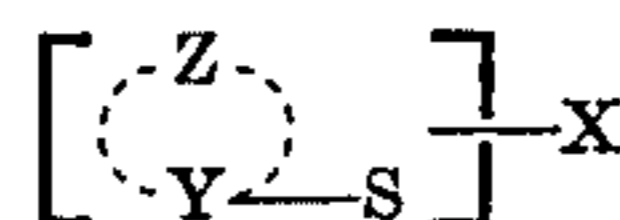


- [54] **POLYCYCLIC HYDROPYRIMIDINE DEVELOPMENT RESTRAINERS**
- [75] Inventor: **Donald O. Rickter**, Arlington, Mass.
- [73] Assignee: **Polaroid Corporation**, Cambridge, Mass.
- [22] Filed: **Jan. 3, 1972**
- [21] Appl. No.: **214,665**
- [52] U.S. Cl. .... **96/3, 96/29 D, 96/66.3, 96/76 R, 96/77**
- [51] Int. Cl. .... **G03d 7/00**
- [58] Field of Search..... **96/66.3, 109, 29 D, 96/3, 77, 76 R**

Primary Examiner—Norman G. Torchin  
 Assistant Examiner—Richard L. Schilling  
 Attorney—Robert M. Ford et al.

[57] **ABSTRACT**

A development restrainer is made available during dye diffusion transfer processing after a predetermined period by incorporating in the photographic film unit, an S-substituted, polycyclic pyrimidine compound of the formula

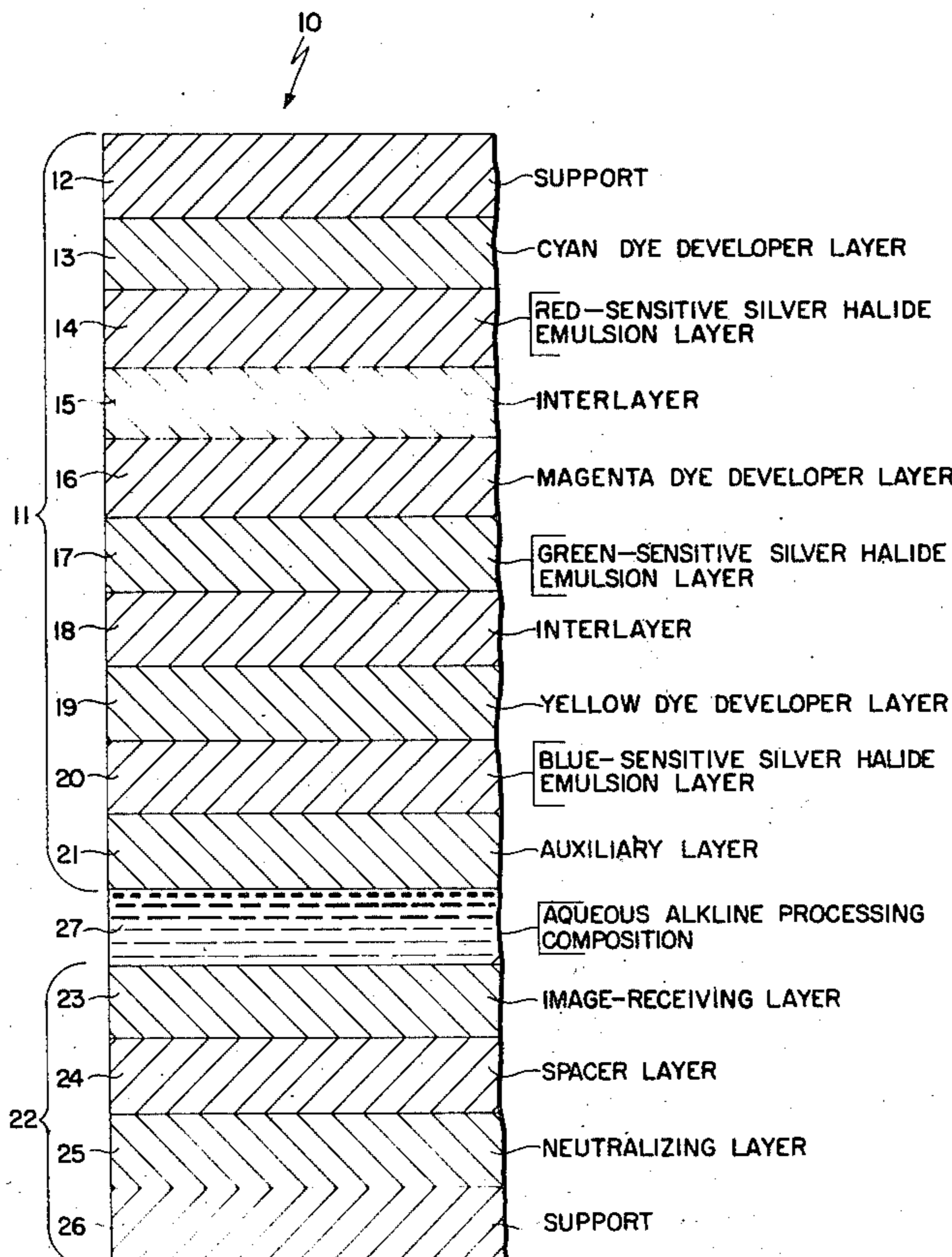


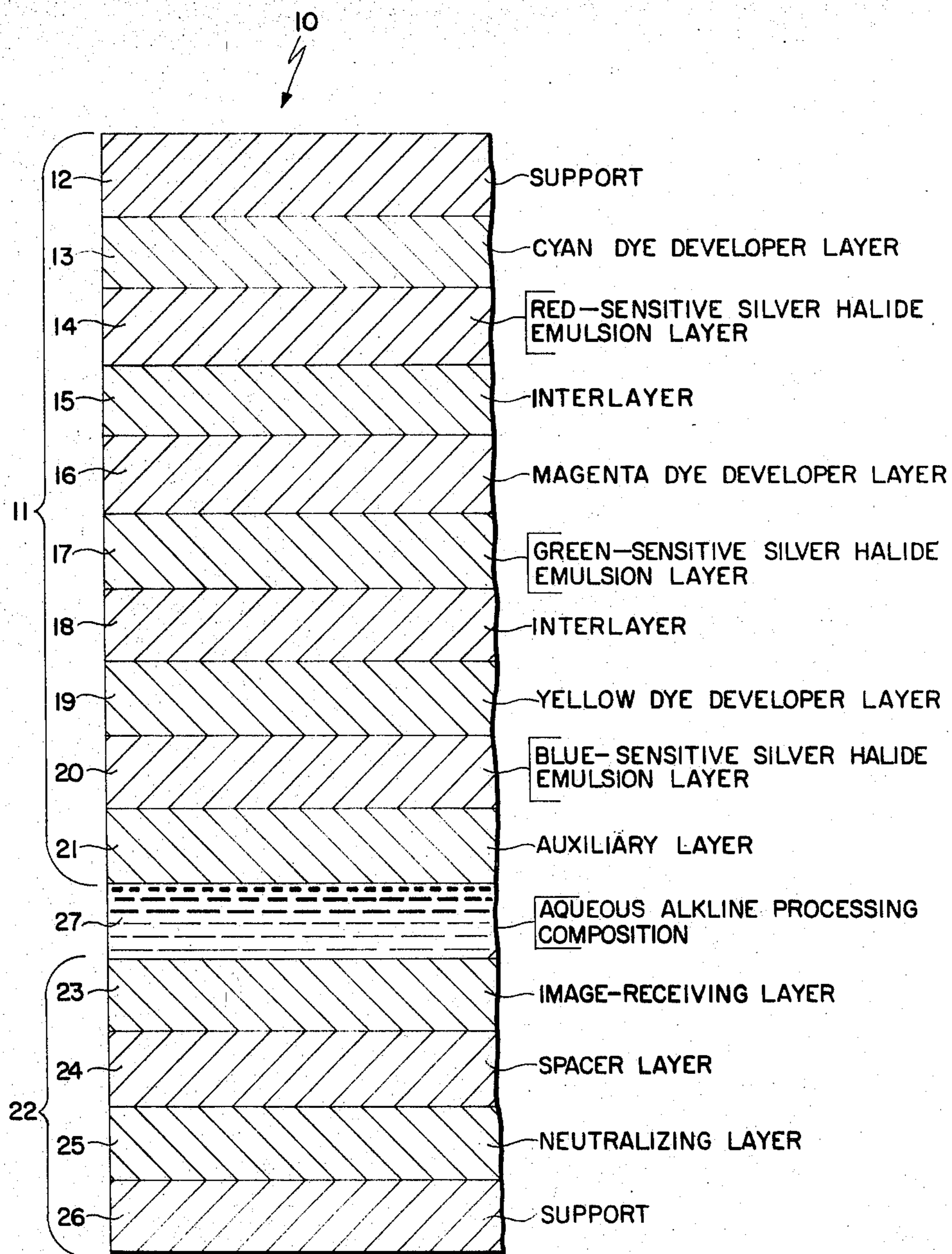
wherein Y is a hydroypyrimidine group, X is hydrogen in its active or unblocked form or a group hydrolyzable by alkaline processing composition as a function of temperature to provide a controlled release of development restrainer during the development process and Z is a ring system attached to the hydroypyrimidine group. Those compounds in which Z is an alicyclic group or a heterocyclic group are novel compositions of matter.

[56] **References Cited**

UNITED STATES PATENTS			
3,669,672	6/1972	Shiba et al. ....	96/109
3,415,644	12/1968	Land .....	96/3
3,415,645	12/1968	Land .....	96/3
3,615,549	10/1971	Ohyama et al. ....	96/109 R
3,331,840	7/1967	Fry et al. ....	96/109 R
3,565,619	2/1971	Johnson et al. ....	96/109 R
3,674,478	7/1972	Grasshoff et al. ....	96/66.3
3,706,557	12/1972	Aron .....	96/66.3

28 Claims, 1 Drawing Figure





## POLYCYCLIC HYDROPYRIMIDINE DEVELOPMENT RESTRAINERS

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to photography and more particularly provides novel products and processes for diffusion transfer photography.

#### 2. Discussion of the Prior Art

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 April 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 processes 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 func-

tioning 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 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 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 anhydride 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 imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 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 above U.S. Patent, 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 layers adhere to each other during storage and use.

The inert spacer layer of the aforementioned U.S. Patent, for example, an inert spacer 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 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 extent 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 be 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.

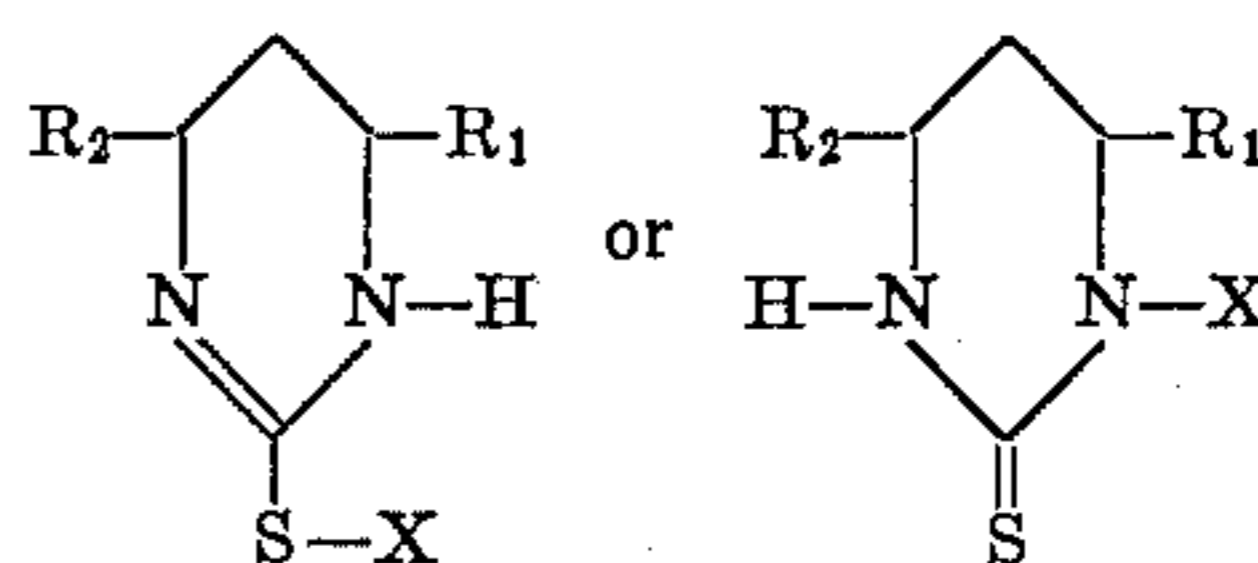
In the preferred embodiments of the above-mentioned processes employing integral multilayer negatives processed with an aqueous alkaline processing composition, unoxidized dye developer diffusion from an underlying emulsion to the superposed image-receiving layer must pass through at least one other 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 diffusing 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 interfer-

ence 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. Patent No. 3,265,498 also teaches the employment of hydrolyzable development restrainers, i.e., development restrainer precursors which are substantially non-diffusible or at least substantially less diffusible in its unhydrolyzed form that 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.

