

March 6, 1973

R. F. W. CIECIUCH ET AL

3,719,489

NOVEL PHOTOGRAPHIC PROCESSES AND PRODUCTS

Filed June 21, 1971

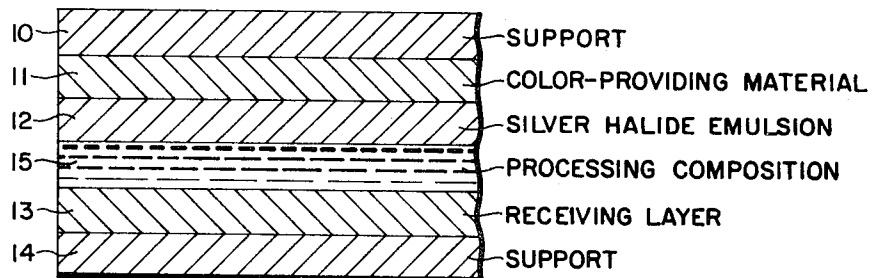


FIG. 1

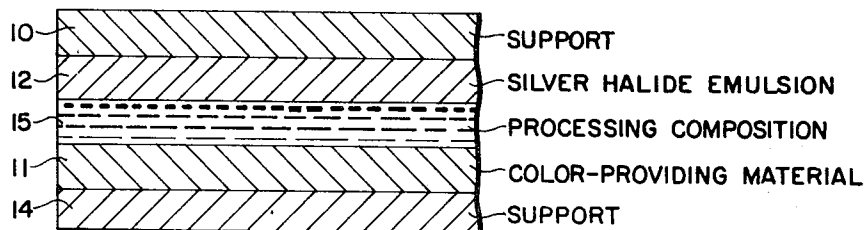


FIG. 2

INVENTORS
RONALD F. W. CIECIUCH
ROBERTA R. LUHOWY
FRANK A. MENEGHINI
and
HOWARD G. ROGERS
BY
Brown and Mikulka
ATTORNEYS

1

3,719,489

NOVEL PHOTOGRAPHIC PROCESSES AND PRODUCTS

Ronald F. W. Ciecuch, Boston, Roberta R. Luhowy,
Watertown, Frank A. Meneghini, Belmont, and Howard
G. Rogers, Weston, Mass., assignors to Polaroid Cor-
poration, Cambridge, Mass.

Filed June 21, 1971, Ser. No. 155,123

Int. Cl. G03c 5/54, 1/40

U.S. Cl. 96—29 D

48 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to photographic processes employing photographically inert compounds which are stable in the photographic processing composition but capable of undergoing cleavage in the presence of an image-wise distribution of silver ions and/or soluble silver complex containing silver ions made available as a function of development to liberate a reagent in an imagewise distribution corresponding to that of said silver ion and/or said complex. In one embodiment, the photographically inert compound is substantially non-diffusible in the photographic processing composition and the reagent released therefrom as a function of development is diffusible in the processing composition. In another embodiment, the diffusible reagent released is a diffusible dye. Compounds particularly useful for liberating a reagent are 1,3-sulphur-nitrogen compounds, e.g., thiazolidines, and their vinyl and phenylene analogs.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to photographic processes for providing an imagewise distribution of a reagent, such as a photographically active reagent or a dye and particularly to processes for the formation of color images and to photographic products useful therein.

(2) Description of the prior art

Diffusion transfer photographic processes are now well-known. In preparing silver images according to such processes, an exposed photosensitive element comprising a light-sensitive silver halide emulsion is developed by treating the emulsion with a processing composition comprising an aqueous alkaline solution of a silver halide developing agent and a silver halide solvent. The developable silver halide of the emulsion is reduced to image silver by the developing agent while the silver halide solvent forms an imagewise distribution of a soluble silver complex with the undeveloped silver halide. This imagewise distribution of soluble silver complex is, at least in part, transferred by imbibition to a superposed image-receiving layer where it is reduced to form a silver transfer image.

It has been proposed in U.S. Pat. No. 3,443,941 of Howard G. Rogers to utilize certain principles of the silver diffusion transfer art in the formation of color images. In particular, it has been proposed to utilize the properties of the imagewise distribution of silver ions in the soluble silver complex to control imagewise transfer of a

2

color-providing substance to a suitable receiving stratum to provide a color image thereon.

Included among the color-providing materials disclosed as useful in such a system are (A) normally diffusible color-providing materials that are rendered non-diffusible upon reaction with silver ions and/or a soluble silver complex containing the same and (B) normally non-diffusible color-providing materials that are rendered diffusible upon reaction with silver ions and/or a soluble silver complex containing the same. Such color-providing materials include complete dyes or dye intermediates which form a complete dye upon subsequent reaction.

It is known that various chemical reactions are assisted by silver ion including reactions involving cleavage of a compound into one or more fragments. One example of a cleavage reaction that is assisted by silver ion is the silver ion-accelerated hydrolysis of mono thio analogs of tetrahydropyranyl ethers as disclosed in U.S. Pat. No. 3,068,099. Other examples of such reactions are the silver ion-accelerated cleavage of disulfides and of thioesters as discussed by L. F. Lindoy, *Coord. Chem. Rev.*, 4 (1969), 41-71 and the silver ion-accelerated elimination of mercaptan in the preparation of carbodiimides, isocyanates and isothiocyanates as discussed by A. F. Ferris et al., *J. Org. Chem.*, 28, 71-74 (1968). Further examples of such reactions are the selective removal of certain S-protecting groups from cysteines using silver ion as discussed by L. Zervas et al., *J. Am. Chem. Soc.*, 84, 3887-3891 (1962) and the silver ion-accelerated hydrolysis of silyl acetylenic compounds as reported in *Rec. trav. chim. des Pays-Bas* 86, 1138 (1967).

Besides the above reactions, it is also known that heavy metal ions, particularly mercuric and silver ions, accelerate cleavage of certain cyclic and linear 1,3-sulfur-nitrogen compounds, i.e., compounds having a sulfur atom and a nitrogen atom, each linked by a single bond to a common carbon atom. Such compounds undergo cleavage in a stepwise fashion between the S atom and the C atom common to the S and N atoms and also between the N atom and the common C atom. As discussed in *The Chemistry of Penicillins*, National Academy of Sciences, Washington, D.C., pages 926 and 927, the cleavage of thiazolidines by mercury salts has become standard practice in the inactivation of penicillin compounds. It is also mentioned in this reference that certain thiazolidine compounds undergo cleavage in the presence of silver ion. The cleavage of benzothiazolines accelerated by the presence of various metal ions including silver ion is reported in the aforementioned Lindoy reference, while the cleavage of certain linear compounds containing the sulfur-carbon-nitrogen configuration assisted by mercuric and silver ions is reported by T. Yamaguichi et al., *Bulletin of the Chemical Society of Japan*, 40, 1952-1954 (1967).

Though certain thiazolidine compounds have been used in photographic processes, for example, to improve ratios of speed to fog as described in U.S. Pat. 3,565,625 such compounds have not been used in a photographic system to provide an imagewise distribution of a reagent.

SUMMARY OF THE INVENTION

According to the present invention, it has been found that cleavage reactions assisted by silver ion may be used

3

in photographic processes to liberate a reagent in an image-wise fashion. For example, it has been found that compounds capable of undergoing cleavage in the presence of ionic silver such as those mentioned above, may be used to release a reagent as a smaller molecule in an imagewise distribution corresponding to the imagewise distribution of silver ions made available as a function of development of an exposed silver halide layer.

It is, therefore, the primary object of the present invention to provide processes employing photographically inert compounds which are stable in the photographic processing solution but capable of undergoing cleavage in the presence of the imagewise distribution of silver ions made available in the undeveloped and partially developed areas of a silver halide emulsion during processing of the emulsion to liberate a reagent as a smaller molecule, preferably, a photographically active reagent or a dye in an imagewise distribution corresponding to said imagewise distribution of silver ions.

It is another object of the present invention to provide processes employing photographically inert compounds to release an imagewise distribution of an aldehyde.

It is another object of the present invention to provide processes for preparing color images by using, as the photographically inert compounds, color-providing compounds which are stable and substantially non-diffusible in the photographic processing solution but capable of undergoing cleavage in the presence of the imagewise distribution of silver ions made available in the undeveloped and partially developed areas of a silver halide emulsion during processing thereof to liberate a more mobile and diffusible color-producing moiety in an imagewise distribution corresponding to said imagewise distribution of silver ions.

It is a further object of the present invention to provide photographic products useful in processes for releasing a photographic reagent which contain photographically inert compounds stable in aqueous media but capable of undergoing cleavage in the presence of silver ions made available in an imagewise distribution during processing of a silver halide emulsion to split off a photographic reagent as a smaller molecule in an imagewise distribution corresponding to said imagewise distribution of silver ions.

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

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

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is an enlarged, diagrammatic, fragmentary sectional view illustrating the preparation of a color image according to one aspect of this invention; and

FIG. 2 is a similar view illustrating another aspect of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As noted previously, the present invention is concerned with utilizing the imagewise distribution of silver ions and/or a soluble silver complex containing the same made available as a function of development to effect cleavage of a photographically inert compound which may be diffusible or non-diffusible in the photographic processing composition to release a reagent as a smaller molecule in an imagewise distribution corresponding to the imagewise

4

distribution of said silver ions and/or said soluble silver complex, which reagent also may be diffusible or substantially non-diffusible in the processing composition.

