsion layer having associated therewith, respectively, cyan, magenta and yellow dyes, each of said dyes being a silver halide developing agent.

16. The product as defined in claim **10** wherein said compound is disposed in at least one of said photosensitive silver halide emulsion layers and X is a group hydrolyzable by alkali.

17. The product as defined in claim **13** wherein said compound is disposed in said image-receiving element and X is hydrogen.

18. The product as defined in claim **11** wherein R_1 is a methyl group and R_2 is hydrogen and X is



wherein R is an alkyl group of 1 to 20 carbon atoms.

19. The product as defined in claim **17** wherein said compound is N-lauroyl 4-methyl-3,4,5,6-tetrahydropyrimidine 2-thiol.

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