Copending application Ser. No. 60,272, now abandoned, discloses the use of hydrolyzable development restrainer precursors of the type described above which comprise S-substituted, tetrahydropyrimidine compounds wherein said compounds are further substituted by a hydrolyzable group. These compounds may be represented by the formula:

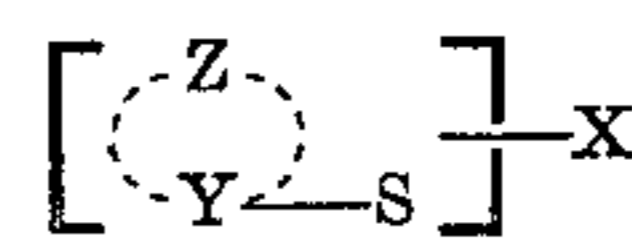


wherein  $R_1$  and  $R_2$  are hydrogen or alkyl groups, preferably lower alkyl groups, more preferably methyl, and X is an alkaline processing composition hydrolyzable group directly bonded to a ring nitrogen or the sulfur, or X is just hydrogen.

#### BRIEF SUMMARY OF THE INVENTION

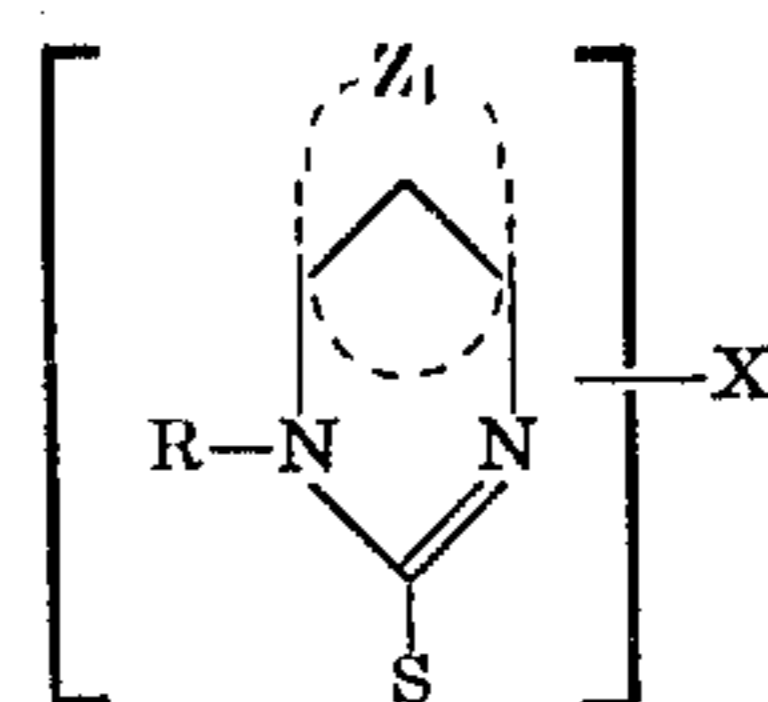
It has now been found that much greater photographic activity, i.e., development restraint, is obtained if the hydroxyprymidine group of the last-mentioned compounds has attached thereto a ring system of one or more rings.

The compounds of the present invention may be generally represented by the formula:



wherein Y is a hydroxyprymidine group, Z is a ring system attached thereto and X is hydrogen in its active or unblocked form or a group replaceable by hydrogen in a hydrolysis reaction with alkaline solution.

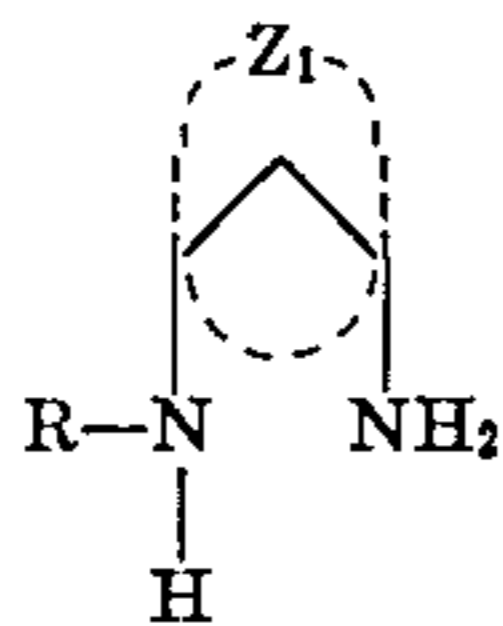
The novel compounds of the present invention may be represented by the formula:



wherein  $Z_1$  represents an alicyclic or heterocyclic ring system; R is hydrogen or an atom which is included in ring system  $Z_1$ ; and X is hydrogen or an alkaline processing composition hydrolyzable group directly bonded to a nitrogen of the hydroypyrimidine group, or the sulfur atom. Prior art compounds also contemplated as within the scope of one aspect of this invention include those polycyclic pyrimidine compounds where the attached ring system  $Z_1$  is a fused aromatic hydrocarbon ring.

X may be bonded to the sulfur atom or to one of the nitrogen atoms of the hydroypyrimidine group. As described before, X refers to a 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 provide the development restrainer activity. The hydrolysis is provided by the alkaline processing composition. Alternatively, X may be hydrogen, in which case the compound is already in its hydrolyzed form and will immediately function as a development restrainer.

The method of preparation of the active development restrainers, i.e., when X is hydrogen, involves the reaction of carbon disulfide with a cyclic diamine compound of the formula:



wherein  $Z_1$  and R have the connotations described above. The development restrainer precursors, i.e., when X is an alkaline processing composition hydrolyzable group, are preferably prepared by reacting the active development restrainers with a compound including said hydrolyzable group.

The photographic unit employing the development restrainers of the present invention preferably 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 the dyeable polymeric layer is at least in superposed relationship with the photosensitive element after exposure and during processing of the exposed photosensitive silver halide emulsion, that is, during contact of said emulsion with the aqueous alkaline processing composition. The development restrainer may be incorporated in a layer of either the photosensitive element or in the image-receiving element or in the processing composition. The hydrolyzed compound is preferably incorporated into the image-receiving element.

#### BRIEF DESCRIPTION OF THE DRAWING

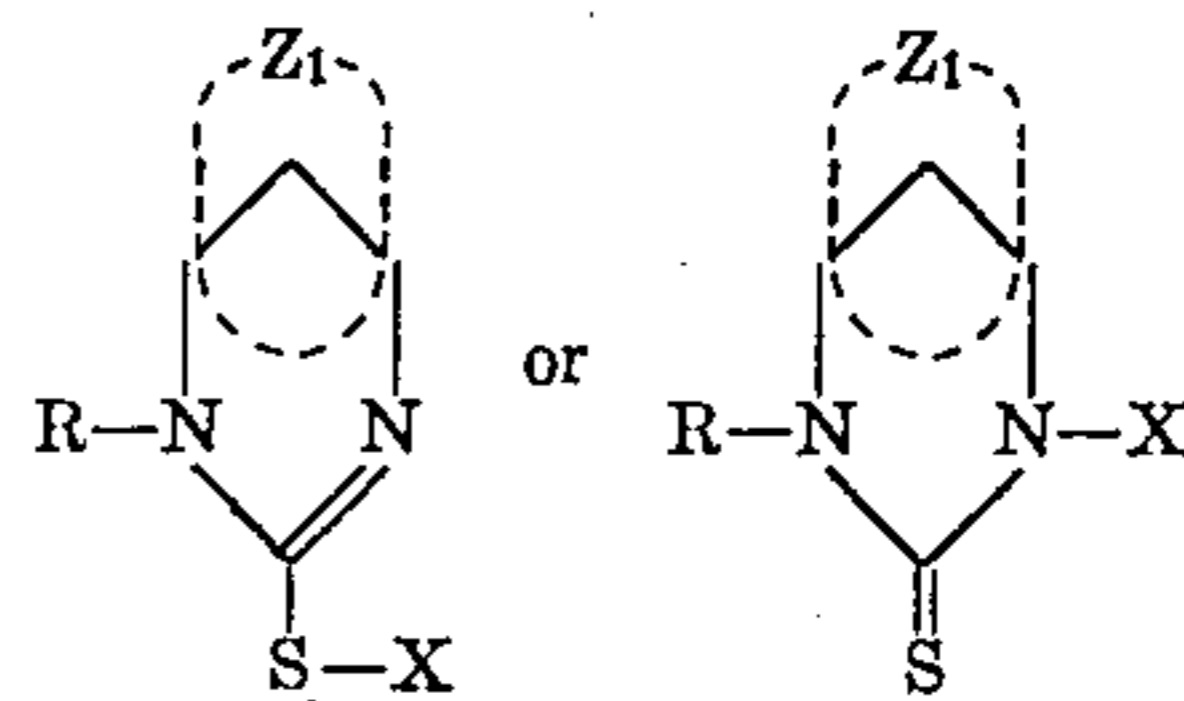
The FIGURE is a diagrammatic enlarged cross-sectional view illustrating the association of elements during one stage of the performance of a diffusion transfer process for the production of a multicolor transfer image according to the present invention, the thickness of the various materials being exaggerated.

#### DETAILED DESCRIPTION OF THE INVENTION

A ring system, represented by Z or  $Z_1$ , in the formulae above, when attached to S-substituted hydroypyrimidine compounds of the type herein described, provides said compound with superior development restraining properties when employed in the products and processes constituting the subject matter of this specification.

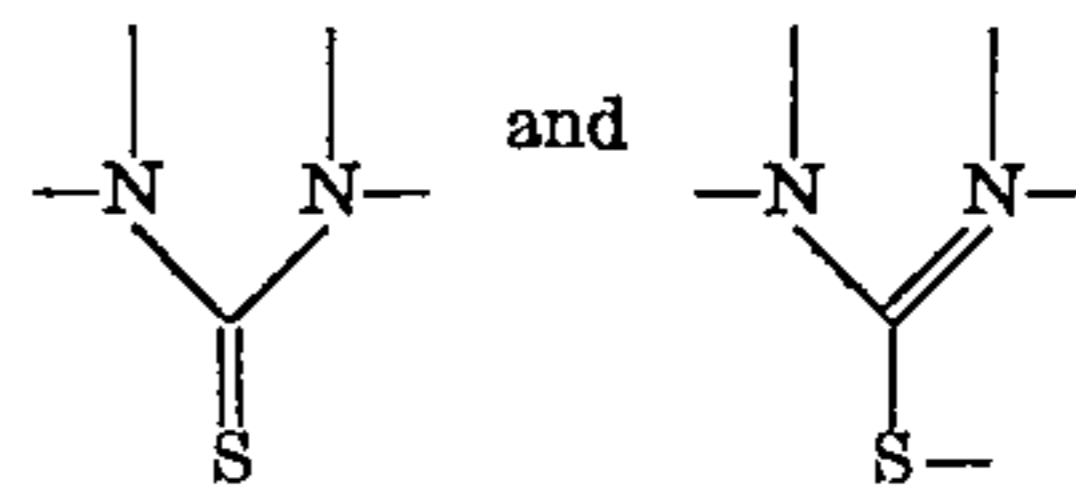
As examples of suitable ring systems contemplated by the present invention, mention may be made of alicyclic, heterocyclic, and arylene radicals. Alicyclic groups are univalent saturated hydrocarbon ring systems. Heterocyclic ring systems are those which contain one or more ring atoms other than carbon, and may be saturated or unsaturated. The prefix "hydro-" designates a heterocyclic ring system whose unsaturation is less than the one corresponding to the maximum number of non-cumulative double bonds, e.g., hydroypyrimidine denotes a pyrimidine group with one or two double bonds deleted.

Preferable compounds contemplated by this invention may be represented by the formula:



wherein  $Z_1$  is a ring system as described above, preferably containing from 3 to 10 atoms (when the atoms common to both the ring system and the hydroypyrimidine group are included in the count), and more particularly, containing 3-10 ring atoms selected from the group consisting of C, N, S and O; said ring system being disposed with respect to the hydroypyrimidine group in a relationship which can be described as ortho-fused, ortho- and peri-fused or bridged; R is hydrogen or an atom which is part of the ring system  $Z_1$ ; and X has the definition given hereinbefore.