According to one system of the present invention, a photographic process for producing an imagewise distribution of a reagent is provided which includes the steps of developing a photosensitive element comprising an exposed silver halide emulsion with an aqueous processing composition; forming in undeveloped areas an imagewise distribution of silver ions; contacting said imagewise distribution of silver ions with a photographically inert compound capable of undergoing cleavage in the presence of silver ions to liberate a reagent; and forming as a function of contacting said imagewise distribution of silver ions with said inert compound, a corresponding imagewise distribution of said reagent.

In forming color images according to this system, a relatively non-diffusible color-providing compound may be present, for example, in a layer associated with a light-sensitive silver halide emulsion which, after being exposed, is developed with an aqueous alkaline processing solution including a silver halide developing agent and a silver halide solvent. The imagewise distribution of silver ions such as contained in the soluble silver complex made available during processing of the emulsion migrates to the associated color-providing material which undergoes cleavage in the presence of the complex to provide an imagewise distribution of a more diffusible color-providing moiety. The subsequent formation of a color image is the result of the differential in diffusibility between the parent material and liberated color-providing moiety whereby the imagewise distribution of the more diffusible color-providing moiety released in undeveloped and partially developed areas is free to transfer. For example, where the imagewise distribution of diffusible color-providing moiety is a complete dye, it may be simply washed away to leave an image associated with the emulsion, or it may be transferred by imbibition to an image-receiving layer, e.g., a dyeable stratum of the character heretofore known in the art to provide a color transfer image thereon.

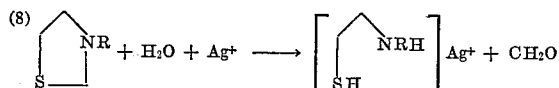
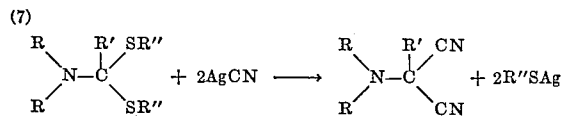
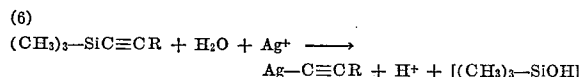
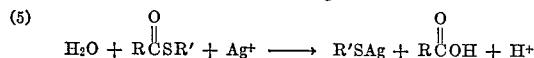
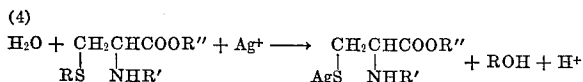
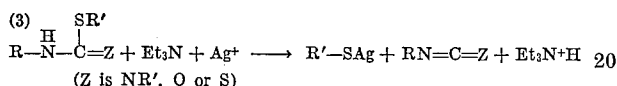
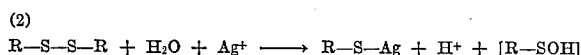
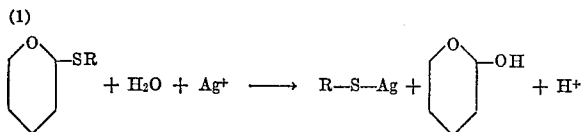
Besides a color-providing moiety, the smaller molecule liberated from the parent compound upon cleavage may be any one of various reagents and preferably is photographically active, such as, a gelatin hardener, a development restrainer, toning agent or antifoggant. Depending upon the reagent it is intended to liberate, the appropriate moiety may be substituted on the parent compound, or the parent compound itself upon cleavage may provide a fragment possessing the desired photographic activity. The respective mobility characteristics of the parent compound and of the liberated reagent may be substantially the same, or they may be different as appropriate for a given photographic process.

A differential in diffusibility between the parent compound and the reagent liberated therefrom may be achieved in various ways, for example, by using a normally immobile and non-diffusible parent compound which upon cleavage releases a diffusible reagent, or conversely, by using a normally mobile parent compound which upon cleavage releases a reagent that is substantially non-diffusible.

To be useful in the present invention, the parent compound should be photographically inert and stable in the processing solution, i.e., should remain intact in the processing composition in the absence of silver ion at least during the processing interval, but should be capable of undergoing cleavage in the presence of the imagewise distribution of silver ions and/or the imagewise distribution of soluble silver complex containing silver ions made available as a function of development to release a reagent, such as, a dye or a photographically active reagent. Its rate of cleavage in the presence of silver ion, however, should be such that an imagewise distribution of reagent is obtained that corresponds to the imagewise dis-

tribution of silver ions or soluble silver complex formed in the partially exposed and unexposed areas of the emulsion. If the rate of cleavage is excessive, reagent may be released to some extent in the exposed areas.

Illustrated below are examples of compounds which may be used to release a reagent, such as, a color-providing moiety and the silver accelerated cleavage reactions which they undergo.



For use in the present invention, the above compounds may be appropriately substituted with the desired color-providing or other moiety it is desired to liberate and with other group(s) as may be necessary to achieve a differential in diffusibility between the uncleaved parent compound and the reagent released therefrom. Where such a differential in diffusibility is necessary or desired for the particular photographic process, the parent compound may be substituted with an immobilizing group or "anchor," that renders the compound substantially non-diffusible in the processing solution, or, rather than a single immobilizing group, the parent compound may be substituted with two or more groups which together preclude migration of the compound from its position in the photographic element. When several groups together are used to immobilize the compound, one or more of the groups may be on the fragment to be released as a diffusible reagent so long as the group(s) does not reduce to any appreciable extent the mobility and diffusibility of the fragment subsequent to cleavage.

It will be appreciated that where a single immobilizing group is used to anchor the parent compound, its position on the compound should be such that upon cleavage, it will be on a fragment different from the fragment to be released as the diffusible reagent. Depending upon the photographic process used and upon the location of the parent compound in the photographic element, it may be preferable to position the immobilizing group on that portion of the parent compound that ultimately forms a complex with the silver ion. For example, when producing positive transfer images using diffusion transfer techniques, it is preferred to anchor the fragment that will complex the silver ion in the photosensitive element to

avoid possible staining of the color images formed in the image-receiving sheet.

The selection of a particular immobilizing group(s) for anchoring the parent compound will depend primarily on whether it is desired to employ only one immobilizing group or to employ two or more groups which together are capable of anchoring the compound. Where two or more groups are employed to immobilize the compound, lower alkyl groups, butyl or hexyl, for example, may be used to achieve the requisite differential in diffusibility between the parent compound and the reagent released. Where only one group is used to immobilize the compound, it is more effective to employ, for example, a higher alkyl radical such as octyl, decyl, dodecyl, stearyl, and oleyl or a carbocyclic or heterocyclic ring having six members or more. Where cyclic compounds are employed the carbocyclic or heterocyclic immobilizing group may be bonded to a single atom or to adjacent atoms of the parent molecule and may be bonded to a single atom by a valence or ionic bond or through a spiro union.

As the "color-providing moiety" in forming color images according to the present invention, there may be used a complete dye or a dye intermediate capable of yielding a complete dye upon subsequent reaction, for example, upon reaction with a suitable coupler to form a complete dye. The coupling reaction may take place directly in the image-receiving layer, or it may take place in the emulsion layer or in the layer of processing composition after which the complete dye formed diffuses to the image-receiving layer.

Complete dyes which may be used as the color-providing moiety may comprise any of the general classes of dyes heretofore known in the art, for example, nitro, azo, thiazole, di- and triphenyl methane, cyanine and anthraquinone dyes. Dye intermediates include any molecule which when released is capable of forming a dye upon reaction with another molecule. For example, a dye intermediate may be released from a sulfur-nitrogen compound, e.g. a thiazolidine, which intermediate in turn reacts with another molecule to produce a complete dye. Photographic processes and products utilizing dye-forming systems wherein an imagewise distribution of a complete dye is produced by the reaction of an aldehyde or ketone dye intermediate and a color-forming reagent comprises the subject matter of copending U.S. Pat. application Ser. No. 155,000 of Louis Locatelli, Jr., Frank A. Meneghini and Howard G. Rogers filed concurrently herewith.

The color-providing moiety, whether a complete dye or dye former, may be linked directly to an atom of the parent molecule by a valence or ionic bond or through a spiro union, or it may be linked indirectly to the parent molecule through an appropriate linking group either acyclic or cyclic. Typical linking groups include cycloalkyl, such as cyclohexyl; —CONH—; —alkylene—CONH—; arylene—CONH—; alkylene; and arylene wherein alkylene may be ethylene, propylene, butylene and arylene may be phenylene. The term color-providing moiety as used herein includes any linking group and the moiety may contain on the color-providing and/or linking portion various solubilizing substituents, e.g., sulfo, hydroxyl or carboxyl groups to adjust its solubility characteristics.

In addition to the above, useful dyes include those which are colorless or of a color other than that ultimately desired in a certain environment, such as at a particular pH level, but upon a change in environment, e.g., from acid to alkaline conditions, take on a color change. Color-providing materials of this nature include indicator dyes and leuco dyes. It is also contemplated that dyes may be employed which undergo a color shift or change in spectral absorption characteristics during or after processing. Such dyes may be referred to as "temporarily shifted" dyes. The temporary shift may, for example, be effected by acylation, the acyl group being removable by hydrolysis in the alkaline processing composition. It is also within the scope of the present invention to employ

7

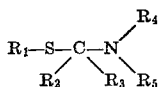
metal complexed or complexable dyes and to employ dyes, the non-complexed forms of which are substantially colorless, but which, when complexed during or subsequent to image formation, are of the desired color.