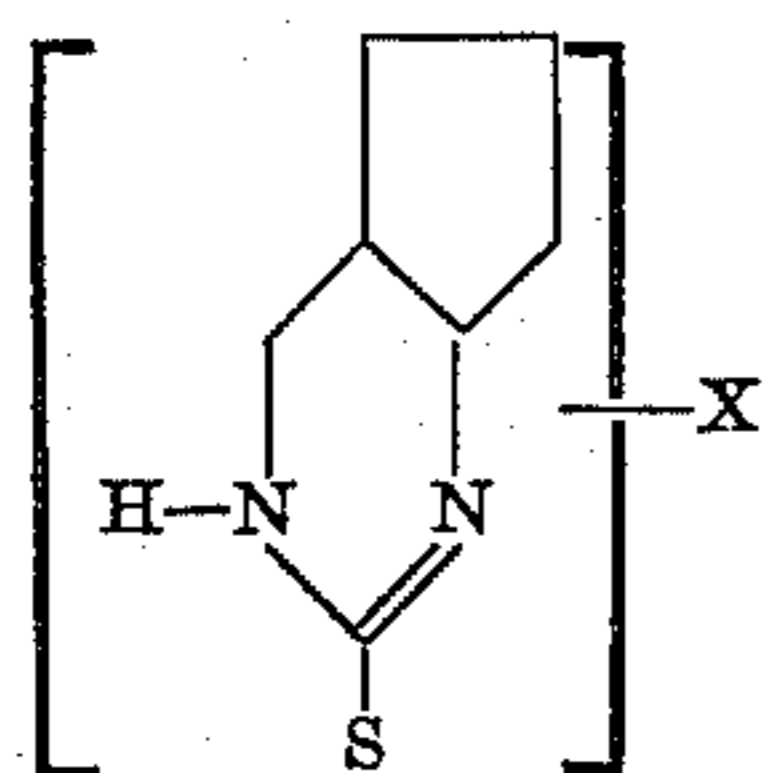
All formulae set forth in this application are intended only to be illustrative of one form of the actual structure of the depicted compound. The "thiourea" grouping contained within the structural formulae of the compounds of the present invention are believed to undergo tautomeric rearrangements and therefore may actually exist in a variety of structures, the extremes of which may be represented, for example, by the formulae:



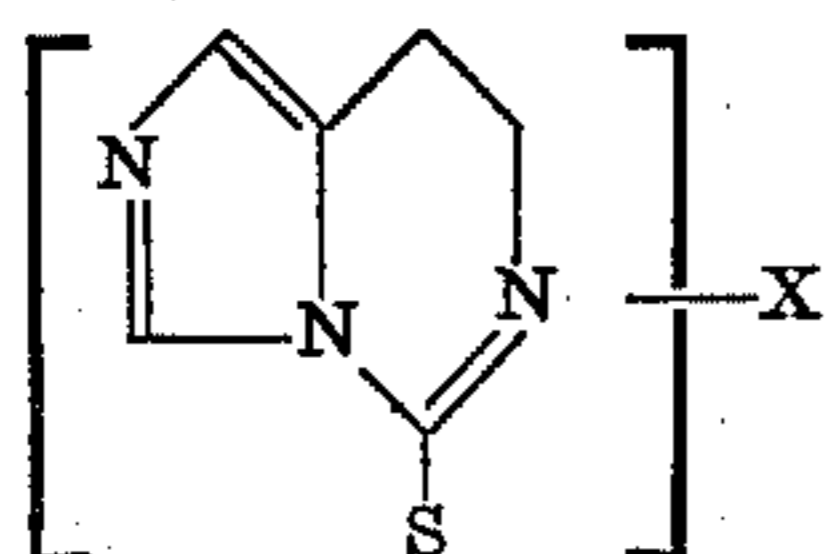
It is to be understood, therefore, that all such formulae contained in this specification and the appended claims represent the depicted structure and any tautomeric equivalent thereof.

The ring system attached to the hydroypyrimidine group may be either monocyclic or polycyclic and the ring or rings which constitute said system may have various alternative sites of attachment to the base hydroypyrimidine group. This position relationship between the above-mentioned ring system and the hydroypyrimidine group is described herein as "ortho-fused," "ortho- and peri-fused" or "bridged." See IUPAC 1957 rules; and *Handbook of Chemistry and Physics*; The Chemical Rubber Co.; 52<sup>nd</sup> Ed. (1971), pp. C-13 and C-18.

Polycyclic compounds in which two rings have two, and only two atoms in common are referred to as ortho-fused. Such compounds have  $n$  common faces and  $2n$  common atoms. Examples of ortho-fused ring systems which may be included within the compounds contemplated by the present invention are:

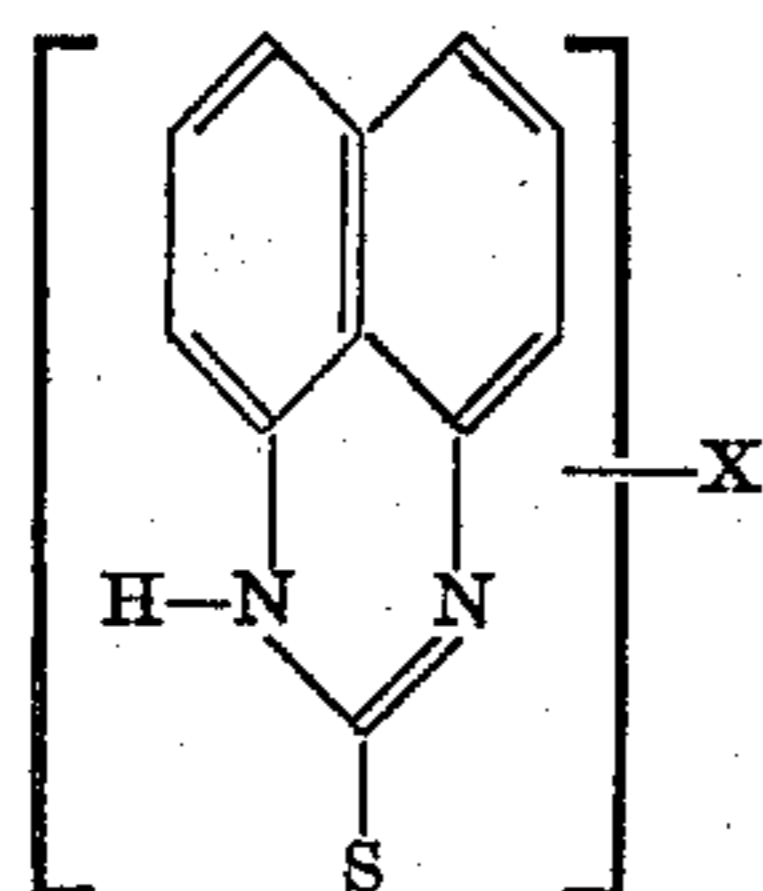


and

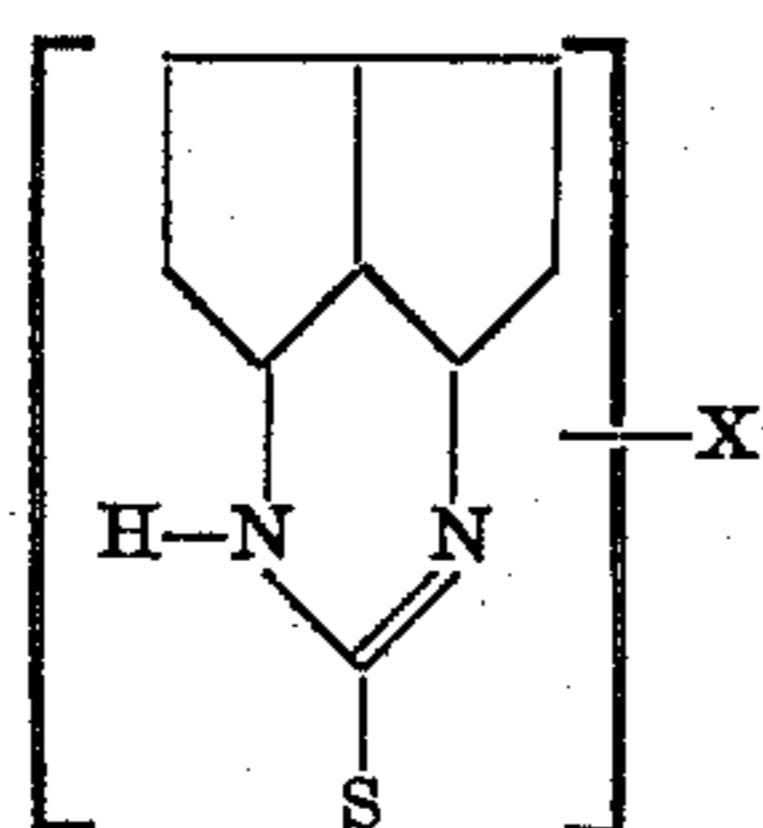


wherein X has the above-described connotation.

Polycyclic compounds in which one ring contains two, and only two, atoms in common with each of two or more rings of a contiguous series of rings are said to be ortho- and peri-fused. These compounds have  $n$  common faces and fewer than  $2n$  common atoms. Examples of ortho- and peri-fused compounds contemplated by the present invention include:

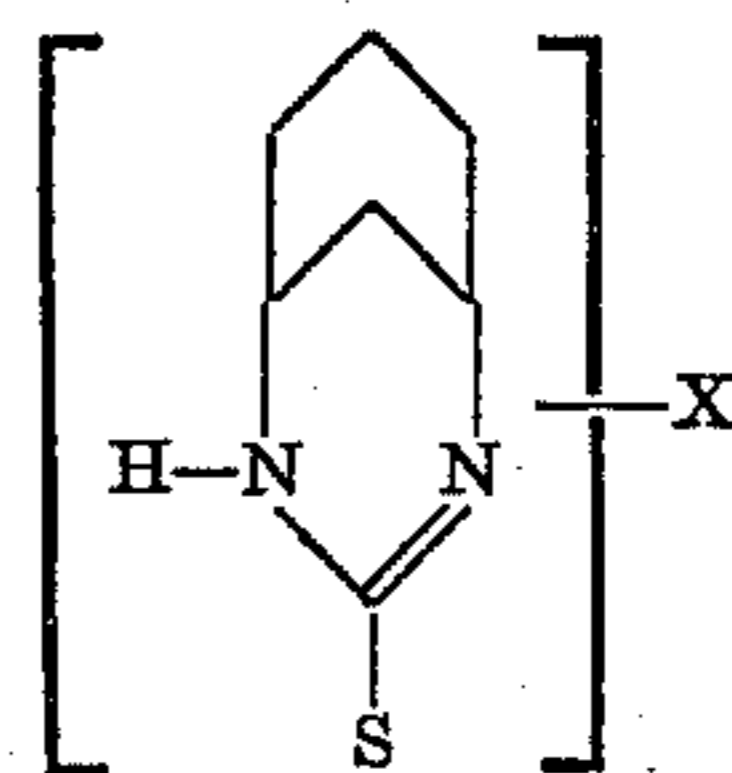


and

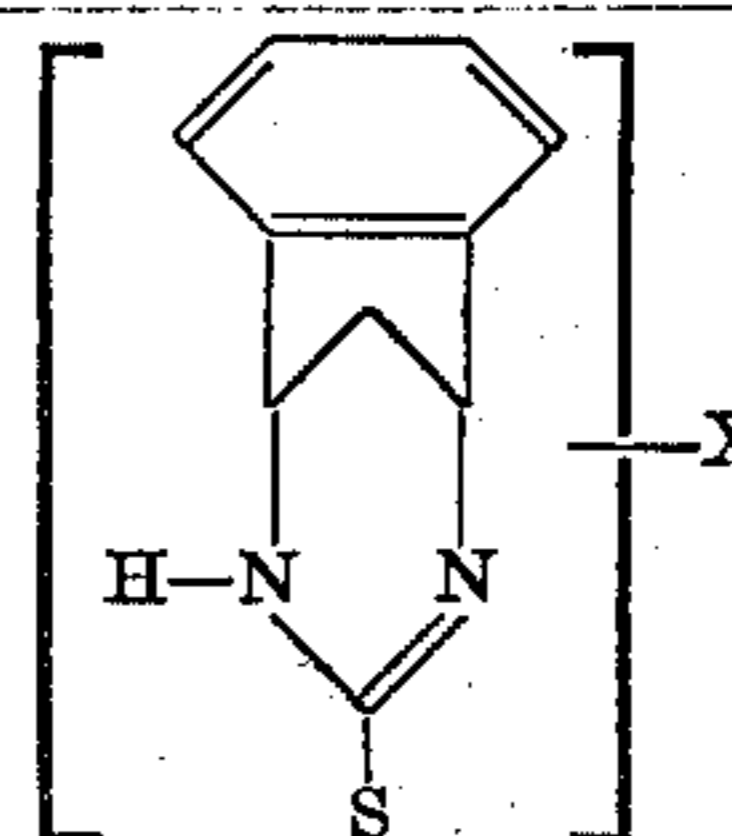


wherein X has the above-defined connotations.

A bridge, as defined for the purposes of this application, is an atom or unbranched chain of atoms connecting two different non-adjacent atoms of the hydroypyrimidine group to form a closed ring. The bridged relationship of the ring system to the hydroypyrimidine group as contemplated by the present invention is exemplified by:

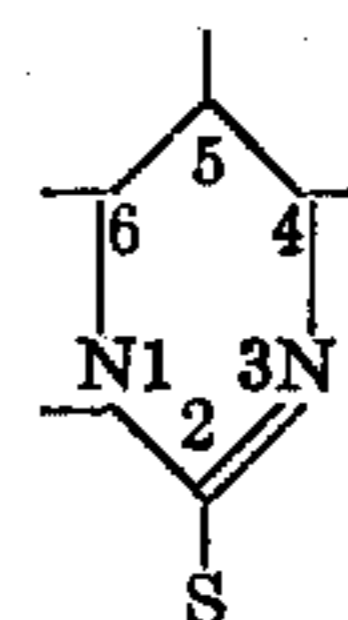


and



wherein X has the above-defined connotations.

To further clarify the relationship of the ring systems of the hereindescribed compounds, the member atoms of the base hydroypyrimidine group may be numbered; for example:



Accordingly, ortho-fused compounds as described above would include, for example, those compounds having ring systems attached to atoms 4 and 5, 5 and 6 and 1 and 6 of the hydroypyrimidine group. Similarly, the above-described bridged compounds would include those compounds having, for example, 4, 6-; 1, 5- and 1, 4-ring attachment. Ortho- and peri-fused compounds would include, for example, compounds having contiguous attached ring systems in the 4, 5, 6- position and the 1, 6, 5- position on the hydroypyrimidine group.

Preferably,  $Z_1$  in the equations supra comprises alicyclic and heterocyclic ring systems containing 3-10 ring member atoms, and more preferably alicyclic or heterocyclic rings containing 5 to 6 member atoms. The preferred member atoms of said ring systems are C, N, S or O atoms, and the most preferred atoms are C and N.

In one embodiment of the present invention,  $Z_1$  is an imidazo, cyclopenta, or cyclohexa group. A particularly preferred embodiment of this invention involves  $Z_1$  as an ortho-fused cyclopenta group.

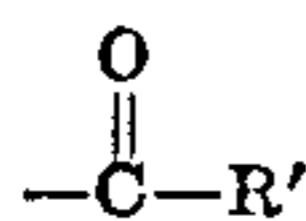
R, as defined above, may be hydrogen or an atom which is a part of the ring system depicted as  $Z_1$ . When R is so defined, a ring which is included in  $Z_1$  may also have as a constituent atom one of the nitrogens of the

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hydropyrimidine group. One of the compounds depicted above is an example of this type of compound wherein an ortho-fused imidazo group shares a nitrogen atom with the hydropyrimidine group.

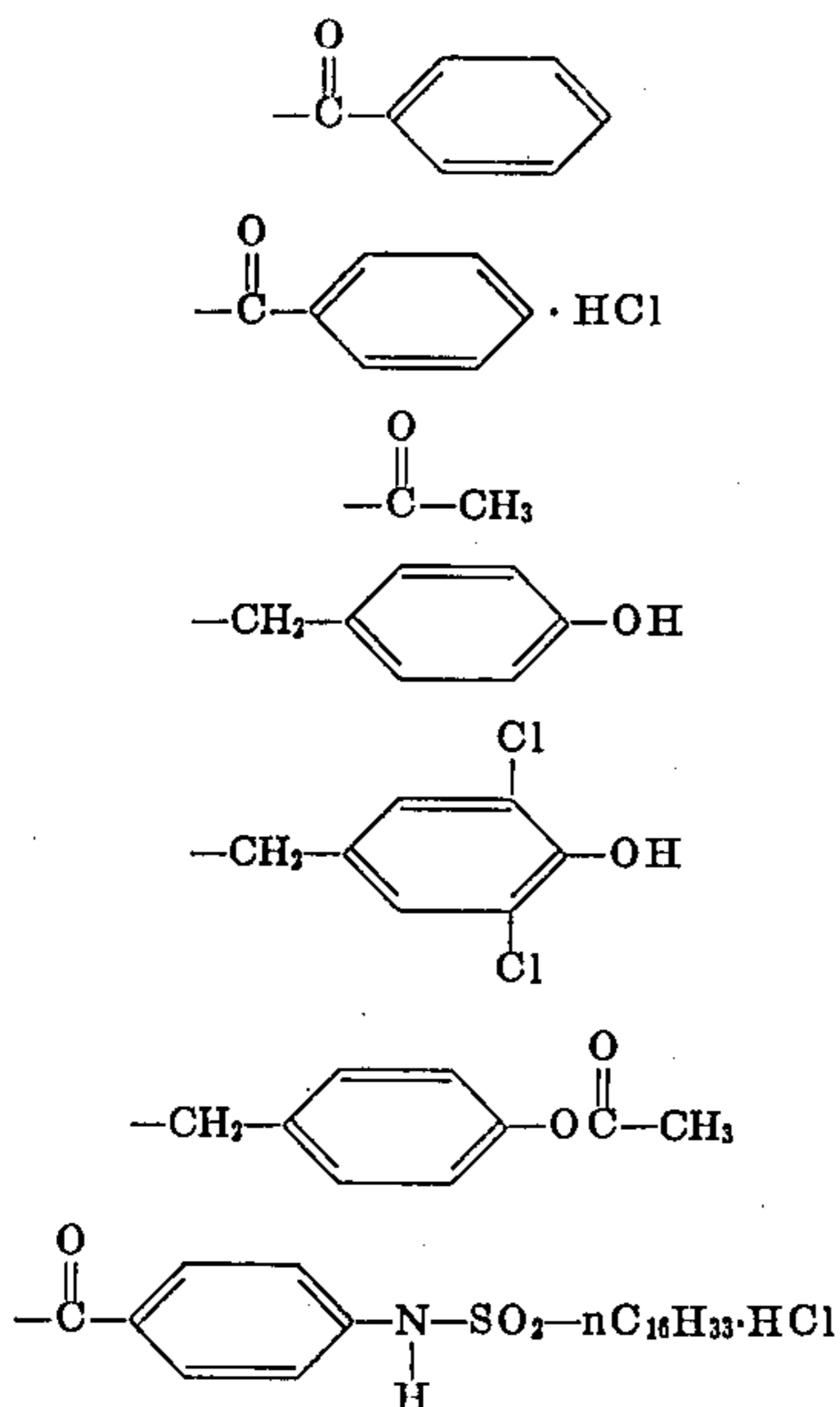
As described hereinbefore, X may be hydrogen, in which case the compound represented by the above formula is in its hydrolyzed form and will function as a development restrainer, or X may be an alkaline processing composition hydrolyzable group which substantially inactivates the development restrainer function. X may also be any 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.

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

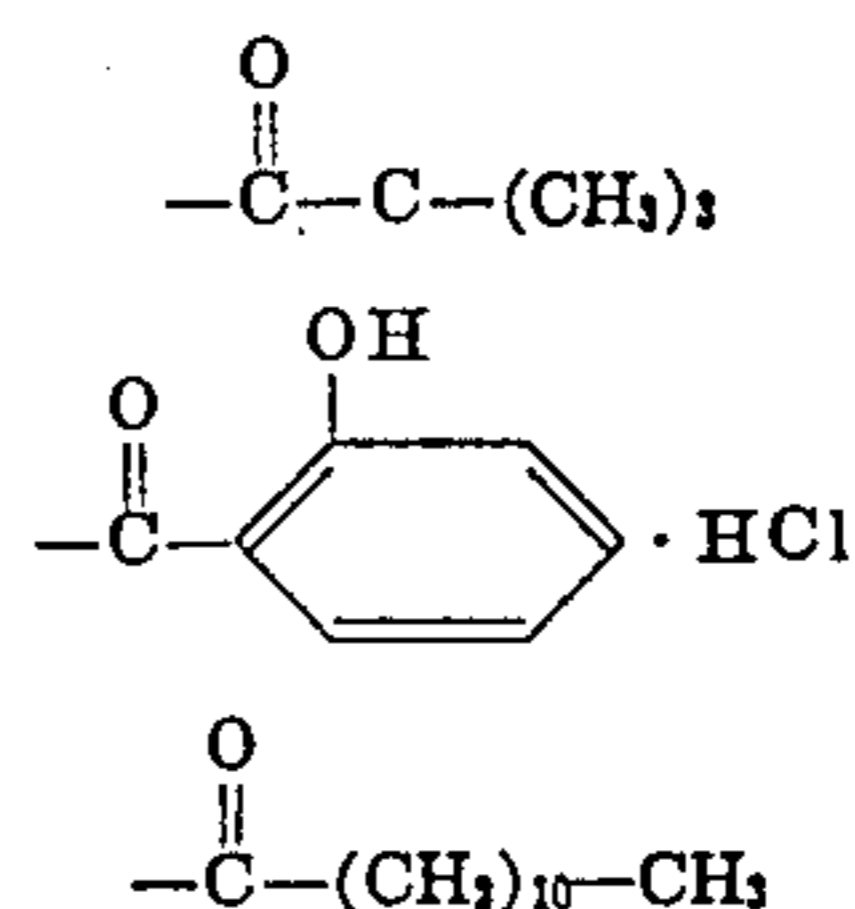


wherein R' is aryl or alkyl. The length of the alkyl group or substituent on the aryl group is selected by the operator to provide the desired rate of solubility in alkaline processing composition and thus provide the desired rate of diffusion or mobility of the compound from its initial location in 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:



12



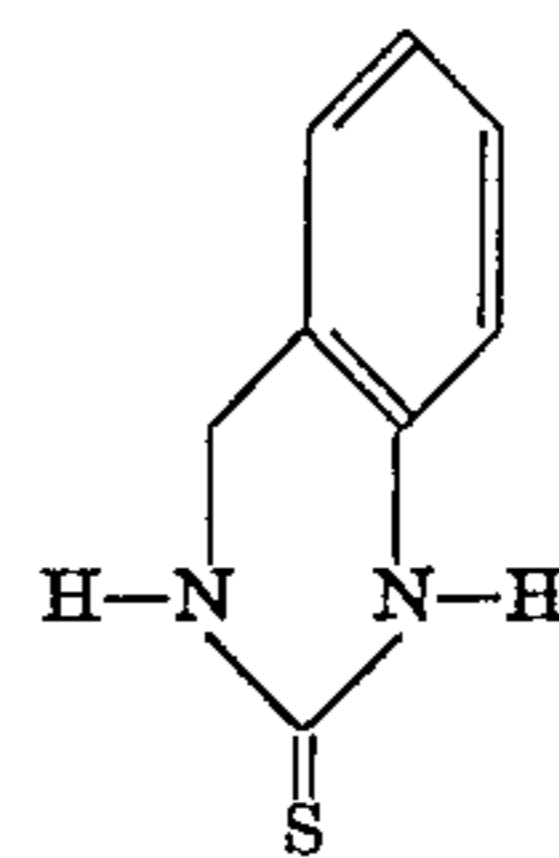
At low temperatures, development and migration of the dye developers is retarded and providing prior art development restrainers under such conditions would impose further restraints on the development process resulting in decreased control of the image-forming process. Similarly, at higher temperatures, 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 temperatures 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.

Compounds wherein the attached ring system is a benzo group, e.g.,

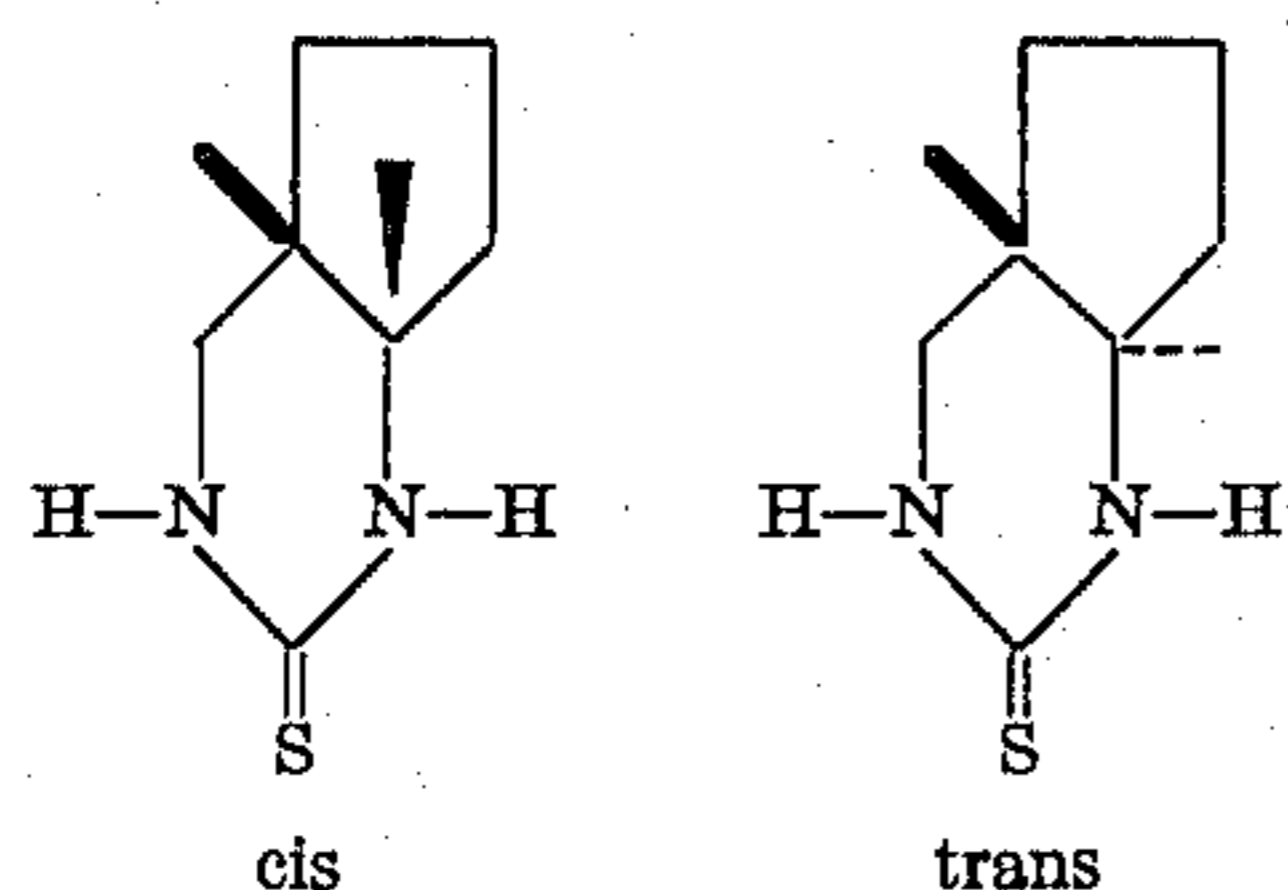


are disclosed in the art. See, for example, Dutch Pat. No. 707,945; Chem. Abstracts, 70, 42844d; Chem. Abstracts, 56, 5964; and J. Pharm. Sci., 50, 866 (1961). The above-mentioned Dutch Pat. No. 707,945, claims compounds of the above-mentioned type as toners in black and white silver diffusion transfer processes.