Though some of the compounds enumerated above may cleave in the absence of silver ion under extreme conditions, such as strong heating, they are sufficiently stable under neutral, acid and alkaline conditions at ambient temperatures to remain intact under the processing conditions encountered in conventional and diffusion transfer photography until silver ion becomes available as a function of development. However, the reactivities of the various compounds toward silver ion may vary and thus, some compounds may cleave more rapidly in the presence of silver ion than others. Accordingly, it will be appreciated that the particular compound selected should have the cleavage rate necessary for obtaining an image-wise distribution of the desired reagent, such as a color-providing moiety, under the particular processing conditions employed. In diffusion transfer processes, it is desirable that the parent compound cleave in the presence of silver ion and/or soluble silver complex containing silver ion to release a diffusible color-providing moiety such that a transfer image is obtained within a reasonable processing time.

Of the aforementioned classes of compounds, the 1,3-sulfur-nitrogen compounds have been found especially satisfactory. As discussed above, these compounds may be linear, or they may be cyclic in structure with either or both of the S and N atoms being constituents of the ring which should contain at least four atoms. The compounds may be saturated or unsaturated provided the S and N atoms each are bonded to the common, i.e., intermediate, carbon atom by a single bond.

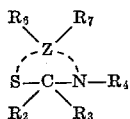
Among the 1,3-sulfur-nitrogen compounds that may be used in the present invention are those represented in the following formulae:

(I)



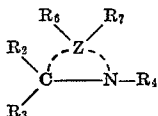
wherein R_1 and R_5 each are a monovalent organic radical and R_2 , R_3 and R_4 each are hydrogen or a monovalent organic radical;

(II)



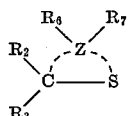
wherein R_2 , R_3 and R_4 have the same meaning as in Formula I above; R_5 and R_7 on the same or different atoms each are hydrogen or a monovalent organic radical and taken together represent a substituted or unsubstituted carbocyclic or heterocyclic ring; Z represents the atoms, preferably carbon atoms, necessary to complete a ring system having up to 20 members;

(III)



wherein R_2 , R_3 , R_4 , R_6 , R_7 and Z have the same meaning as in Formula II above; and

(IV)



wherein R_2 , R_3 , R_6 , R_7 and Z have the same meaning as in Formula II above.

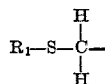
Examples of cyclic compounds which may be used in

8

the present invention are thiazolidines, tetrahydro-1,3-thiazines, benzothiazolines, benzimidazolines, tetrahydrothiophenes, s-trithianes, 1,3-dithianes, tetrahydrothiopyrans, 1,3-dithiolanes, pyrrolidines, imidazolidines, hexahydro-s-triazines, piperazines, piperidines, and morpholines. Where the ring contains a nitrogen atom but no sulfur atom or where the ring contains a sulfur atom but no nitrogen atom, the compound will be appropriately substituted with a sulfur or nitrogen-containing group to obtain the 1,3-sulfur-nitrogen configuration. For example, in Formula IV above, the sulfur-nitrogen configuration may be obtained by selecting as the R_2 or R_3 group, a monovalent organic radical



or $-N=R$ wherein R_4 and R_5 have the same meaning given above and R is a divalent organic radical. Likewise, the desired configuration may be obtained with compounds of Formula III by selecting as R_4 , a monovalent organic radical



or by selecting as the R_2 or R_3 group, a monovalent organic radical $-S-R_1$ wherein R_1 has the same meaning given above. It will be appreciated that the compound may contain more than one sulfur-nitrogen configuration if it is desired to release several smaller molecules. As an illustration, the compound of Formula II may be substituted with a cyclic 1,3-sulfur-nitrogen substituent in the 2-position through a linking group, such as a methylene group, to give, e.g., a bis compound.

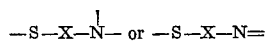
It will be understood that at least one of the substituents of the compounds illustrated in the above formulae will be the color-providing or other moiety it is desired to release as the reagent from the parent compound, which moiety may be released as an amine, aldehyde, ketone, etc., depending upon the position of the substituent on the parent. Also, one or more of the R substituents may be selected to immobilize the compound in processes where it is desired to render the uncleaved parent compound substantially non-diffusible in the processing solution, or one or more of the R substituents may be selected to enhance the solubility of the compound in processes where it is desired to render the parent compound diffusible in the processing solution. Suitable immobilizing and solubilizing groups have been enumerated above. The positioning of these groups on the parent compound will depend upon the diffusibility characteristics desired for the parent compound and for the smaller molecule released upon cleavage in a given process. As noted previously, the parent and the reagent liberated therefrom may exhibit the same or different diffusibility characteristics in the photographic processing solution. Both may be non-diffusible, both may be diffusible or one may be diffusible and the other non-diffusible. In addition to the immobilizing and/or solubilizing groups, it will be appreciated that R groups may comprise other substituents which do not interfere with the use of the compound to liberate a selected reagent, such as, a color-providing moiety or a photographically active reagent.

Typical of the substituents that may be used in the above formulae include carboxy, sulfo, nitro, hydroxy, halo, e.g., chloro and bromo, cyano and hydrocarbon radicals including aliphatic, cycloaliphatic, aromatic and heterocyclic radicals. The radicals may possess ethylenic or acetylenic unsaturation, and the carbon chains may be interrupted by heteroatoms or heteroatom groups, such as S, O, N, SO, NH and so forth. Also, the radicals may contain substituents, e.g., phenyl, alkyl, alkyl ether,

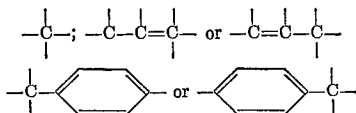
aryl ether, carbalkoxy, carboxy, hydroxy, sulfo, halo, cyano, nitro, and alkylamino.

Examples of suitable radicals are substituted and unsubstituted alkyl groups, such as methyl, ethyl, octyl, dodecyl; substituted and unsubstituted cycloalkyl radicals, such as, cyclohexyl, cyclopentyl, cyclooctyl; substituted and unsubstituted alkenyl groups, such as, vinyl, allyl, butenyl, decenyl, octadienyl, hexatrienyl; substituted and unsubstituted cycloalkenyl groups, such as, cyclopentenyl, cycloheptenyl, cyclohexadienyl; substituted and unsubstituted alkynyl groups, such as, ethynyl, hexynyl, octynyl; substituted and unsubstituted aryl radicals, such as, phenyl, tolyl, benzyl and naphthyl; and substituted and unsubstituted heterocyclic groups, such as those having a 4-, 5- or 6-membered ring and containing O, N, S, and combinations thereof derived from, e.g., pyrrole, pyrazole, oxazole, thiazole, imidazole, pyrimidine, piperidine, piperazine, thiophene, pyrrolidine, azetidine. Where a single hydrocarbon moiety is used as the immobilizing group, higher acyl radicals such as oleoyl and stearoyl groups have been found useful.

It will be appreciated by those skilled in the art that the vinyl and phenylene analogs of the above sulfur-nitrogen compounds, including those exemplified in Formulae I-IV, are useful in the present invention. The 1,3-sulfur-nitrogen compounds and their vinyl and phenylene analogs may be defined as containing the group,



wherein X is

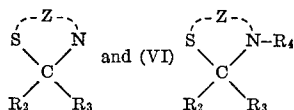


As in the compounds illustrated in Formulae I-IV, the above analogs may be substituted with an immobilizing group and/or a solubilizing group and with a moiety it is desired to release as the reagent, e.g., a color-providing moiety.

Compounds found especially suitable for forming images by diffusion transfer are certain cyclic sulfur-nitrogen compounds where both the S and N atoms are included in the ring, particularly thiazolidines and benzothiazolines. These compounds exhibit the desired stability in the processing composition, and in the presence of silver ions undergo cleavage at the desired rate to release a reagent, e.g., a color-providing moiety in an imagewise distribution corresponding to that of the silver ions and/or soluble silver complex containing the same made available in the undeveloped areas of the emulsion. Besides exhibiting these characteristics under the highly alkaline conditions ordinarily employed in diffusion transfer processes, they may be employed under neutral and acid conditions as well. Also, it will be appreciated that these and other 1,3-sulfur-nitrogen compounds, both cyclic and linear, and their vinyl and phenylene analogs may be used to liberate an aldehyde in an imagewise fashion to produce relief or transfer images by utilizing the hardening effect of aldehydes on gelatin and similar emulsion binders.

Illustrative of the aforementioned cyclic compounds particularly useful in forming dye images are those represented in the following Formulae V and VI, and preferably VI.

(V)



wherein R₂, R₃, R₄ and Z have the same meaning given

above. It will be appreciated that the ring system represented by Z may be substituted if desired as in the illustrative compounds of Formulae I to IV. When using these compounds in the production of dye images, the color-providing moiety is preferably but not necessarily substituted on the carbon atom common to the sulfur and nitrogen atoms. If the color providing moiety selected as the organic radical R₂ and/or R₃ is a diffusible dye then R₄ and/or a group or groups substituted on the ring Z should be capable of rendering the parent compound substantially immobile in the photographic processing solution. Alternatively, if the color-providing moiety is a non-diffusible dye, the R₄ and/or a group or groups substituted on Z should be capable of rendering the parent compound diffusible in the processing solution.

In the present invention, the parent compound may be present initially in the photosensitive element in a layer or layers other than the layer containing the light-sensitive silver halide emulsion. For example, it may be in a layer over the emulsion, in a layer between the support and the emulsion, or in two layers, one on either side of the emulsion. It may be present in the photosensitive layer itself if the compound is inert, that is photographically innocuous in that it does not adversely affect or impair image formation to any appreciable or unacceptable extent. If not photographically innocuous, the compound may be modified in a manner which does not interfere with the development process in any way, but which deactivates the compound so that it does not affect adversely the light-sensitive emulsion. Preferably, the parent compound is contained in a layer separate from the silver halide emulsion. If desired, it may be separated from the emulsion layer by one or more spacer layers, or it may be contained in a layer associated with the image-receiving layer in processes such as diffusion transfer where receiving elements are employed.