However, the novel compounds of the present invention, i.e., wherein  $Z_1$  is an alicyclic or heterocyclic ring system are preferably employed as development restrainers as detailed in this specification.

Examples of the novel compounds of the present invention are the isomers of 4,5-cyclopentahexahydro-2-thione, represented by the formulae:



Both of the above-depicted isomers are prepared, as illustrated in Example I, by reacting carbon disulfide with 2-aminomethyl cyclopentylamine, which may be obtained commercially or prepared from adiponitrile by cyclization and hydrogenation. See. JACS, 80, 5483 (1958).

#### EXAMPLE I

One mole of 2-aminomethyl cyclopentylamine (114 gms; or approx. 120 ml. of the amine available from BASF) was dissolved in 1 liter of ethanol. About 120 ml. of carbon disulfide was then added to this solution over a period of one-half hour. This mixture was refluxed overnight in a hood, and then refluxed for another 1 to 5 hours with 10 ml. of concentrated hydrochloric acid added to ensure that any dithiocarbamate present was completely ring-closed. (Each fraction may be tested with aqueous cupric sulfate. There should be no brown color observed).

The solid formed was filtered from the hot reaction mixture. This product was determined to be the crude trans isomer having a melting point of approximately 200°-220° C. Other crops collected after cooling, melted at approximately 180°-200° C.

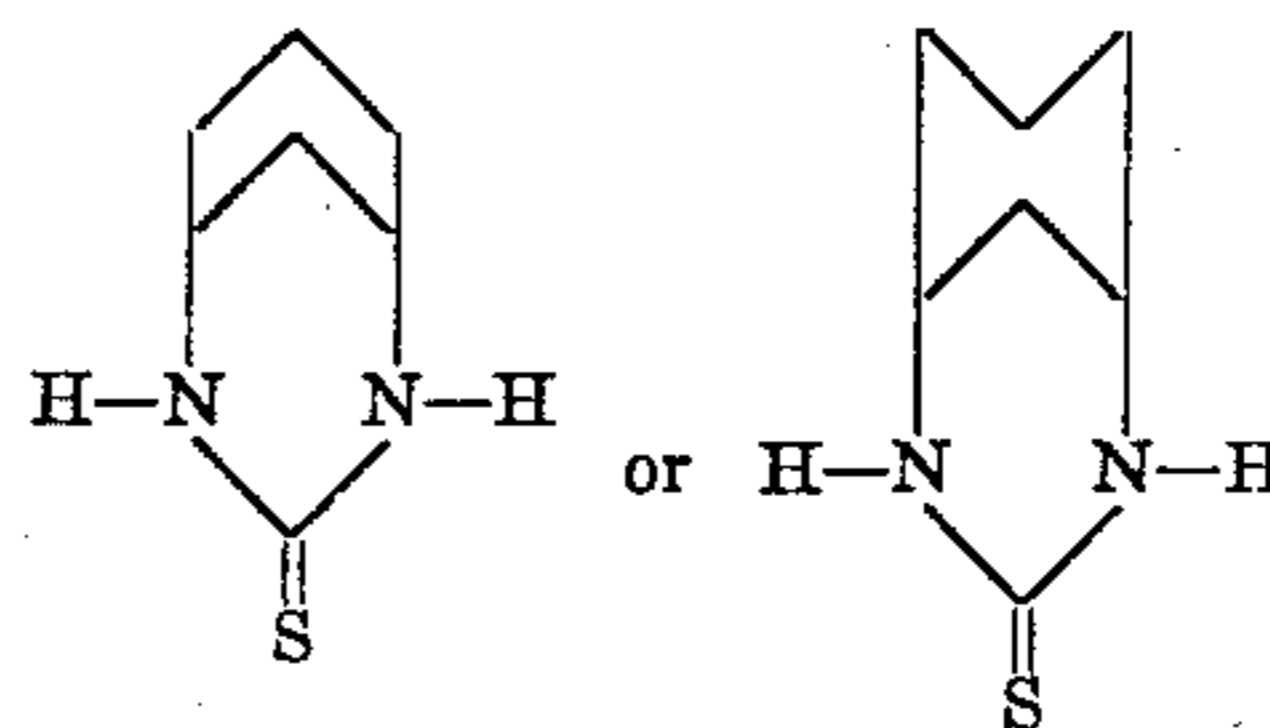
Evaporation of the filtrate gave the crude cis isomer which melted at about 150°-180° C. Although the crude products above were satisfactory for the preparation of various derivatives for photographic use, several recrystallizations from alcohol gave the pure compounds which had the following properties:

Isomer	M.P.	Color and State	U.V.-Vis Spec (3A ethanol)	
			$\lambda_{max}$	$\epsilon$
Cis	165-7°	white crystals	243 m $\mu$	14,600
Trans	236-8°	white crystals	247 m $\mu$	14,400
Equimolar mixture of isomers	150-220°	white crystals	245 m $\mu$	14,400

#### Elemental Analysis of the trans isomer gave:

	C	H	N	S
Found	53.8%	8.0%	17.7%	20.2%
Theoretical	53.81%	7.75%	17.92%	20.52%

The reaction of 1,3-diaminocyclohexane (BAYER Ag.) with carbon disulfide similar to Example I above forms another novel compound within the scope of the present invention and represented by:



#### EXAMPLE II

12 ml of  $CS_2$  was added over a period of 5 minutes to about 200 ml of a 2B ethanolic solution containing 11.4 gms (0.10 moles) of 1,3-diaminocyclohexane. There was an instant reaction to form a white solid. Another 100 ml of 2B ethanol was added and the mixture refluxed for an hour. Since the resultant product produced a positive test with  $Cu^+$ , indicating the presence of unclosed dithiocarbamate, 200 ml of ethanol and 5 mls of concentrated HCl were added and the mixture refluxed for 2½ hours. The white crystalline solid was filtered from the reaction mixture and evaporated to give a crude product which had a melting point of 281°-286° C. This material was recrystallized from acetone to give a product with essentially the same melting point, and a U.V.-Visible spectrum in 3A ethanol exhibiting a  $\lambda_{max}$  of 243 m $\mu$  and molar extinction coefficient ( $\epsilon$ ) of 14,800.

Compounds within the scope of this invention may be formed from heterocycles that have amino groups placed where they can form 6-membered rings when reacted with carbon disulfide as illustrated in Example III, the preparation of imidazo (1,5-c) tetrahydro-2'-thione from histamine:

#### EXAMPLE III

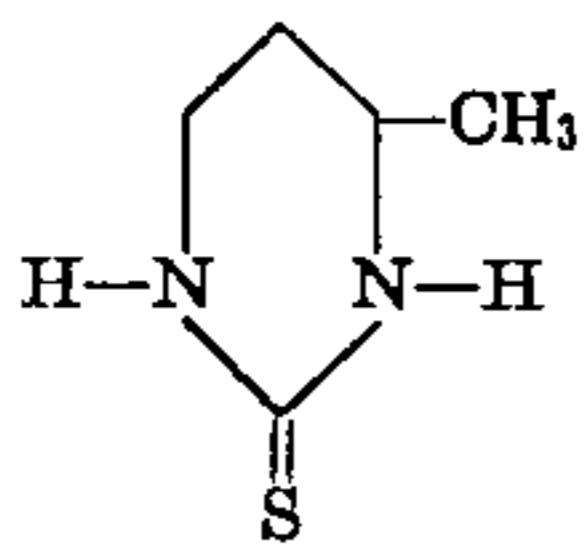
About 2.9g (0.026 mole) of histamine (Eastman Kodak No. 3404) was dissolved in 50 ml of alcohol 2B. Then, 5 gms of  $CS_2$  (4 mls at 1.26 g/ml) was added to the boiling solution. After about 1 hour of reflux, the clear yellow solution was poured into a beaker and chilled in ice. The pale yellow solid product filtered from the reaction mixture had a melting point of 219°-21° C. A representative elemental analysis confirmed the product composition to be that of imidazo [1,5-c] tetrahydro-2'-thione:

	C	H	N	S
Found:	47.4%	4.6%	27.4%	20.6%
Theoretical:	47.04%	4.61%	27.42%	20.93%

The reasons behind the much increased photographic activity of the novel compounds of this invention over development restrainers in the prior art are not as yet fully understood. However, several observations may be made.

The compounds constituting the subject matter of this application unexpectedly exhibit a much lower sol-

ubility in alkaline processing compositions than those compounds disclosed in the aforementioned copending application Ser. No. 60,272, e.g.,



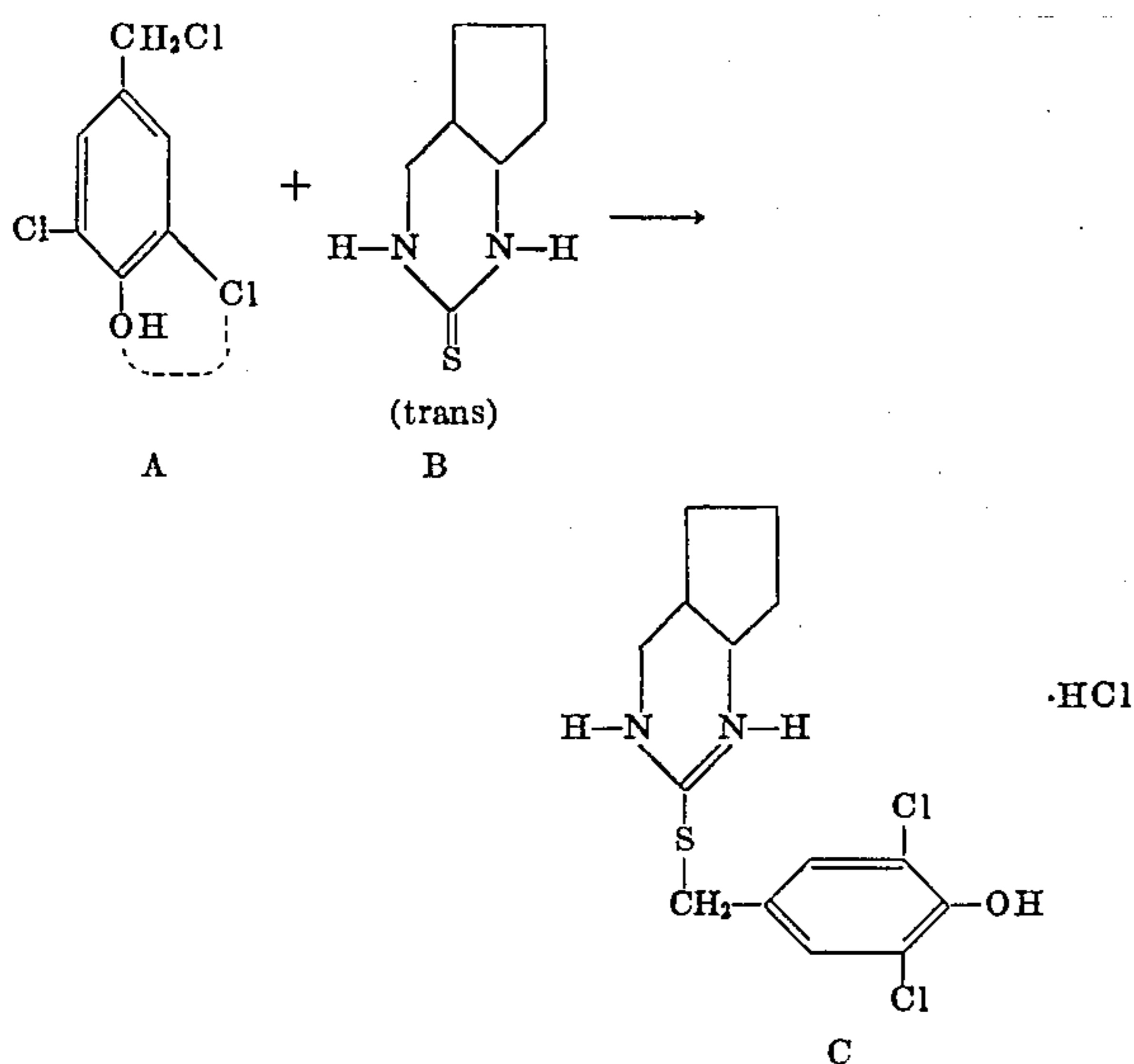
This behavior may be explained, for example, by the fact that the additional fused rings of the instant compounds distort the geometry of the bonds in the base hydroprymidine group, thus making these compounds less soluble in alkali than analogous prior art compounds without said additional ring.