As mentioned previously, the processing compositions customarily employed in silver diffusion transfer processes comprise an aqueous alkaline solution of a silver halide solvent and a silver halide developing agent. The named ingredients may be present initially in the aqueous medium or may be present initially elsewhere in the photographic product, for example, in the emulsion and/or image-receiving and/or spacer layers as heretofore suggested in the art. When such ingredients are present initially in the film unit, the processing composition is formed by contacting the product with a suitable aqueous medium to form a solution containing these ingredients. Though the use of a silver halide solvent is preferred in the processes of the present invention, it is not essential since cleavage may be assisted by the silver ion contained in the unexposed portions of the emulsion.

The alkali employed in the processing composition may be any of the alkaline materials heretofore used, such as sodium or potassium hydroxide. The silver halide solvent also may be any of the heretofore known materials, such as sodium or potassium thiosulfate, sodium thiocyanate and uracil. Also, a silver halide solvent precursor may be used, such as described in copending U.S. patent application Ser. No. 99,310 filed Dec. 17, 1970. The silver halide developing agent may be selected from those commonly employed, such as the diamino benzenes, e.g., paraphenylenediamine; aminophenols, e.g., methyl-p-aminophenol; and dihydroxybenzenes, e.g., hydroquinone. In addition to the aforementioned ingredients, the composition may contain antifoggants, preservatives, viscosity-imparting reagents, and other adjuncts as conventionally used in the art. It will be understood that the selection of the above materials is not critical to the practice of this invention.

In the accompanying drawings, FIG. 1 illustrates the processing of a photosensitive element to prepare a color transfer image in accordance with one embodiment of the present invention. As shown therein, an exposed photosensitive element including a support 10, a layer of color-

11

providing material 11 and a light-sensitive silver halide emulsion layer 12 is placed in superposition with a receiving element comprising an image-receiving layer, e.g., a dyeable stratum 13 and a support 14 therefor. A processing composition 15 is distributed between the two elements as they are brought into superposition. In exposed areas of emulsion layer 12, silver halide is reduced to image silver while an imagewise distribution of soluble silver complex is formed in terms of unexposed areas. This imagewise distribution is, at least in part, transferred by imbibition to layer 11 where it accelerates cleavage of the color-providing material to release a diffusible color-providing moiety, e.g. a dye, in areas corresponding to unexposed areas of emulsion layer 12. This, in turn, produces an imagewise distribution of the diffusible color-providing moiety, corresponding to unexposed areas of the emulsion layer, which is transferred to the receiving layer 13 to form a positive color transfer image.

Processing composition 15 may be applied to the emulsion layer by coating, dipping, spraying or any or all of the ingredients thereof may be confined initially in a frangible container such as disclosed in U.S. Pat. No. 2,543,181, the container being positioned in the film unit so as to be capable upon rupturing of spreading its contents in a substantially uniform layer between the superposed layers. It will be appreciated that the respective elements may be placed in superposition following impregnation with the processing composition according to procedures known in the art.

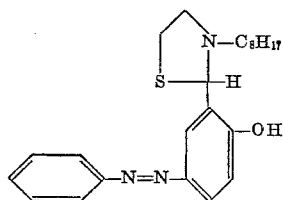
Negative color images also may be obtained by employing a film unit where the layer of cleavable color-providing compound is associated with the receiving element, such as illustrated in FIG. 2. As shown therein, an exposed silver halide emulsion 12 on a support 10 is processed by spreading a processing composition 15 between the emulsion layer and a layer of a colored color-providing material 11 on a support 14. In exposed areas of emulsion layer 12, silver halide is reduced to image silver, while an imagewise distribution of soluble silver complex is formed in terms of undeveloped areas of silver halide. This imagewise distribution is transferred, at least in part, by imbibition, to layer 11 where it accelerates cleavage of the cleavable color-providing compound to provide a diffusible color-providing moiety, e.g., dye, in areas corresponding to undeveloped areas of the emulsion-layer. Diffusion of the diffusible color-providing moiety from the image-receiving element into the processing composition leaves a negative color image in layer 11.

The film structures shown in the figures may be varied, for example, by employing one or more interlayers between those of the emulsion and cleavable parent compound as suggested above or by varying the order of the layers and is intended to be illustrative only of product structures useful in the preparation of color images according to the present invention.

The following examples are given to illustrate the present invention and are not intended to limit the scope thereof.

EXAMPLE 1

A solution containing 0.4 g. cellulose acetate hydrogen phthalate; 10.0 cc. methanol; 10.0 cc. 2-methoxyethanol and 0.4 g. of color-providing compound,



was dip coated on a cellulose acetate support at a rate of ten feet per minute. On top of the resulting layer was dip coated a solution containing 0.2 g. cellulose acetate

12

hydrogen phthalate; 10.0 cc. methanol, and 10.0 cc. 2-methoxyethanol also at a rate of ten feet per minute. Finally, a blue-sensitive silver iodobromide emulsion layer was applied which contained 100 mg. per square foot silver and 30 mg. per square foot gelatin.

To determine the difference in transfer of color-providing moiety obtained with a processing composition containing a silver halide solvent, e.g., sodium thiosulfate, and one without silver halide solvent, one portion of the photosensitive element prepared above was processed without exposure using the processing composition designated Solution A and the other portion processed without exposure using the processing composition designated Solution B.

Ingredients	Solution A	Solution B
Water, cc.-----	100.0	100.0
Sodium hydroxide, g.-----	2.5	2.5
Hydroxyethyl cellulose, g.-----	3.9	3.9
Sodium thiosulfate, g.-----	2.0	-----

Processing was carried out by spreading each solution in a layer 0.0016 inch thick between the photosensitive element and the receiving element containing a dyeable stratum that had been superposed therewith. The image-receiving elements used with the two portions of photosensitive material comprised a layer of a 2:1 mixture by weight, of polyvinyl alcohol and poly-4-vinyl pyridine over a layer of polyvinyl alcohol coated on a baryta paper support. After an imbibition period of about 30 seconds each of the image-receiving and photosensitive elements were separated and the transfer densities measured. The resulting transfer densities for the units processed with Solution A and Solution B were 1.56 and 0.26, respectively. These results illustrated that substantially greater transfer of diffusible dye was obtained in the presence of soluble silver hypo complex.

EXAMPLE 2

A further experiment was conducted to demonstrate the cleavage of the color-providing compound used in Example 1. For this experiment, a photosensitive element was prepared in the same manner as in Example 1 above except that an interlayer comprising 100 mgs. per square foot of gelatin was provided between the gelatino silver iodobromide emulsion layer and the underlying layer of cellulose acetate hydrogen phthalate. The outer silver halide emulsion layer was then removed from the element with an enzyme solution after which the element was divided into three portions. Each of the three portions was superposed with an image-receiving element and treated with Solutions C, D and E, respectively, by spreading solution, between the superposed materials in a layer 0.0016 inch thick. The image-receiving element was prepared in the same manner as that in Example 1 above except that an additional layer of a half-butyl ester of poly-(ethylene/maleic anhydride) was provided between the layer of polyvinyl alcohol and the baryta support.

The solution employed comprised the following:

Ingredients	Solution C	Solution D	Solution E
Water, cc.-----	100.0	100.0	100.0
Hydroxyethyl cellulose, g.-----	3.9	3.9	3.9
Sodium hydroxide, g.-----	5.0	5.0	5.0
Sodium thiosulfate, g.-----	-----	4.0	4.0
Silver chloride, g.-----	-----	-----	0.7

After an imbibition time of 30 seconds, the superposed elements were separated and the transfer densities measured for each. The densities obtained were 0.15, 0.13 and 0.95 for the units treated with Solutions C, D and E, respectively. From these results it is readily apparent that the presence of silver ions as in the soluble silver-hypo complex is necessary for cleavage to liberate the color-providing moiety in image-forming quantities in reasonable process times.

EXAMPLE 3

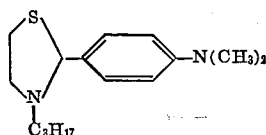
A photosensitive element was prepared by coating a cellulose acetate support with 186 mgs. per square foot of the color-providing compound used in Example 1 above. On top of the layer of compound there was applied a layer containing 100 mgs. per square foot of gelatin, and finally there was applied a blue-sensitive layer of silver iodobromide emulsion containing 33 mgs. per square foot of silver and 30 mgs. per square foot of gelatin. This element was exposed for one one-hundredth of a second to blue light through a density step tablet. Thereafter, the exposed element was superposed with an image-receiving element and a 0.0016 inch layer of processing composition was spread therebetween. The image-receiving element was the same as that used in Example 2. The processing composition comprised the following:

Hydroxyethyl cellulose	G.
Sodium hydroxide	3.9
p-Methylamino-phenol	5.0
Sodium sulfite	1.6
Sodium thiosulfate	2.0
4-amino-2-methyl-6-methoxy-phenol	2.0
Water, 100.0 cc.	0.5

After an imbibition period of about 30 seconds, a positive yellow image was obtained which had a $D_{\max}$ of 2.75 and a $D_{\min}$ of 0.92 as measured at 400 $m\mu$.