Furthermore, it is known in the art that, generally, 5-membered monocyclic development restrainers function more satisfactorily than 6-membered cyclic development restrainers. See, for example, J. Org. Chem., 34:3549 (1969). This behavior may be explained again by the fact that the pentagonal structure has a more nearly planar configuration than the hexagonal structure.

The foregoing observations, therefore, lead one to hypothesize, without intending to be bound by theory, that the increased photographic activity of the compounds of the present invention is due, at least in part, to a modification of molecular geometry, particularly an increase in the planarity of the molecule.

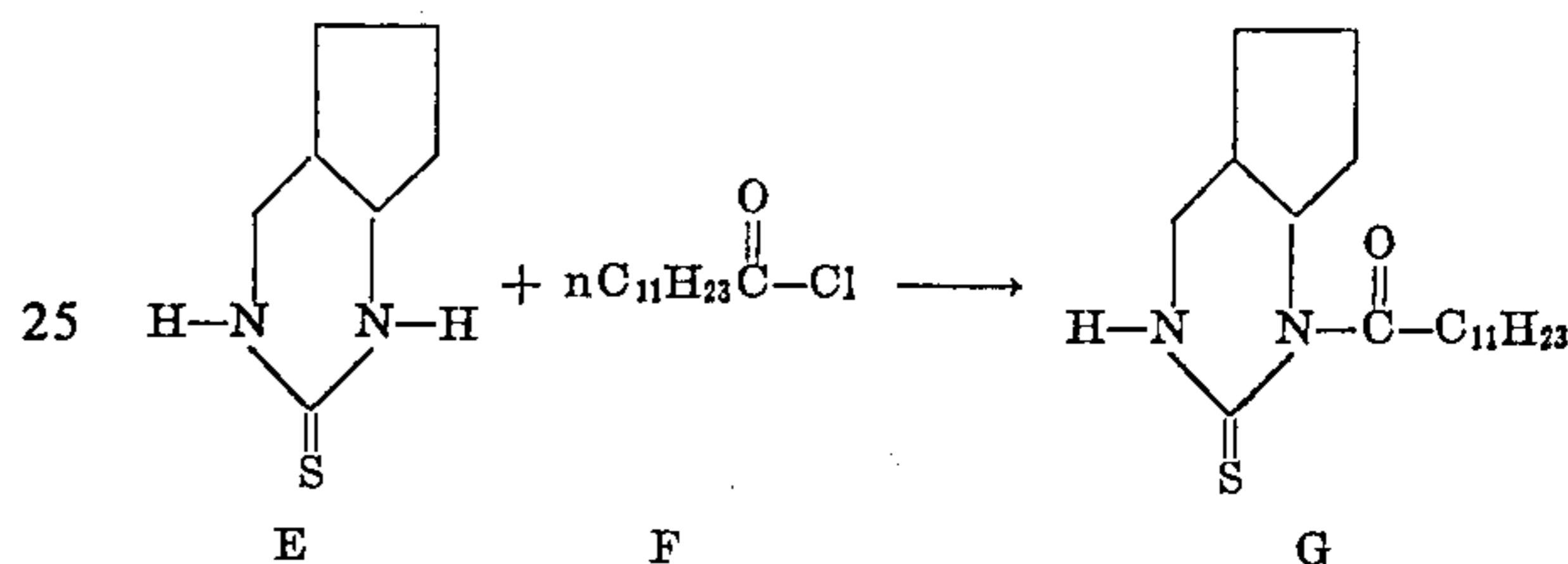
Those compounds in which the position designated as X in the equations supra is a group which is replaceable by hydrogen in a hydrolysis reaction with alkaline processing composition, i.e., development restrainer precursors, are preferably prepared by employing, for example, a method disclosed hereinbefore to form the active development restrainer, and then including an additional step which comprises reacting the product of said method with a compound including said hydrolyzable group. Typical reactions of the type described above are illustrated by the following examples:

## EXAMPLE IV



About 1.1 gms of compound A (0.005 mole) and 0.78 gms of compound B (0.005 moles) were put in a flask and 25 ml reagent grade acetone was added thereto. A white solid formed, the mixture was shaken occasionally and then left to sit overnight at room temperature. The white solid product was then removed by filtration and dried in a vacuum oven at room temperature. The product has a melting point of 229°-233°C and was confirmed by elemental analysis to be 2-(3',5'-dichloro-4'-hydroxy-benzylmercapto) - trans 4,5 - cyclopenta-3,4,5,6, -tetrahydropyrimidine hydrochloride, i.e., compound C in the equation above.

## EXAMPLE V



To a solution of 6.25 gms (0.040 mole) of compound E and 4.00 gms. (0.040 mole) of triethylamine (E.K. No. 616) in 100 ml of AR chloroform, 8.75 g (0.040 mole) of compound F (lauroyl chloride -EK No. 2217) in 25 ml of chloroform is added dropwise with continual stirring. The stirring is then continued for about 2½ hours after the addition is completed. The product, compound G is then washed, separated from the reaction mixture, recrystallized from alcohol and dried.

Adding the alkaline hydrolyzable group to the development restrainer in its active form by other methods will be obvious to those skilled in the art.

All examples set forth hereinabove are intended to be illustrative and are not to be interpreted in a limiting sense.

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 multi-color 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 of 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 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 comprise 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.

#### 5 DETAILED DESCRIPTION OF THE DRAWINGS

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

10 As illustrated in the FIGURE, film unit 10 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.

25 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.

30 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.

35 In the performance of a diffusion transfer multicolor process employing film unit 10, the unit is exposed to radiation, actinic to photosensitive laminate 11.

40 Subsequent to exposure, film unit 10 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.

45 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 neutraliza-

tion, 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.

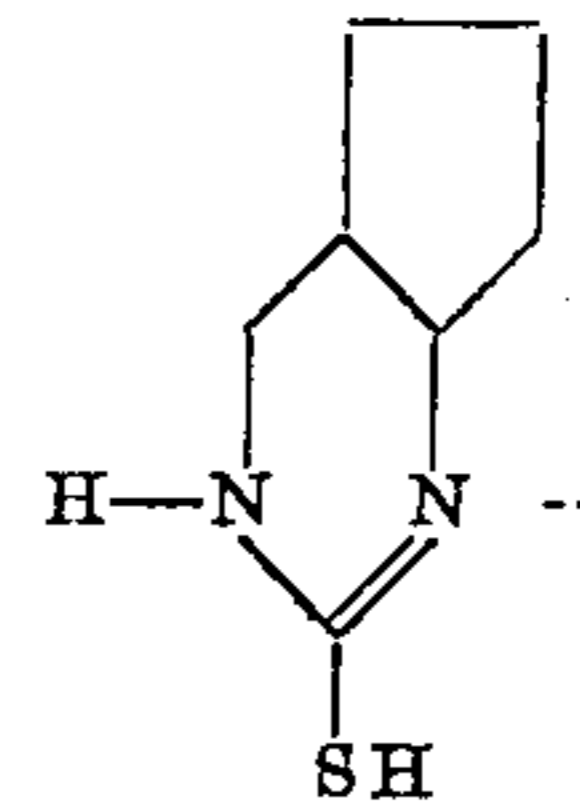
Assuming in the above-indicated photographic unit in a given unit area of the negative, exposure is effected only of the green-sensitive emulsion, unoxidized cyan dye developer will eventually diffuse into and through such exposed areas of the green-sensitive emulsion on route to the image-receiving 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 percent 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 percent solution of partial acetaldehyde acetal of polyvinyl alcohol in water-methanolisopropanol 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.<sup>2</sup>, to provide a polymeric image-receiving layer approximately 0.40 mils. thick.

The development restrainers of the present invention may be incorporated within the image-receiving element as prepared above. For example, an equimolar

mixture of the cis and trans isomer of the compound of the formula:



may be present therein at a coverage of approximately 70 mg./ft.<sup>2</sup>. This incorporation may be accomplished, for example, by dissolving an appropriate amount of the above-mentioned compound in a warm methanol-acetone mixture to form a solution with a development restrainer concentration in the range of about 3 percent, and incorporating said solution in one of the coating solutions detailed above.

A multicolor, multilayer photosensitive element may then be prepared in a manner similar to that disclosed in U.S. Pat. No. 3,345,163. In general, the photosensitive elements of said patent 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-( $\alpha$ -methyl- $\beta$ -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- $\alpha$ -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. and 100° F. employing an imbibition period of 1 minute or less.

For purposes of comparison, an image-receiving element may be fabricated in accordance with the last-mentioned procedure with the exception that a prior art development restrainer may be employed, for example, phenyl mercaptotetrazole or a compound of the aforementioned application Ser. No. 60,272.

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

The film units having image-receiving elements containing development restrainers of the present invention show a greater degree of photographic activity and maintain image density and speed more uniformly over the temperature ranges than does the image-receiving elements containing prior art development restrainers.

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 particularly 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 process-

ing 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.

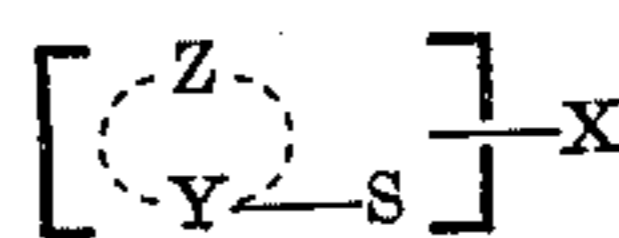
Although the invention has been discussed in detail throughout employing dye developers, the preferred image-providing materials, it will be readily recognized that other, less preferred, image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the 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; 2,698,798; 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. No. 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.

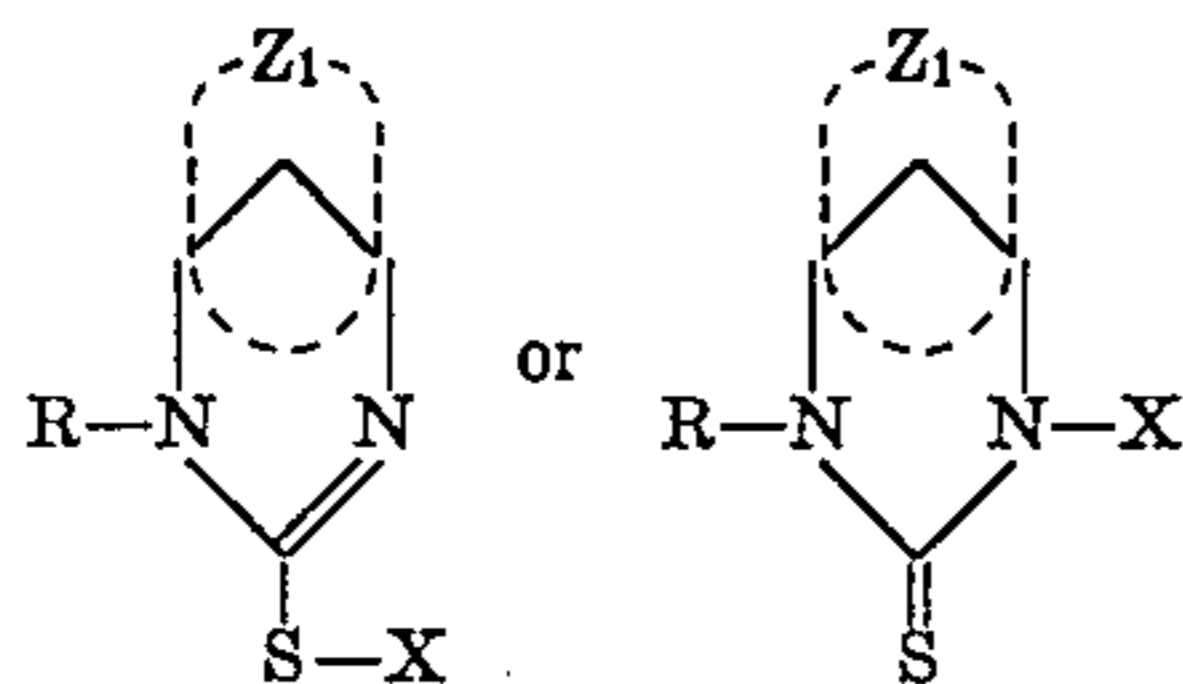
What is claimed is:

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 hydroypyrimidine group, Z is a ring system attached to said hydroypyrimidine group and X is hydrogen or a group replaceable by hydrogen in an hydrolysis reaction with said aqueous alkaline solution, said X being bonded to said compound through the sulfur or a nitrogen of said hydroypyrimidine group with the unsatisfied valence on said sulfur or nitrogen being satisfied by the formation of a double bond.

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

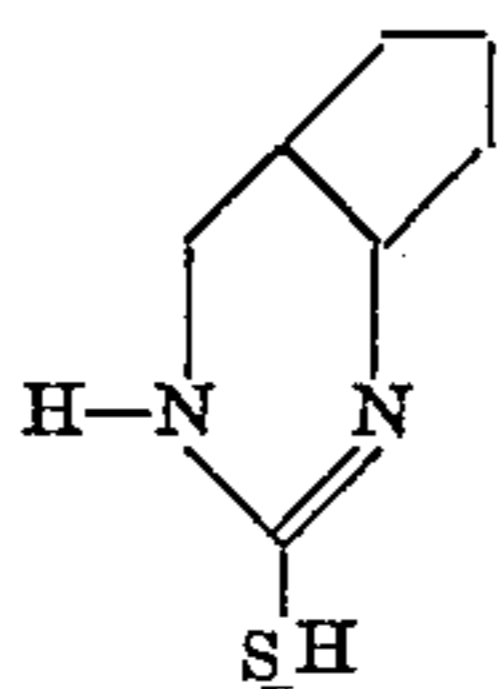


wherein Z<sub>1</sub> is an alicyclic, heterocyclic, or aryleno ring system in ortho-fused, ortho- and peri-fused, or bridged relationship with said hydroypyrimidine group; and R is hydrogen or a ring atom of Z<sub>1</sub>.

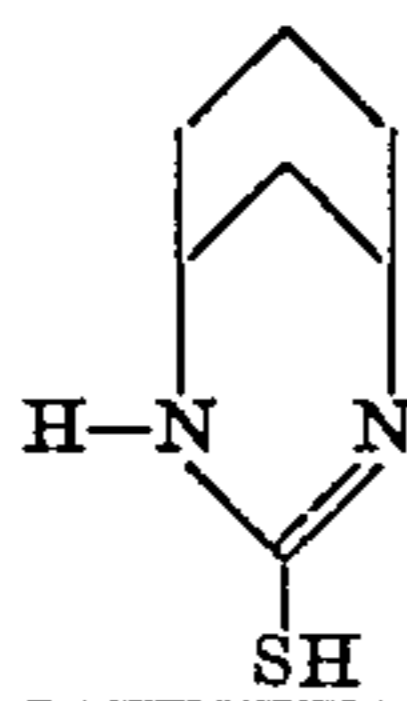
3. A process as defined in claim 2 wherein Z<sub>1</sub> comprises 3 to 10 ring atoms selected from the group consisting of C, N, S and O.

4. A process as defined in claim 1 wherein Z<sub>1</sub> is a heterocyclic or alicyclic ring system having 5 or 6 ring atoms.

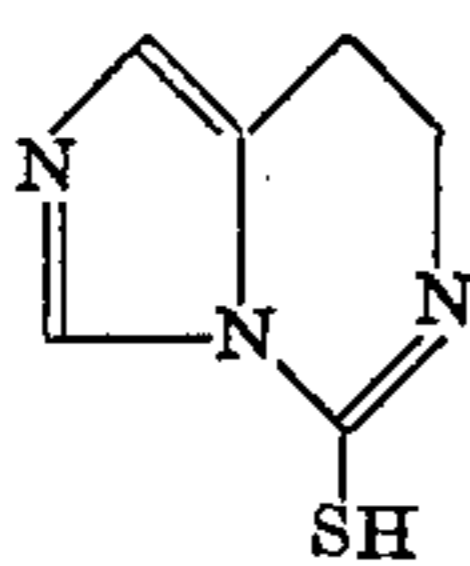
5. A process as defined in claim 4 wherein said compound is:



(cis or trans) 4,5-cyclopentatetrahydropyrimidine-2-thiol  
or,



4,6-cyclohexatetrahydropyrimidine-2-thiol  
or,



Imidazo [1,5-c] tetrahydropyrimidine-2'-thiol

6. 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.

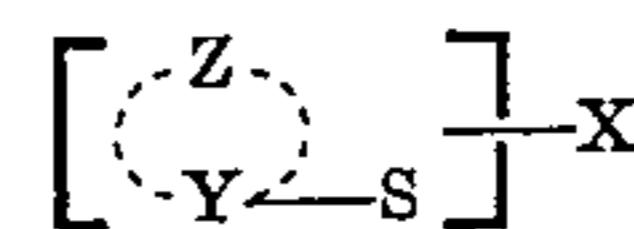
7. A process of forming a multicolored image by diffusion transfer comprising:

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;

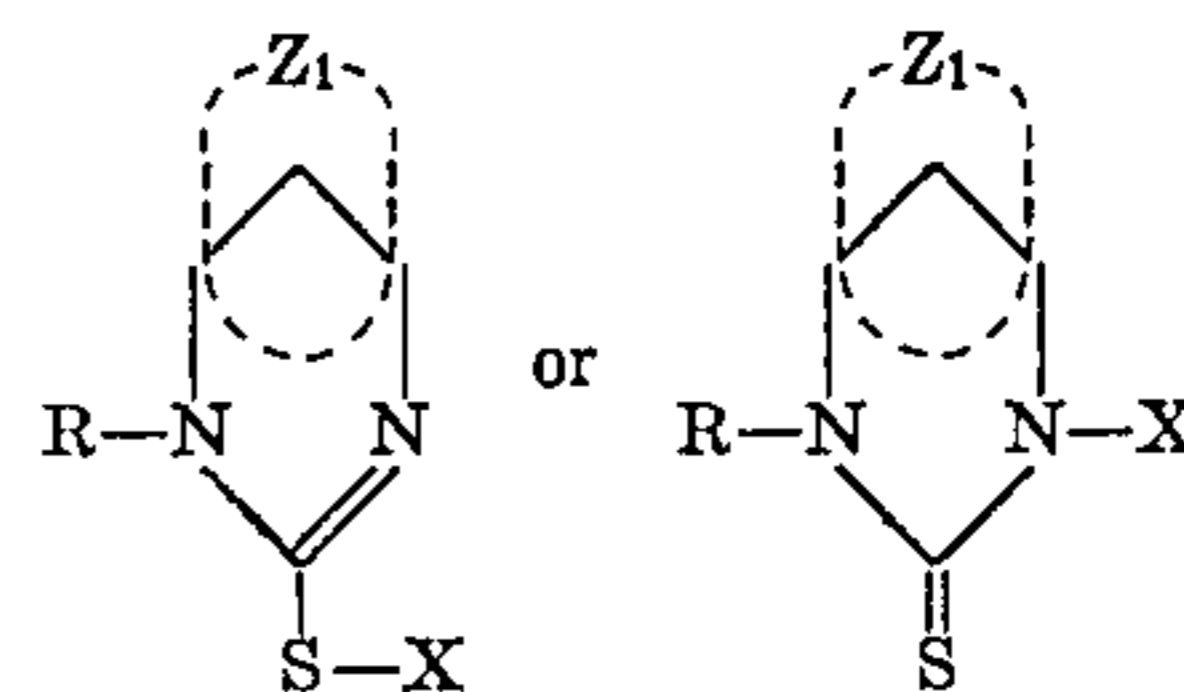
c. continuing said development of exposed silver halide for a predetermined period, said predetermined development period being sufficiently long to form an imagewise distribution of diffusible unoxidized dye developer in undeveloped areas of each of said silver halide emulsion layers as a function of 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:



wherein Y is a hydroypyrimidine group, Z is a ring system attached to said hydroypyrimidine group, and X is hydrogen or a group replaceable by hydrogen in an hydrolysis reaction with said aqueous alkaline solution; said X being bonded to said compound through the sulfur or a nitrogen of said hydroypyrimidine group with the unsatisfied valence on said sulfur or said nitrogen being satisfied by the formation of a double bond.

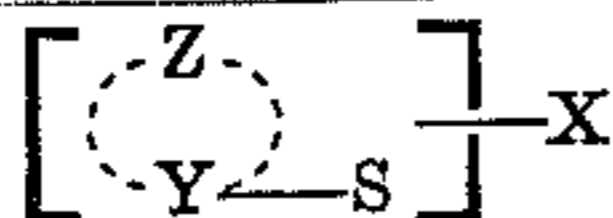
8. A process as defined in claim 7 wherein said compound is represented by:



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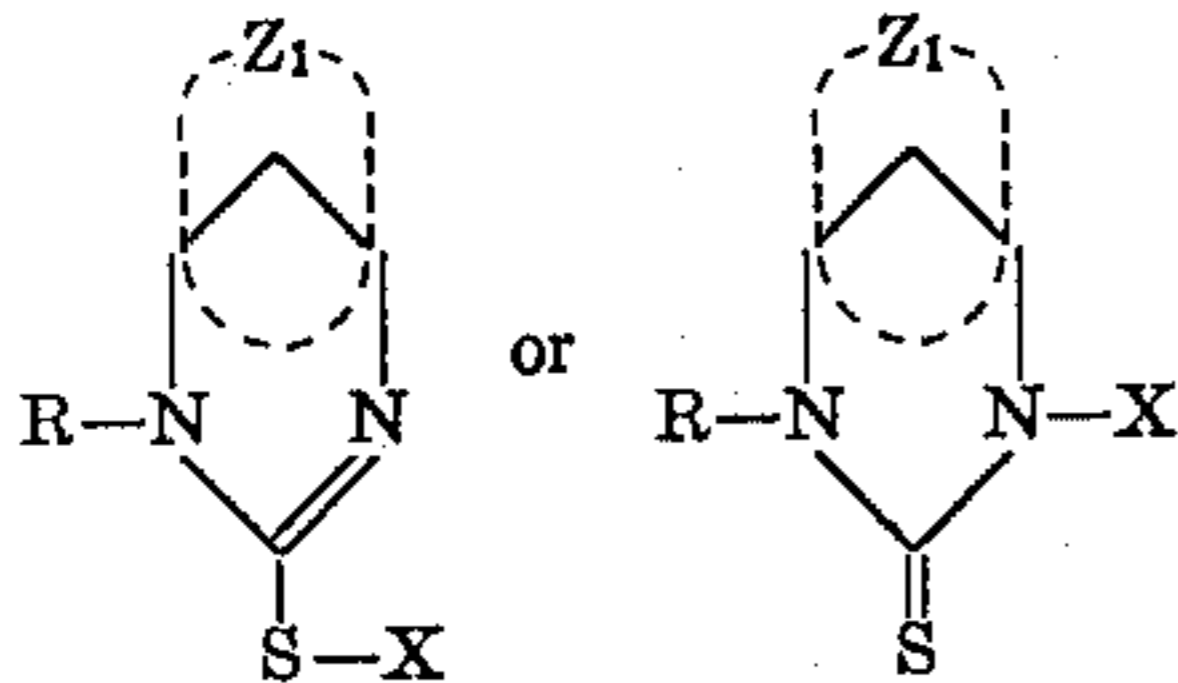
wherein  $Z_1$  is an alicyclic, heterocyclic, or arylene ring system in ortho-fused, ortho- and peri-fused or bridged relationship with said hydroypyrimidine group; R is hydrogen or a ring atom of  $Z_1$  and X is hydrogen or a group hydrolyzable by said aqueous alkaline processing composition at a temperature dependent rate to provide for the restraining of further development of exposed silver halide after said predetermined development period.

9. A photographic film unit comprising a support carrying on one surface at least two selectively sensitized silver halide layers, each having a dye of predetermined color associated therewith, which dye is a silver halide developing agent, said film unit including a compound of the formula:



wherein Y is a hydroypyrimidine group, Z is a ring system attached to said hydroypyrimidine group and X is hydrogen or a group replaceable by hydrogen in an hydrolysis reaction with alkali; said X being bonded to said compound through the sulfur or a nitrogen of said hydroypyrimidine group with the unsatisfied valence on said sulfur or nitrogen being satisfied by the formation of a double bond.