EXAMPLE 4

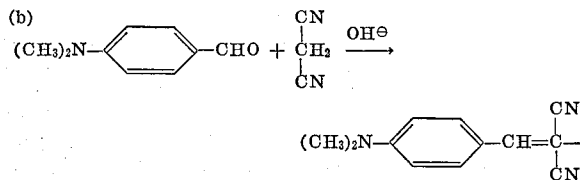
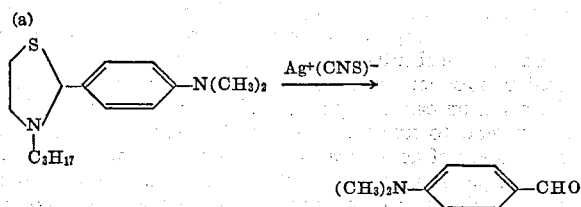
Malononitrile and 2-(p-dimethyl-aminophenyl)-3-propylthiazolidine,



were dissolved in N-ethyldecylamide and dispersed in gelatin. The resulting dispersion was coated on a transparent base comprising cellulose triacetate. A photosensitive element comprising a gelatino silver iodobromide emulsion carried on a paper base was totally fogged and one-half was then developed for ten minutes in a mixture of hydroquinone and methyl p-aminophenol, stopped with dilute acetic acid, rinsed and dried. Thereafter, the dried photosensitive element was superposed with the coated sheet prepared above and a 0.034 layer of processing composition was spread therebetween. The processing composition comprised the following:

Hydroxyethyl cellulose	G.
Sodium hydroxide	3.4
Titanium dioxide	5.0
Potassium thiocyanate	50.0
Water, 100.0 cc.	4.0

Almost instantaneously, a yellow image was produced in the area of the coated sheet corresponding to the undeveloped portion of the photosensitive element by the following sequence:



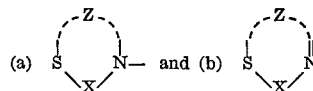
Substantially no yellow dye was visible in the area of the coated sheet corresponding to the portion of the photosensitive element where silver had been developed.

It will be appreciated that dye images may be prepared in accordance with Example 6 above using different color-forming reagents, e.g., different methylene couplers and different dye intermediates, e.g., different aldehydes.

As disclosed in aforementioned copending U.S. patent application Ser. No. 155,000, dye images may be produced by the reaction of an aldehyde or a ketone with a color-forming reagent, e.g., a methylene coupler. In one embodiment cyclic sulfur-nitrogen compounds containing the group $-S-X-N-$ or preferably



as part of the ring may be used to release one or both of these reagents in an imagewise distribution, which reagents upon subsequent reaction produce a corresponding imagewise distribution of a complete dye. Typical cyclic sulfur-nitrogen compounds are illustrated in the following formulae:



wherein Z represents the atoms, preferably carbon atoms necessary to complete a ring-system containing at least 4 members and usually containing up to about 20 members and X has the same meaning given above and preferably is



As the color-forming reagent, any compound may be used that will react with aldehydes and/or ketones to give a colored product. Suitable compounds include methylene couplers and those reagents used in color tests for identifying aldehydes and ketones as reported in the literature. The term "methylene coupler" as used herein is intended to include compounds containing an active methylene group and also compounds containing a reactive methyl group capable of forming a methylene base in alkaline media. Typical of compounds possessing a reactive methyl group are quaternary ammonium compounds, such as, pyridinium quaternary ammonium compounds having a methyl substituent in the 2 and 4 positions of the heterocyclic ring. Examples of 2 and 4 methyl-substituted pyridinium compounds are those wherein the nitrogen atom is substituted by groups, such as, alkyl, e.g., methyl, ethyl and propyl; aryl, e.g., phenyl; and aralkyl, e.g., phenethyl and benzyl. These compounds may be used as the free base or a salt where the anion is a derivative of any acid, e.g., a tosylate.

The couplers containing an active methylene group may be characterized as compounds containing a methylene ($-CH_2-$) group bonded directly to at least one activating group, such as, a keto, aldehyde, ester or nitrile group and usually a carbonyl or nitrile group. The methylene group also may be bonded to two such activating groups, the same or different, and the methylene group may be part of an open chain structure or a member of a ring system.

These compounds containing at least one active methylene group are generally known in the photographic art as useful couplers with color developing agents, e.g., the p-phenylene diamine series, to form a dye, as discussed in

15

Mees, *The Theory of the Photographic Process*, revised edition, 1966, pp. 382-395. Any of the methylene couplers commonly used for this purpose may be employed in the present invention such as the acylacetic esters; acylacetoacetic esters; malonic acid esters; acetonitriles; acylacetonitriles; aroylacetonitriles; cyanacetic esters; cyanacetophenones; cyanacetyl coumarones; cyanacetyl hydrazones; acetoacetamides; cyanoacetamides, 1,3-indandiones; thioindoxyls; oxindoles; indazoline-3-ones; isoxazole-5-ones; pyrimidazolones; and homophthalimides. The coupler employed preferably is colorless, though it may be colored depending upon its location in the photographic element.

Rather than being coated on the transparent receiving element, the layer of color-providing compound and coupler may be associated with the emulsion layer in the photosensitive element, e.g., to yield a dye capable of diffusing in the processing composition to form a transfer image. By using a transparent receiving element, the resulting image, when stripped from the photosensitive element, may be viewed by transmitted light as a transparency. If the photosensitive element and/or processing composition contains a translucent layer of a material providing the requisite background, e.g., a white pigment such as titanium dioxide, the image may be viewed as a reflection print without separating the image-receiving and photosensitive elements. Color transparencies and reflection prints of this type also may be produced in this manner where the diffusible color-providing moiety released in a complete dye.

In the various embodiments of the present invention, other silver halide emulsions may be used, such as silver chloride, silver bromide, silver bromoiodide, silver chlorobromide and silver chlorobromoiodide. Rather than the conventional silver halide emulsions, direct positive silver halide emulsions may be employed. By using such an emulsion in Example 4 above, for instance, a negative rather than a positive transfer image may be produced. Typical materials that may be used as the support for the emulsion are paper, glass and plastic materials, e.g., cellulose nitrate, cellulose acetate, polyvinyl acetal, polystyrene, polyethyleneterephthalate, polyethylene and polypropylene.

While in the foregoing, reference is made to the preparation of a monochromatic image, it will be appreciated that the invention is applicable to the formation of multicolor images. For example, the above-described color-providing compounds may be employed in photographic systems utilizing integral multilayer photosensitive elements comprising at least two selectively sensitized silver halide emulsion strata with associated color-providing material which are processed simultaneously and without separation to provide a multicolor image on a single common image-receiving element. In such a structure, there is preferably used a barrier interlayer of silver complex scavenger, e.g., silver precipitant, to confine diffusion of soluble silver complex to the appropriate thiazolidine stratum. Another useful structure for obtaining multicolor images is the screen type negative described in U.S. Pat. No. 2,968,554 issued Jan. 17, 1961 to Edwin H. Land or that described in U.S. Pat. No. 3,019,124 issued Jan. 30, 1962 to Howard G. Rogers.

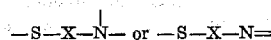
The expression "color" as used throughout the foregoing specification and in the appended claims is intended to include the use of a plurality of colors to obtain black.

As discussed above, rather than liberating a color-providing moiety as the reagent, the system of the present invention may be used to form an imagewise distribution of another reagent, preferably a photographically active reagent, in the same manner as color images were formed in the foregoing examples. The parent compound, such as the compounds illustrated in Equations 1 to 8 above may be appropriately substituted to yield the desired photographic reagent upon cleavage in the presence of silver

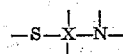
16

ions, or the unsubstituted compound itself may be used to provide the photographic reagent desired.

As in the formation of color images, the compounds found especially useful in diffusion transfer processes for releasing various photographic reagents are those containing the group



and especially

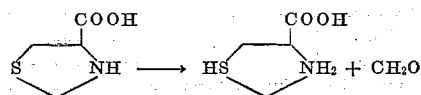


particularly where X is

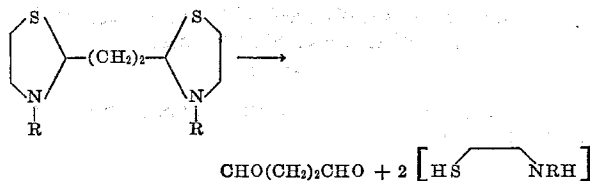


Such compounds, as exemplified by thiazolidine, may be employed in aqueous media in the presence of silver ion, to liberate, for example:

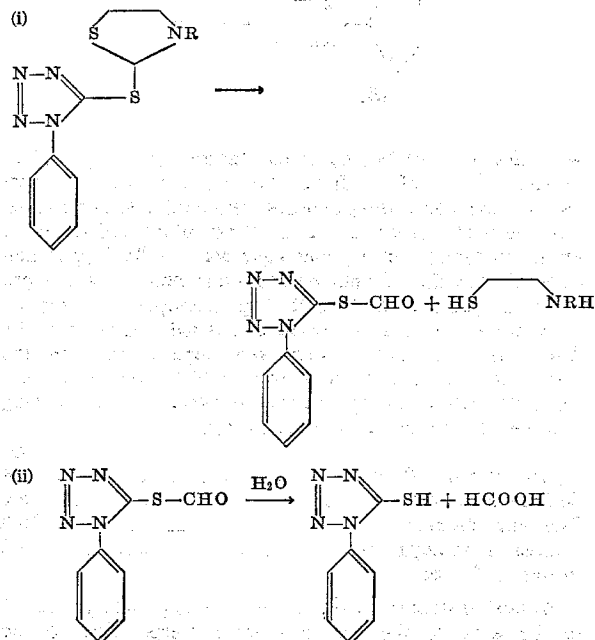
(a) a silver halide solvent



(b) a gelatin hardener



(c) an antifoggant



Thiazolidine itself upon cleavage, as illustrated in Equation 8 above, yields a fragment containing a mercapto group which fragment finds use as a development restrainer or antifoggant. This compound also may be used to produce a secondary amine or a tertiary amine, depending upon the N-substituent, and as illustrated above, may be used to produce an aldehyde, or where the hydrogen on the common carbon atom is replaced by phenyl or other substituent, to liberate a ketone. Releasing in imagewise distribution of active reagent in this manner affords many advantages. For example, relief images may be prepared by liberating a gelatin hardener in the unexposed areas, and as noted previously, fogging may be controlled more

effectively by releasing the antifoggant in an imagewise fashion during processing.