10. The product of claim 9 wherein said compound is represented by:

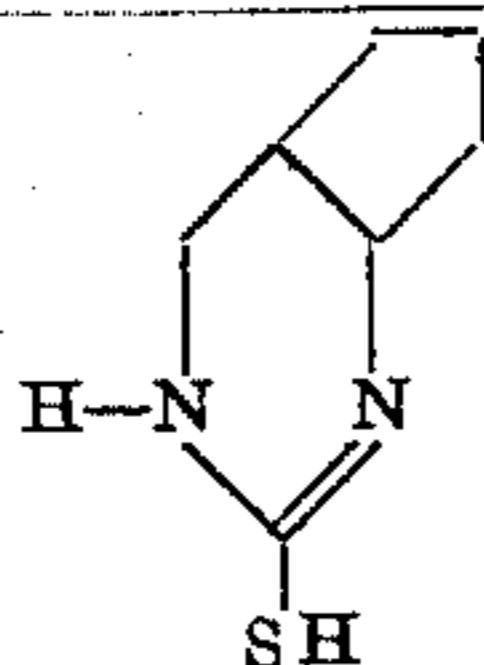


wherein  $Z_1$  is an alicyclic, heterocyclic, or arylene ring system in ortho-fused, ortho- and peri-fused or bridged relationship with said hydroypyrimidine group, and R is hydrogen or a ring atom of  $Z_1$ .

11. The product of claim 10 wherein  $Z_1$  comprises 3 to 10 ring atoms selected from the group consisting of C, N, S and O.

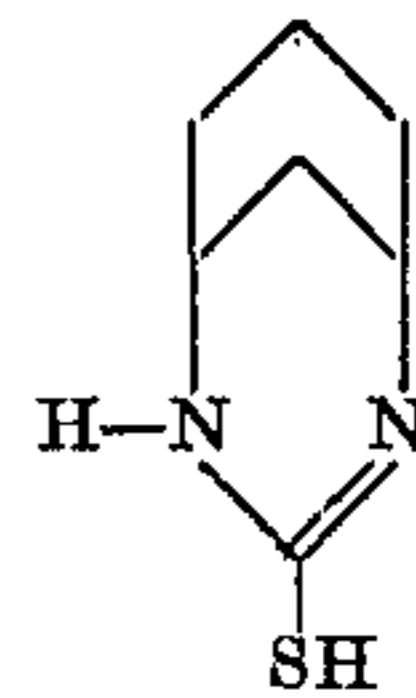
12. The product of claim 11 wherein  $Z_1$  is a heterocyclic or alicyclic ring system having 5 or 6 ring atoms.

13. The product of claim 12 wherein said compound is

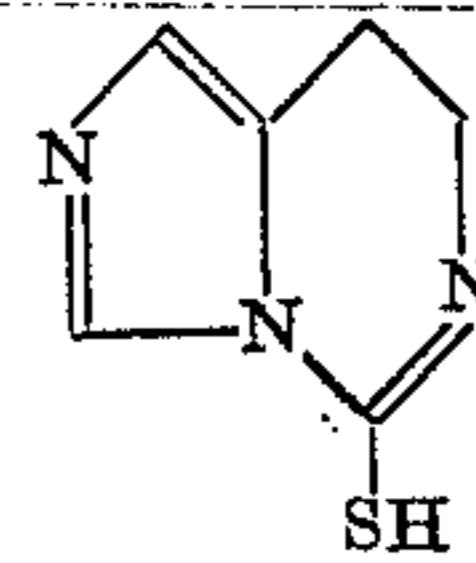


(cis or trans) 4,5-cyclopentatetrahydropyrimidine-2-thiol  
or,

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4,6-cyclohexatetrahydropyrimidine-2-thiol  
or,



Imidazo [1,5-c] tetrahydropyrimidine-2'-thiol

14. The product of claim 9 which includes a diffusion transfer image-receiving element fixed to at least one edge of said photosensitive element.

15. The product of claim 14 wherein said compound is disposed in said image-receiving element and X is hydrogen.

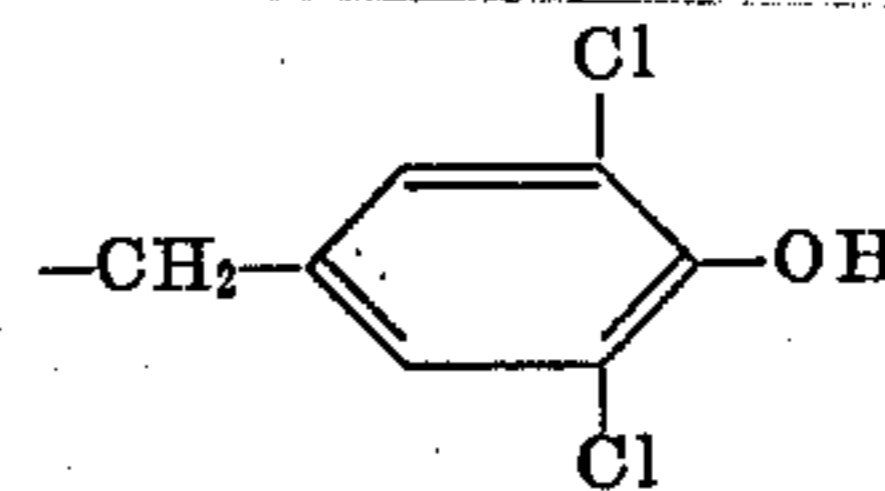
16. The product of claim 14 which includes a rupturable container retaining an aqueous alkaline processing composition fixed to one edge of said photosensitive and said image-receiving elements and adapted upon rupturing to distribute its contents intermediate said photosensitive element and said image-receiving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

17. The product of claim 16 wherein said compound is disposed in said aqueous alkaline processing composition and X is hydrogen.

18. The product of claim 9 wherein said photosensitive 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.

19. The product of claim 18 wherein said compound is disposed in at least one of said photosensitive silver halide emulsion layers and X is a group hydrolyzable by alkali.

20. The product of claim 19 wherein X is:



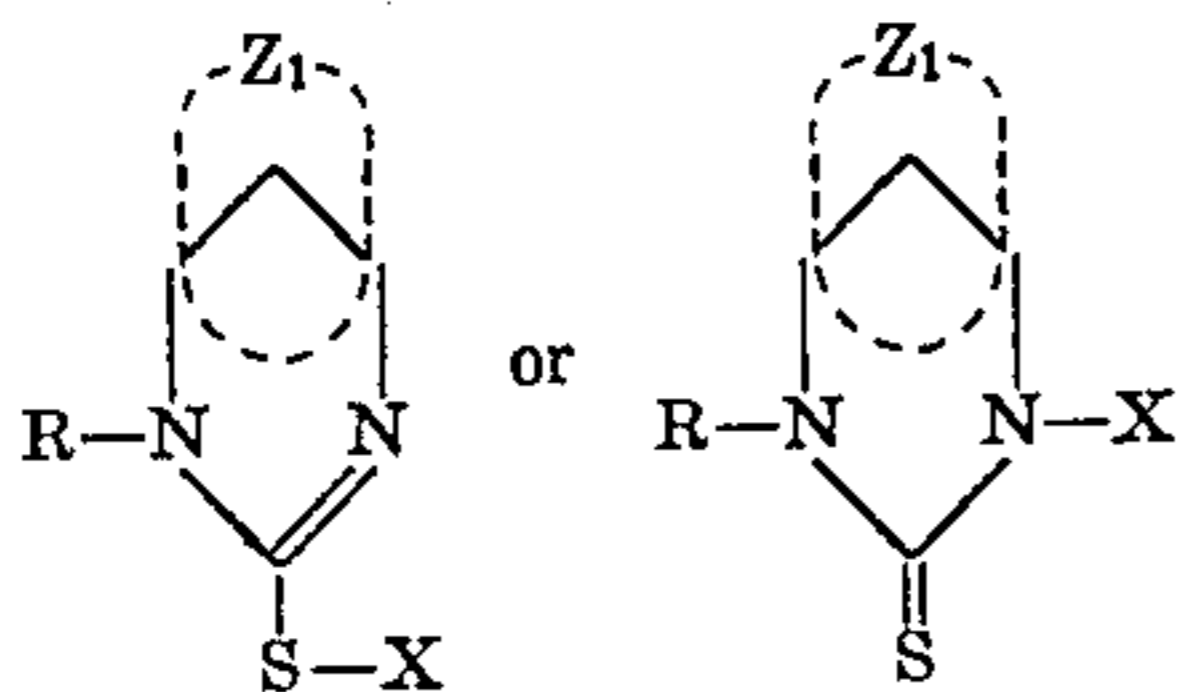
21. An image-receiving element for use in color diffusion transfer processes comprising a support carrying an image-receiving layer, a layer on said support containing a compound of the formula:



wherein Y is a hydroypyrimidine group, Z is a ring system attached to said hydroypyrimidine group, and X is hydrogen or a group replaceable by hydrogen in an hydrolysis reaction with alkali, said X being bonded to said compound through the sulfur or a nitrogen of said hydroypyrimidine group with the unsatisfied valence on said sulfur or said nitrogen being satisfied by the formation of a double bond.

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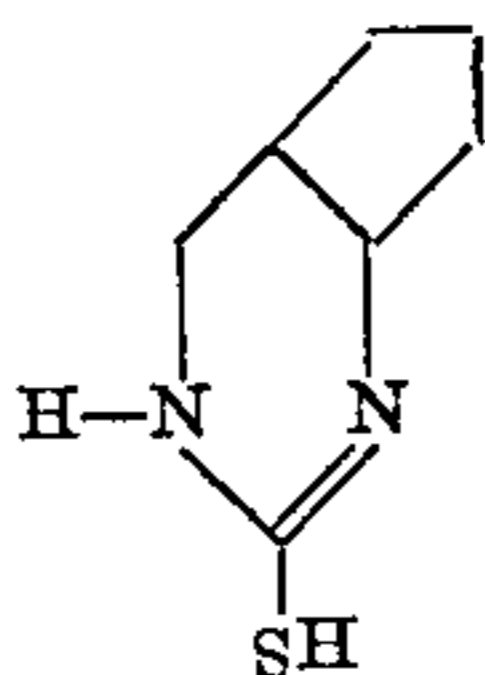
22. The product of claim 21 wherein said compound is represented by:



wherein  $Z_1$  is an alicyclic, heterocyclic, or arylene ring system in ortho-fused, ortho- and peri-fused or bridged relationship with said hydroxypyrimidine group, and R is hydrogen or a ring atom of  $Z_1$ .

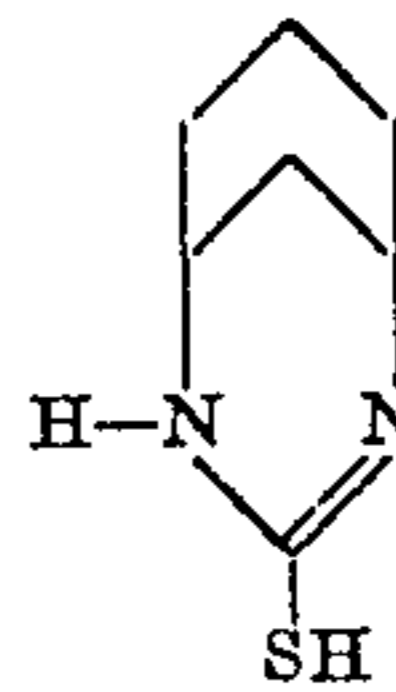
23. The product of claim 22 wherein  $Z_1$  is a heterocyclic or alicyclic ring system having 5 or 6 ring atoms.

24. The product of claim 22 wherein said compound is:



(cis or trans) 4,5-cyclopentatetrahydropyrimidine-2-thiol or,

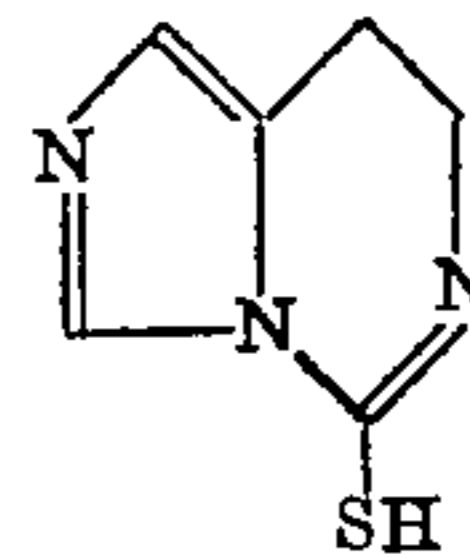
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4,6-cyclohexatetrahydropyrimidine-2-thiol or,

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imidazo[1,5-c]tetrahydropyrimidine-2'-thiol or tautomeric equivalents thereof.

25. The product of claim 21 wherein said compound is disposed in said image-receiving layer.

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26. The product of claim 21 wherein said compound is disposed in a layer between said image-receiving layer and said support.

27. The product of claim 26 wherein said layer containing said compound is an alkaline solution permeable polymeric spacer layer positioned between said image-receiving layer and a polymeric acid neutralizing layer.

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28. The product of claim 27 wherein said spacer layer has decreasing permeability to alkaline solution with increasing temperature.

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