It will be appreciated that the photographic system of the present invention may be used to liberate reagents other than those specifically mentioned and that the present system for releasing a reagent in an imagewise fashion may be used with film structures other than those illustrated. For example, in diffusion transfer film units the negative component comprising at least one light-sensitive layer and the positive component comprising an image-receiving layer may be separate elements as shown above which are brought together during processing and thereafter either retained together as the final print or separated following image formation.

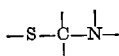
Rather than the photosensitive layer and the image-receiving layer being in separate elements, they may be in the same element. In such a film unit, the image-receiving layer is coated on a support and the photosensitive layer is coated on the upper surface of the image-receiving layer. The liquid processing composition is applied between the combined negative-positive element and a spreading sheet which assists in spreading the liquid composition in a uniform layer adjacent the surface of the photosensitive layer.

Illustrative of still other film units are those where the negative and positive components together may comprise a unitary structure, e.g., integral negative-positive film units wherein the negative and positive components are laminated and/or otherwise physically retained together at least prior to image formation. Generally, such film units comprise a plurality of essential layers including a negative component comprising at least one light-sensitive layer, e.g. a silver halide layer and a positive component comprising an image-receiving layer which components may be laminated together or otherwise secured together in physical juxtaposition as a single structure. In the formation of color transfer images, the dye image-providing compounds of the present invention may be associated with the silver halide layer or layers of the negative component.

Included among such structures are those adapted for forming a transfer image viewable without separation, i.e. wherein the positive component containing the transfer image need not be separated from the negative component for viewing purposes. In addition to the aforementioned essential layers, such film units include means for providing a reflecting layer between the image-receiving and negative components in order to mask effectively the silver image or images formed as a function of development of the silver halide layer or layers and any remaining associated dye image-providing material and also to provide a background for viewing the transfer image in the receiving component, without separation, by reflected light. This reflecting layer may comprise a preformed layer of a reflecting agent included in the essential layers of the film unit or the reflecting agent may be provided subsequent to photoexposure, e.g. by including the reflecting agent in the processing composition.

These essential layers are preferably contained on a transparent support closest to the image-receiving layer and preferably include another support positioned on the opposed surface of the essential layers so that the layers are sandwiched or confined between the support members, at least one of which is transparent to permit viewing of the final image. Such film units usually are employed in conjunction with means, such as, a rupturable container containing the requisite processing composition and adapted upon application of pressure of applying its contents to develop the exposed film unit.

Among the color-providing compounds discussed above, those compounds comprising a complete dye and a cyclic moiety containing the group

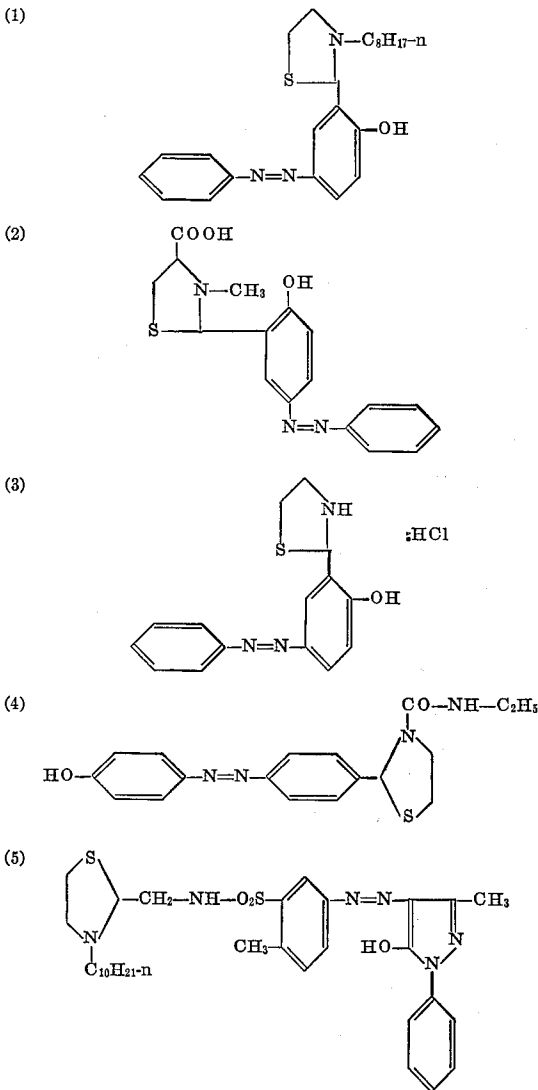


included in the ring wherein the cyclic moiety is capable

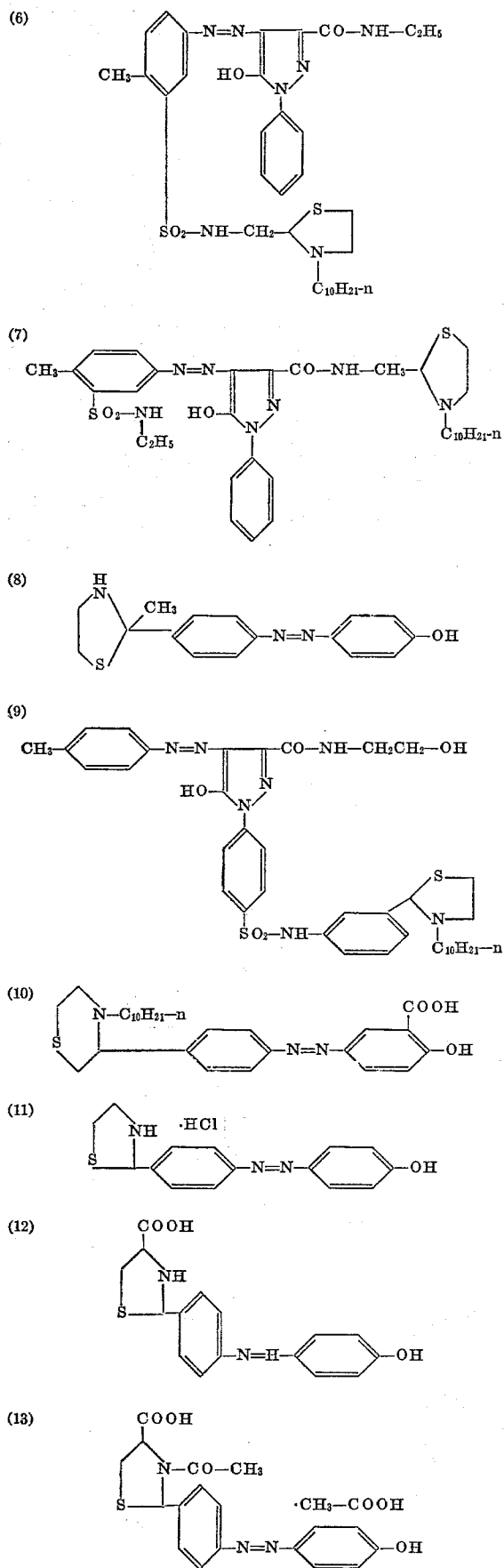
of undergoing cleavage in the presence of silver ions are novel compounds. The dye portion may comprise any one of the various classes of dyes, such as, azo, anthraquinone and the other dyes enumerated above. The cyclic moiety may be derived from any cyclic 1,3-sulfur-nitrogen compound containing at least four members in the ring system and containing the aforementioned group as part of the ring, the cyclic compound being capable of undergoing cleavage in the presence of ionic silver.

As discussed above, the dye may be linked directly to an atom of the cyclic 1,3-sulfur-nitrogen ring system by a valence or ionic bond or through a spiro union, or the dye may be linked indirectly to the ring system through an appropriate linking group either cyclic or acyclic. Preferably, the dye is substituted in the 2-position of the ring system, i.e., on the carbon atom common to the sulfur and nitrogen atoms. The novel dyes may be diffusible or non-diffusible in aqueous processing solution and if non-diffusible, may contain a bulky group linked directly or indirectly to the molecule, usually on the cyclic portion. Likewise, the novel dyes may contain solubilizing groups to adjust the solubility characteristics, as may be desired.

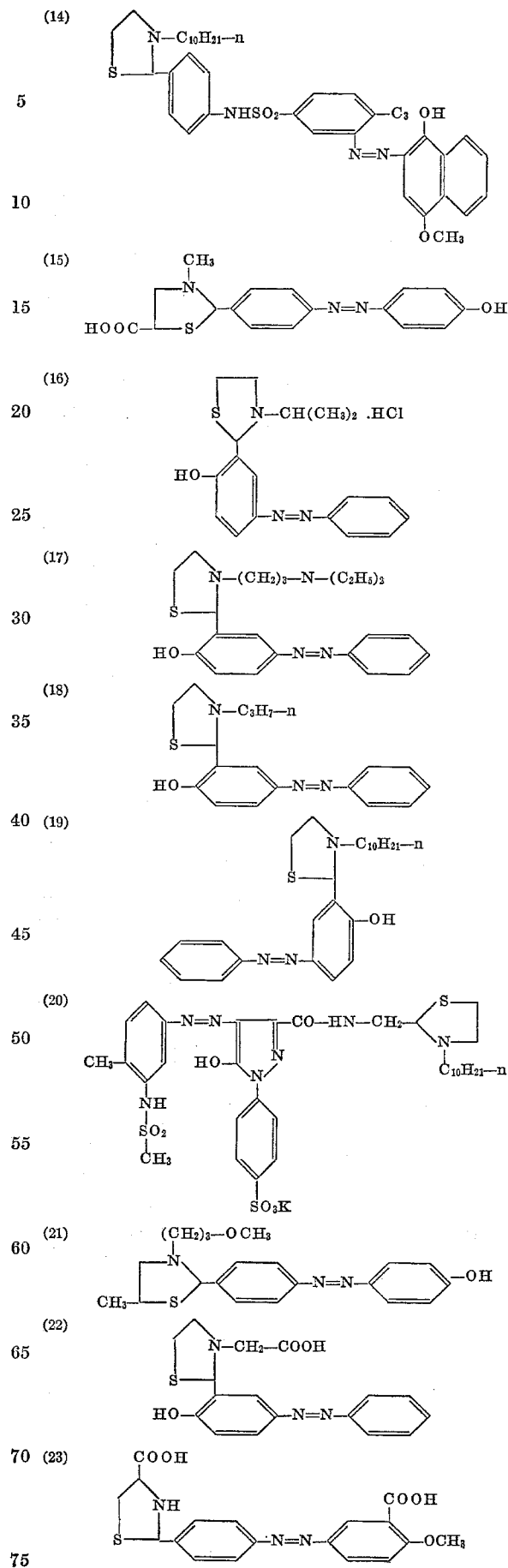
Illustrative of the novel dyes containing the specified cyclic moiety are the dye-substituted compounds of Formula VI above, as exemplified by dye-substituted thiazolidines and benzothiazolines. Specific examples of novel dyes within the scope of the present invention are as follows:



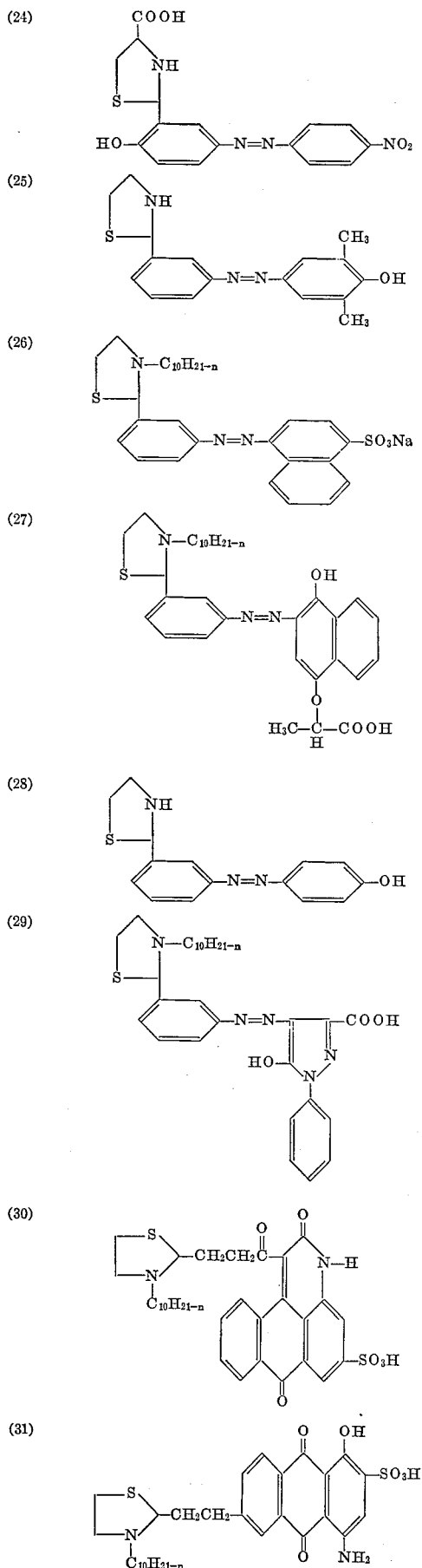
19



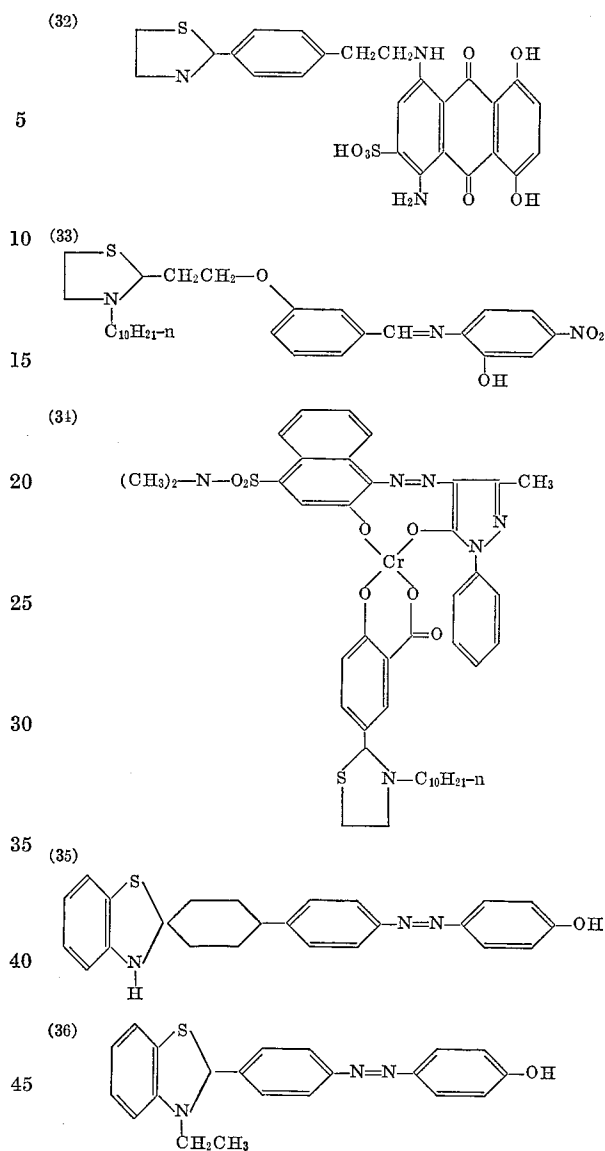
20



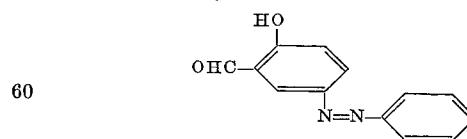
21



22



The novel dyes may be synthesized in a known manner by condensing an aldehyde, for example, a dye-substituted aldehyde, such as, DYE-CHO with a compound HS-Z-NH₂ wherein Z represents the atoms, preferably carbon atoms to complete a cyclic 1,3-sulfur-nitrogen moiety having up to about 20 members in the ring system. For example, the novel dyes may be prepared by condensing an aldehyde,



with 2-amino-ethanethiol or with ortho-amino-thiophenol to yield, for example, an azo dye possessing a cyclic moiety comprising a thiazolidine or a benzothiazoline nucleus. It will be appreciated that a dye-substituted ketone may be substituted for the aldehyde in the above condensation including cyclic ketones, such as, cyclohexanone where it is desired to prepare spiro derivatives. The following detailed example is given to illustrate the preparation of the preferred compounds within the scope of this invention, and is not intended to be in any way limiting.

Preparation of the compound of Formula 1:

(a) 52 grams of aniline hydrochloride was dissolved

23

in 165 cc. of 40% hydrochloric acid and cooled to about 0° C. 28 grams of sodium nitrite was slowly added while maintaining the temperature below 5° C. After stirring for one hour, a solution of 50 grams of salicylaldehyde dissolved in 270 cc. of 10% potassium hydroxide was added. Stirring was continued for approximately 15 minutes. Hydrochloric acid was added to precipitate the aldehydic azo dye which was then recrystallized from ethanol.

(b) 15.2 grams of N-decylamino ethanethiol and 15.8 grams of 2-hydroxy-p-phenylazo benzaldehyde prepared in step (a) was dissolved in 250 ml. of ethanol. The solution was stirred overnight. The title compound, which precipitated out, was recrystallized from ethanol, melting range 65°-66.5° C.

In addition to the above, the specific dyes of Formulae 2 to 29 above also were prepared in accordance with the foregoing procedure by condensing the appropriate aldehydic dye with the selected amino-ethanethiol.

It will be appreciated that other dyes, either aldehyde or ketone dyes, for example, other azo dyes or anthraquinone dyes, azomethine dyes, etc., such as, those commonly employed in photographic processes for producing color images may be condensed with the amino-ethanethiol according to the above procedure. Rather than the amino-ethanethiol, amino-thiophenol or other appropriate amino-mercapto compound may be used in the condensation reaction to obtain the desired cyclic 1,3-sulfur-nitrogen moiety.

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 shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic process for producing an imagewise distribution of a reagent, including the steps of developing a photosensitive element comprising an exposed silver halide emulsion with an aqueous processing composition; forming in undeveloped areas an imagewise distribution of silver ions and/or soluble silver complex; contacting said imagewise distribution of silver ions and/or said complex with an initially photographically inert compound capable of undergoing cleavage in the presence of said silver ions and/or said complex to liberate a reagent; and forming as a function of contacting said imagewise distribution of silver ions and/or said complex with said compounds, a corresponding imagewise distribution of said reagent.

2. A process according to claim 1 wherein said reagent is photographically active.

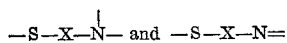
3. A process according to claim 1 wherein said initially inert compound is present in a layer in said photosensitive element.

4. A process according to claim 1 wherein said processing composition is an aqueous alkaline solution of a silver halide developing agent and a silver halide solvent.

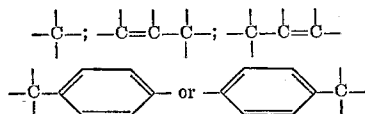
5. A process according to claim 1 wherein one of said initially inert compound and said reagent is diffusible in said processing composition and the other is substantially non-diffusible in said processing composition.

6. A process according to claim 1 wherein a sheet-like element is in superposed relationship with said photosensitive element and said processing composition is distributed between said photosensitive and sheet-like elements.

7. A process according to claim 1 wherein said initially photographically inert compound is a compound containing a group selected from

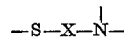


wherein X is



24

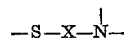
8. A process according to claim 7 wherein said compound contains the group



9. A process according to claim 8 wherein X is



10. A process according to claim 9 wherein said compound is a cyclic compound having a ring system containing up to 20 members and said



group is included in the ring.

11. A process according to claim 10 wherein said cyclic compound is a thiazolidine.

12. A process according to claim 10 wherein said cyclic compound is a benzothiazoline.

13. A process according to claim 9 wherein the reagent liberated is an aldehyde.

14. A photographic process for producing an imagewise distribution of a color-providing moiety including the steps of developing a photosensitive element comprising an exposed silver halide emulsion with an aqueous processing composition; forming in undeveloped areas an imagewise distribution of silver ions and/or soluble silver complex; contacting said imagewise distribution of silver ions and/or said complex with an initially photographically inert compound capable of undergoing cleavage in the presence of said silver ions and/or said complex to liberate a color-providing moiety; and forming as a function of contacting said imagewise distribution of silver ions and/or said complex with said compound, a corresponding imagewise distribution of said color-providing moiety.

15. A process according to claim 14 wherein one of said initially inert compound and said color-providing moiety is diffusible in said processing composition and the other is substantially non-diffusible in said processing composition.

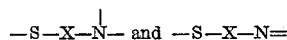
16. A process according to claim 15 wherein said compound is substantially non-diffusible and said color-providing moiety is diffusible in said processing composition.

17. A process according to claim 16 wherein said color-providing moiety is a diffusible dye.

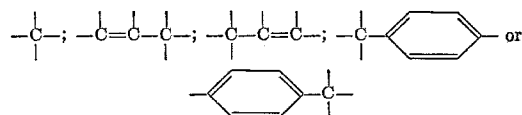
18. A process according to claim 17 wherein a sheet-like element comprising a dyeable stratum is superposed with said photosensitive element and at least a portion of said imagewise distribution of diffusible dyes transferred to said dyeable stratum to form a color transfer image thereon.

19. A process according to claim 18 wherein said processing composition is an aqueous alkaline solution of a silver halide developing agent and a silver halide solvent.

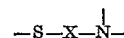
20. A process according to claim 14 wherein said initially photographically inert compound is a compound containing a group selected from



wherein X is



21. A process according to claim 20 wherein said inert compound contains the group



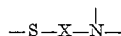
22. A process according to claim 21 wherein X is



23. A process according to claim 22 wherein said com-

25

compound is a cyclic compound having a ring system containing up to 20 members and said



group is included in the ring.

24. A process according to claim 23 wherein said cyclic compound is a thiazolidine.

25. A process according to claim 23 wherein said cyclic compound is benzothiazoline.

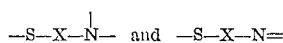
26. A photographic product comprising first and second sheetlike elements, said first element comprising a plurality of layers including a support; a photosensitive silver halide emulsion in a layer on said support; in a layer in one of said first and second sheet like elements, an initially photographically inert compound capable of undergoing cleavage in the presence of an imagewise distribution of silver ions and/or soluble silver complex to liberate a reagent in an imagewise distribution corresponding to said distribution of silver ions and/or said complex; and means for applying a photographic processing composition comprising an aqueous alkaline solution of a silver halide developing agent and a silver halide solvent in a substantially uniform layer between said emulsion layer and said second sheet like element in superposed relationship therewith.

27. A product as defined in claim 26 wherein one of said initially inert compound and said reagent is diffusible in said processing composition and the other is substantially non-diffusible in said processing composition.

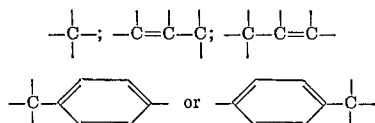
28. A product as defined in claim 27 wherein said compound is non-diffusible and said reagent is diffusible in said processing composition.

29. A product as defined in claim 26 wherein said reagent is photographically active.

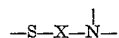
30. A product as defined in claim 26 wherein said initially inert compound is a compound containing a group selected from



wherein X is



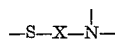
31. A product as defined in claim 30 wherein said compound contains the group



32. A product as defined in claim 31 wherein X is



33. A product as defined in claim 32 wherein said compound is a cyclic compound having a ring system containing up to 20 members and said



group is included in the ring.

34. A product as defined in claim 33 wherein said cyclic compound is a thiazolidine.

35. A product as defined in claim 33 wherein said cyclic compound is a benzothiazoline.

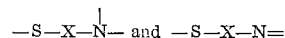
36. A product as defined in claim 26 wherein said initially inert compound is present in said first element in a layer on the same side of said support as said silver halide emulsion layer.

37. A product as defined in claim 26 wherein said cyclic compound is present in a layer in said second element.

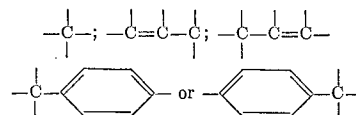
26

38. A photographic product comprising a photosensitive element comprising a plurality of layers including a support; a silver halide emulsion in a layer on said support; and in a layer on the same side of said support as said silver halide emulsion, an initially photographically inert compound capable of undergoing cleavage in the presence of an imagewise distribution of silver ions and/or soluble silver complex to liberate a color-providing moiety in an imagewise distribution corresponding to said distribution of silver ions and/or said complex.

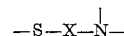
39. A product as defined in claim 38 wherein said initially inert compound is a compound containing a group selected from



wherein X is



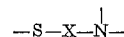
40. A product as defined in claim 39 wherein said initially compound contains the group



41. A product as defined in claim 40 wherein X is



42. A product as defined in claim 41 wherein said compound is a cyclic compound having a ring system containing up to 20 members and said



group is included in the ring.

43. A product as defined in claim 42 wherein said compound is a thiazolidine.

44. A product as defined in claim 42 wherein said compound is a benzothiazoline.

45. A product as defined in claim 39 wherein one of said initially inert compound and said color-providing moiety is diffusible in aqueous alkaline solution and the other is substantially non-diffusible in aqueous alkaline solution.

46. A product as defined in claim 45 wherein said compound is substantially non-diffusible and said color-providing moiety is diffusible in aqueous alkaline solution.

47. A product as defined in claim 46 wherein said color-providing moiety is a diffusible dye.

48. A photographic product as defined in claim 47 including a superposed image-receiving layer so positioned as to be capable of receiving by diffusion transfer an imagewise distribution of said diffusible dye and means for applying a photographic processing composition comprising an aqueous alkaline solution of a silver halide developing agent and a silver halide solvent in a substantially uniform layer between said silver halide and said imagewise receiving layer.

References Cited

UNITED STATES PATENTS

3,379,529 4/1968 Porter ----- 96-36 X

J. TRAVIS BROWN, Primary Examiner

A. T. SURO PICÓ, Assistant Examiner

U.S. Cl. X.R.

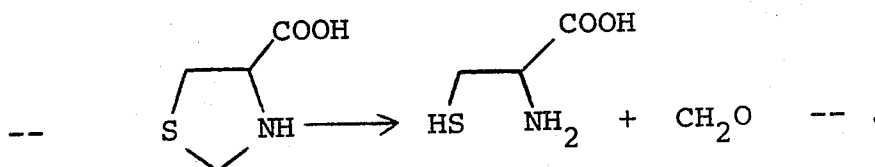
96-3, 74, 76 C, 77; 260-158

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,719,489 Dated 3/6/73
Inventor(s) Ronald F. W. Cieciuch, Roberta R. Luhowy,
Frank A. Meneghini, and Howard G. Rogers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

- Col. 1, line 20, "ion should be --ions--.
- Col. 3, line 31, "color-producing" should be --color-providing--.
- Col. 3, line 32, "distribtuion" should be --distribution--.
- Col. 4, line 2, "diffusable" should be --diffusible--.
- Col. 6, line 1, after "color" change "images" to --image--.
- Col. 11, line 6, "brough" should be --brought--.
- Col. 12, line 59, "solution" should be --solutions--.
- Col. 14, line 72, "continuing" should be --containing--.
- Col. 15, line 30, "in" should be --is--.
- Col. 16, line 21, the formula should read as



Signed and sealed this 12th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents