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PHOTOGRAPHIC ELEMENTS CONTAINING
PROTEIN COLOR FORMERS

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This invention relates to color yielding compositions and to photographic elements and processes for producing colored images utilizing the same. More particularly, it relates to hydrophilic vegetable protein dye intermediate derivative radiation sensitive compositions and to photographic elements and processes of color photography utilizing the same.

Various types of color formers have been proposed for use in color coupling development processes of color photography since the investigators Homolka, Fisher and Siegrist discovered the utility of and established the practicability of forming dye images simultaneously with the development of latent silver salt images. Color formers which are immobile in the conventional gelatin silver salt layers of photographic elements during photographic processing have received considerable attention by the research workers in the art. It has been found, however, that the addition of color formers often has a deleterious effect on the light sensitivity of emulsions.

This invention has for an object the preparation of new hydrophilic color formers or dye intermediate compositions containing light-sensitive silver salts or grains. A further object is to provide such compositions from available raw materials by a simple and economical procedure. A still further object is to provide new color former compositions from vegetable proteins. Another object is to provide new and useful color forming silver salt layers. Yet another object is to prevent the coagulation and sedimentation of silver salts in photographic layers. Still other objects are to provide new photographic elements and photographic processes and to make a general advance in the art of color photography and high molecular weight, water-permeable dye intermediates.

The above objects may be accomplished in accordance with this invention which will be described below with greater particularity.

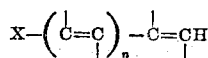
It has been found that vegetable proteins which are capable of being cast into transparent films which are water-permeable can be converted into novel hydrophilic color formers by condensing them with a bi-functional condensation agent and a color former either simultaneously or stepwise. The bi-functional condensing agents link with vegetable protein molecule to the color former nucleus thus forming a single organic compound. In general, the condensation can be advantageously carried out by means of aldehydes, e. g., formaldehyde or a formaldehyde-yielding material or substance such as paraldehyde, trioxane, hexamethylene-tetramine, etc.; dimethylolurea and its mono- and di-methyl and -ethyl ethers.

hyde, trioxane, hexamethylene-tetramine, etc.; dimethylolurea and its mono- and di-methyl and -ethyl ethers.

The condensation may effectively be carried out in the presence of a solvent medium such as water, acids such as acetic or formic; a volatile alcohol, e. g., methanol, ethanol, etc.; an ether, e. g., di-isopropyl ether, dioxane, etc., or mixtures of the aforementioned. Alternatively, non-solvents for the protein may be employed such as a hydrocarbon, e. g., benzene, benzene, toluene, tetrahydronaphthalene, etc. Condensation agents or catalysts which are known to promote esterification or saponification reactions such as organic or inorganic acids, e. g., hydrochloric, sulfuric, phosphoric, acetic, etc.; alkalis such as sodium carbonate, sodium hydroxide, etc., may be employed as desired or if necessary to facilitate the reaction.

The invention can be applied with any dye intermediate or color former which will condense with formaldehyde to form bis or polymeric compound without permanently destroying the dye coupling structure of said intermediate. For instance, any color former which is capable of coupling with the development products of primary aromatic amino developing agents that are formed upon the color coupling development of silver salt latent images and form azomethine or quinoneimine (including indophenol, indoamine and indoaniline) dyes can be used. It is advisable to use non-colloidal simple dye intermediates or color formers because the colloidal type and high molecular weight type tend to form resinous water-impermeable condensation products. The simple crystalline color formers which are useful in color-developer solutions thus can be easily converted into hydrophilic color formers which can be used as the sole binding agents for light-sensitive silver salts in thin photographic layers.

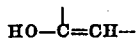
The dye intermediate nuclei or color former components of the vegetable protein-dye intermediates have as the active coupling groups a structure which may be represented by the general formula



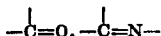
where X is an HO radical or an RHN radical; where R is hydrogen, an alkyl or substituted alkyl group, e. g., methyl, ethyl, dodecyl, betachloroethyl, betahydroxyethyl, benzyl, etc.; and n is 0 or 1. Thus X may be a primary or secondary amino group. These groups are found in reactive methylene dye intermediates or color formers and in

aromatic hydroxyl and amino compounds and includes reactive ethenol, aminoethenyl, 4-hydroxy- and 4-amino-1,3-butadienyl groups. These groups occur in phenols, naphthols, anilines, naphthylamines, acylacetamides, cyanoacetamides, beta-ketoesters, pyrazolones, N-homophthalylamines, homophthalylimides, coumaranones, indoxyls, thioindoxyls, etc.

The reactive ethenol group represented by



occurs in phenols and naphthols which couple in the ortho positions and in the alkali-soluble or enol form of most reactive methylene dye intermediates. These reactive methylene groups have a hydrogen rendered mobile by the proximity of certain unsaturated groups such as for example,

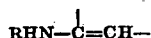


$-\text{C}\equiv\text{N}$ and others. The $-\text{CH}_2-$ group is usually present between two such groups, for example, $-\text{COCH}_2\text{CO}-$, $-\text{COCH}_2\text{CN}$,



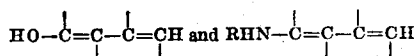
in a cyclic or acyclic system.

The reactive aminoethenyl group,



occurs in aromatic amino compounds which couple in the ortho position.

The 4-hydroxy- and 4-amino-1,3-butadienyl groups represented as



occur in phenolic, naphtholic and aromatic amino compounds which couple in the para position.

In all of these dye intermediate groups the hydrogen atoms in the coupling reactive position may be replaced by groups readily eliminated in the coupling reaction, e. g., halogen, sulfonic acid, carboxylic acid, etc.

Vegetable proteins such as gluten, gliadens, glutenins, globulins, legumins, glutins, and especially the zeins can be converted into protein-dye intermediates or color formers which form strong self-supporting and/or supported thin films which are freely water permeable but do not dissolve in cold water e. g., below 30° C. They have a softening point of at least 50° C. which is an advantage since it enables the photographic elements to be processed at tropical temperatures with safety. The vegetable protein color formers are soluble to the extent of at least 5 parts per hundred of an aqueous alcohol solvent mixture containing 50% or less ethanol.

Light-sensitive silver halides can be precipitated in an aqueous alkanol solution of the hydrophilic vegetable protein color formers by adding an aqueous solution of a water-soluble bromide, e. g., ammonium bromide and then an aqueous solution of a water-soluble silver salt, e. g., silver nitrate can be added from an aqueous solution. Silver halide, e. g., silver bromide is precipitated in a finely divided state in the protein derivative and forms a stable dispersion therewith. The dispersion can be diluted with a water-alkanol mixture to a proper viscosity for coating and cast onto a support such as a transparent film base or a baryta coated paper, etc., and dried. Before coating however the dispersion can be ripened, digested and modified by the addition of general emulsion sensitizers, e. g., sodium sulfite, sodium hyposulfite, allyl thiourea, isothiocyanates, etc.,

fog inhibiting agents, e. g., benzimidazoles, etc., spectral sensitizing dyes, stabilizers, and/or other emulsion constituents. Instead of using the dispersion it may be set and/or shredded and stored for later use.

Instead of precipitating the silver salts directly in the hydrophilic vegetable protein dye intermediate derivatives, they may be precipitated in a sensitive gelatin solution which is diluted and centrifuged and the silver salts made into a paste and redispersed in the aforesaid derivatives by admixing from an aqueous solution.

The novel dye intermediates hereof have two components (1) the protein nucleus and (2) a plurality of dye intermediate nuclei which are joined by the residue of the bi-functional condensation agent. In the case of formaldehyde the linking radical is a $-\text{CH}_2-$ radical.

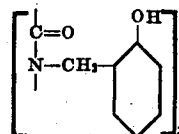
Various useful characteristics are possessed by the novel chemical products hereof. Thus the hydrophilic protein dye intermediates have (1) the ability to form strong coherent supported films, (2) a good protective colloid action with respect to silver halide grains or crystals, (3) good permeability in the form of layers or films to water and aqueous developing and fixing solutions, (4) optical clarity, (5) good resistance to deformation in water or aqueous media at ordinary temperatures, (6) good dye coupling properties yielding dyes of good saturation of color, and (7) good resistance to abrasion.

The invention will be further illustrated but is not intended to be limited by the following examples in which all operations were carried out under conditions which would not expose the silver salts.

Example 1

A solution of 8.0 gms. of saligenin, M. P. 85-86° C. in 125 cc. of alcohol and 175 cc. of water was added at 15-20° C. to 55.5 cc. of 37% formaldehyde solution containing 0.25 gm. of sodium carbonate monohydrate. The mixture was stirred for two hours at room temperature, a little dilute carbonate solution being added from time to time to keep the mixture just alkaline to litmus.

The above solution was poured into 480 cc. of a stirred solution of zein prepared by dissolving 125 gms. of zein in 375 cc. of ethanol and 25 cc. of water. The mixture was stirred and heated to reflux for five hours and then poured into cold water. The plastic mass which separates was washed with water and upon drying a somewhat brittle, brownish mass was obtained. It contained structural units of the probable structure:



wherein the free bonds form a part of the protein residue.

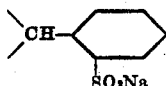
Example 2

To 100 cc. of dioxane, 11 gms. of zein were added at room temperature, followed by 15 gms. of saligenin. The mixture was stirred for one and one-half hours at room temperature and then heated to 80° C. At this temperature, 75 cc. of 85% phosphoric acid was added and after stirring and heating for five minutes a plastic mass separated from the liquid. To the mixture were added 50 cc. of alcohol whereupon partial solution took place. Heating was continued for five hours more and after cooling the liquid was decanted and the

remaining solid washed with acetone and alcohol and then dried. The product was similar in appearance and properties to that described in Example 1.

Example 3

In a manner similar to that described in Example 2, zein (11 gms.) and saligenin (15 gms.) were treated in dioxane with the addition of 4 gms. of benzaldehyde-o-sulfonic acid to the reaction mixture. The resulting product was somewhat more water-sensitive than the products of Examples 1 and 2. It had the unit structure set forth in Example 1 except that a portion of the $-\text{CH}_2-$ radicals were replaced by



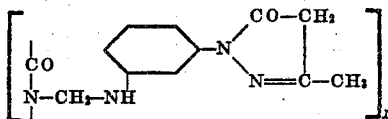
radicals.

Example 4

A solution of 20 gms. of zein in 50 gms. of 85% formic acid was treated at 45–50° C. with 10 gms. of saligenin. The mixture was stirred and heated to 65° for one-quarter of an hour. After cooling and diluting with two liters of acetone, a viscous solid separated. The solid was washed with fresh acetone and dried.

Example 5

A warm solution of 245 gms. of 3-methyl-1-(m-aminophenyl)-5-pyrazolone and 5 gms. of potassium carbonate in 1500 cc. of water was cooled to room temperature whereupon a fine crystalline precipitate was obtained. The suspension was added gradually at 20–30° C. to a stirred solution of 37% formaldehyde (111 cc.) containing 5 gms. of sodium carbonate. After stirring for three-fourths of an hour, the mixture, which was acid to litmus, was poured into a stirred zein solution comprising 750 cc. of alcohol, 50 cc. of water and 250 gms. of zein. A pasty solid separated, but when stirred and heated, the solid broke up into granular particles. The mixture was stirred and heated to 80° C. for several hours. After cooling and filtering and washing with water, the buff, granular solid (305 gms.) was dried in the open air. It contained structural units of the probable structure:

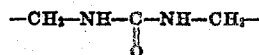


wherein the free bonds form part of the protein residue.

Example 6

A solution of 24.5 gms. of 1-(m-aminophenyl)-3-methyl-5-pyrazolone and 5 gms. of sodium carbonate in 250 cc. of water was added slowly to a solution of 18 gms. of dimethylolurea in 75 cc. of water. The resulting suspension was stirred at room temperature for three-fourths of an hour and was then added to 96 cc. of a zein solution of the same composition as that employed in Example 5. Sufficient sodium carbonate was added to make alkaline, and the mixture was stirred and heated for eight and one-half hours on a steam bath. The pale brownish yellow granular solid (49 gms.) was filtered, washed and dried. It had a structure similar to that of Ex-

ample 5 except that the $-\text{CH}_2-$ radical was replaced by a radical of the formula:



Example 7

If in Example 6 the dimethylolurea was replaced by an equivalent quantity of bis-methoxymethylurea (22 gms.), and 44 gms. of a product was obtained which was similar in properties and appearance and contained the same linking radical as that in said example.

Example 8

To 200 cc. of dioxane which has been dried with solid sodium hydroxide, 20 gms. of zein and 5 gms. of benzaldehyde-orthosulfonic acid were added with stirring. To this mixture were then added 25 gms. of saligenin. After stirring for ten minutes and then adding 1.5 cc. of 85% sulfuric acid the mixture was warmed slightly. The suspended solid became pasty and 100 cc. of alcohol were added which partially dissolved the suspended solids. Heating was continued at 100° for five to six hours with vigorous stirring. After cooling, acetone was added to coagulate the product which was separated and washed well with fresh acetone. A total of 23 gms. of a pale plastic material was obtained.

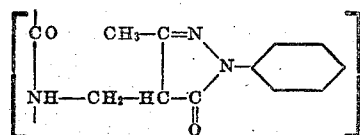
Example 9

A solution was made containing 378 gms. (4 mols) of m-amino-phenyl-methyl-pyrazolone, 4 liters of H_2O , 50 gms. of sodium carbonate (monohydrate), 300 cc. of 15.8% piperidine-alpha-carboxylic acid. The mixture was stirred and made just alkaline by addition of 500 cc. of 5% sodium carbonate. At 35–40° C., a solution of 240 gms. of dimethylolurea in 1600 cc. of water was added rapidly. After adding 500 cc. of alcohol the entire mixture was filtered to remove a small amount of dark solid. After stirring for one hour a solution of 1420 cc. of zein in alcohol was added with stirring at such a rate that no heavy clumping took place. The zein solution had the following compositions: alcohol 750 cc., water 50 cc., zein 250 gms. During the addition of the zein solution 250 cc. more of alcohol were added. The mixture was then heated with stirring to reflux for four to five hours. After cooling, precipitating with acetone and washing with the same solvent, 724 gms. of a yellow granular solid were obtained.

If in the previous example formaldehyde is used in place of dimethylolurea, the reaction mixture sets to a firm gel. After heating for two to three hours at this point, heating is interrupted, the mixture is diluted with alcohol and then with acetone, slurried with acetone and filtered.

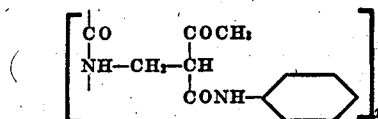
Example 10

In the manner described for Example 4, zein, formaldehyde and phenyl-methyl-pyrazolone were caused to react in formic acid solution. At the end of the reaction period, the product was precipitated with acetone, washed and dried as usual. It contained structural units of the probable structure:



wherein the free bonds form a part of the protein residue.

In the same manner zein, formaldehyde and acetoacetanilide were treated in formic acid solution and the product recovered as before and a product containing the following probable color former units:



wherein the free bonds form a part of the protein residue.

Example 11

A solution was made from the film-forming protein color-former obtained by the interaction of zein, formaldehyde and meta-amino-phenyl-methyl-pyrazolone after the manner described in Example 5 as follows:

Protein color former.....	gms..	10
Sodium hydroxide (20%).....	cc..	10
Ethyl alcohol.....	cc..	100
Water.....	cc..	100

After stirring and warming until solution was complete, the liquid was filtered and treated with 5 gms. of light-sensitive silver bromide which is substantially free from gelatin and was coated on a paper support at room temperature. The resulting photographic element may be exposed through a negative or to an original subject and processed in a developer such as the following:

	Grams
p-Amino diethylaniline hydrochloride.....	2
Sodium carbonate (anhydrous).....	20
Potassium bromide.....	5
Sodium sulfite.....	1

A very powerful magenta dye image is obtained. Alternatively, the element may be processed by reversal as follows:

Develop five minutes with intermittent agitation in the following first developer:

N-methyl-p-aminophenol sulfate.....	gms..	5.0
Hydroquinone.....	gms..	7.5
Sodium sulfite.....	gms..	60.0
Potassium bromide.....	gms..	4.5
Water to.....	cc..	1,000

After washing in the dark for ten minutes, the film is exposed to light and developed for ten minutes in the following:

p-Amino diethylaniline hydrochloride.....	gms..	2.0
Sodium carbonate (anhydrous).....	gms..	20.0
Sodium sulfite.....	gms..	.5
Water to.....	liters..	1.0

After washing for fifteen minutes in running water, the film is bleached in neutral or alkaline potassium ferricyanide, rinsed, fixed in plain hypo, washed and dried. A reversed magenta dye image of excellent strength and color purity is obtained.

Example 12

A solution of the protein color former obtained as in Example 5 was used in the preparation of a light-sensitive element as follows:

To a solution comprising 10 gms. of the protein color former in 100 cc. of water, 25 cc. of alcohol and 10 cc. of sodium hydroxide, was added 10 cc. of 9% potassium bromide. In darkness was then added 8 cc. of ammonical silver nitrate pre-

pared from 3N silver nitrate and 20% ammonia solution. The mixture was treated further with 2 cc. of electrolyte free sodium dodecyl sulfate (10%) and the resulting emulsion was coated at room temperature on a cellulose acetate film base having a substratum coating of the type described in United States Patent No. 1,947,160. When this element is processed as in Example 11 by negative color development, a powerful magenta dye image is obtained. Alternatively as in Example 11 the element may be processed by reversal to yield a positive magenta image.

Example 13

Any of the products described in Examples 1 through 4 may be used as dispersing and binding media for light-sensitive silver salts either by precipitation of said salts therein or by addition of centrifuged silver salts to solutions of the protein color-formers. These blue-green color forming protein polymers were treated in the manner of Example 12, by precipitating silver bromide therein. When developed in an N-diethyl-para-phenylenediamine developer as described in Example 11, blue-green images were obtained.

Example 14

A two-color component photographic element was obtained as follows:

On one side of a transparent support was coated a light-sensitive magenta protein color-forming layer similar to that described in Example 11 or in Example 12. On the opposite side of the support was coated a blue-green protein color-forming layer similar to those obtained as described in Example 13, using the protein color-formers as described in Examples 1 through 4. The resulting two-color component element may be used, for example, for printing from color separation negative records of an original subject using the red and green record for printing on the blue-green and magenta side respectively, of the two color element. After developing in an N-diethyl-para-phenylenediamine developer as described in Example 11, blue-green and magenta images remained in superposition. The blue record negative may be converted into a positive yellow component image on the two color image by toning, imbibition, or other suitable means.

Example 15

A multilayer film for the reproduction of colored objects by reversal processing may be made by coating on a support such as cellulose acetate or nitrate or on paper the following separate strata: (A) A light-sensitive hydrophilic protein color-forming layer made by the addition of precipitated silver halide which has been sensitized for red by means of naphthoselenocarbocyanine iodide to a composition derived from one of the blue-green protein color formers described above. (B) Over this layer is coated a separating strata consisting of partially hydrolyzed ethylene-vinyl-acetate interpolymers. (C) Next is coated a color yielding layer similar to that described in Example 11 with the exception that the pre-precipitated silver bromide has been made sensitive to blue and green by means of erythrosine. (D) Next in order is coated a yellow resin colloidal silver element such as that which may be obtained by reducing a solution of silver nitrate in a water-insoluble, water-permeable colloid, e. g., by means of diphenyl carbazide. (E) Finally there is coated a layer of a

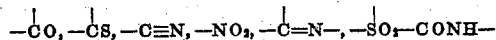
yellow protein color former containing light sensitive silver salts. The color former which is employed may be that described in Example 10 as obtained from acetoacetanilide. This film may be exposed and developed in negative color developer as described in Example 11, whereupon a negative image in complementary colors will be obtained. The film may also be processed by reversal using the black and white first developer and color developer described in Example 11. In this case, a positive color image giving an approximate reproduction of the original subject will be obtained.

In place of the zein described in the above examples may be substituted other vegetable proteins in similar amounts whereby color formers are directly linked to the protein nuclei through an ether linkage. Suitable proteins include gliadins or prolamines such the gliadin of wheat, zein of maize, and hordein of barley which are soluble in 70-80% alcohol; glutelins such as gluten from wheat and maize and oryzenin from rice, which are soluble dilute alkalies and acids but not in neutral media; globulins such as edestin from hemp, phaseolin from beans and the globulins of wheat which are soluble in dilute acids and alkalies; albumins such as ricin from castor beans, leucosin from wheat, legumelin from peas and vetches which are soluble in water. Zein derivatives such as piperidylmethylzein, dimethylaminomethylzein and dimethylaminoethylzein and related derivatives can be used.

A wide variety of color formers or dye intermediates can likewise be substituted in the above examples or with the alternative proteins described above to form similar hydrophilic protein color formers. The preferred reaction for preparing these new color forming binding agents involves formation through formaldehyde to give a compound having each of the color forming nuclei attached through a methylene ($-\text{CH}_2-$) group to a nitrogen atom of an amido group or to a carbon atom which is in turn attached to a nitrogen atom in the chain of atoms forming the polymeric protein molecule. The color-forming nuclei need not, however, be attached directly to the methylene group. For instance, non-color-forming formaldehyde reactive groups, e. g., amide, mercapto, or aliphatic amino or hydroxyl may be present in the dye intermediate or color former and react with formaldehyde to form methylol derivatives capable of condensing with the amino groups of the protein to form a lateral color forming substituent. The solubility and permeability of the protein derivatives may vary considerably depending upon the properties of the initial protein used, the nature of the bi-functional condensing agent, and the nature and number of color formers condensed. If color formers which contain solubilizing groups, e. g., sulfonic acid or carboxylic acid groups are used the water-sensitivity of the resulting protein derivative is increased. If the protein color formers do not have sufficiently high water-sensitivity or solubility, solubilizing groups such as carboxylic or sulfonic acid, groups can be introduced, e. g., by reaction with glyoxal, or with formaldehyde and hydroxyethane sulfonic acid or glycolic acid. If the products are too water-sensitive, insolubilizing groups may also be introduced, for instance, by an amidation reaction, e. g., by condensation with fatty acid chlorides such as acetyl chloride, lauryl chloride, stearyl chloride, etc., or with aromatic acyl halide, e. g.,

benzyl chloride. The modification of the solubility characteristics of the proteins can be accomplished prior or subsequent to the condensation of the dye intermediate or color former therewith.

In addition to the color formers or dye intermediates used in the above examples, there may be employed many of the other well-known compounds of this type. Thus the dye intermediate nucleus may be any phenol, naphthol, or aromatic amine having a coupling position available ortho or para to the aliphatic hydroxyl or amine group or any active methylene compound, i. e., any compound having a $-\text{CH}_2-$ group activated by two vicinal unsaturated groups taken from the class consisting of



$-\text{COO}$ alkyl, COO aryl connected either directly or through a conjugated system. Such active methylene compounds are distinct by their ability to have one of the hydrogen atoms of the methylene groups replaced by alkali metals in an aqueous solution and include a host of acyclic and heterocyclic compounds. Examples of such active acyclic and intercyclic methylene compounds include (1) beta-ketoacylamides of the type $\text{RCOCH}_2\text{CONHR}$, where R is a hydrocarbon or heterocyclic radical and R is preferably aromatic, e. g., benzoylacetanilide, p-nitrobenzoylacetanilide, p-nitroacetoacetanilide, naphthoylacetanilide p-acetoacetamidobenzoic acid, furoylacetanilide, (2) pyrazolones, e. g., 1-phenoyl-3-methyl-5-pyrazolone, 1-p-chlorophenyl-3-methyl-5-pyrazolone, 1-phenyl-3-carboxy-5-pyrazolone, 1-m-sulfophenyl-3-methyl-5-pyrazolone, (3) indoxyl and thionindoxyl, (4) N-homophthalylamines, e. g., N-homophthalylaniline, N-homophthalyl-n-dodecylamine, N-homophthalyl-beta-naphthylamine, (5) 2,4-dihydroxyquinoline, (6) p-nitrobenzylcyanide, (7) diketohydrindene, (8) malonamides, e. g., ethyl N-phenylmalonamate, N,N-diphenylmalonamide, (9) phenacylpyridinium bromide, (10) hydroxypyridine, (11) cyanoacetanilide, ethyl/cyanoacetate.

In the method of preparing these polymeric color-forming binding agents employing formaldehyde to connect the color former to the vegetable protein chain, the formaldehyde may be in any form. Thus, it can be used as solid paraformaldehyde or dissolved or suspended in water or solvents for the color former, or as formaldehyde-releasing compounds such as trioxane, hexamethylenetetramine, methylene diacetate. Compounds which form methylol derivatives such as chloromethyl ether may be used. Alternatively, other bi-functional condensing agents, e. g., dimethylol derivatives of amides, ureas, etc., e. g., dimethylolurea, dimethyloladipamide, dimethyloloxamine and their ethers such as bismethoxymethylurea may be used in place of formaldehyde for linking the dye intermediates to the polymer chain.

The light-sensitive color yielding compositions described above which consist of a hydrophilic protein dye intermediate or color former and a light-sensitive silver salt can be made with a wide variety of silver salts. Thus simple and mixed silver chlorides, bromides and iodides can be incorporated with the novel color former as binding agents. The dispersion may advantageously be made by dissolving the hydrophilic protein color former in a solvent therefor and mixing a water soluble inorganic halide there-

with followed by the admixture of a solution of a water-soluble silver salt. Suitable solvents for the protein derivatives include water containing 10-50 per cent of a water-miscible volatile alcohol, e. g., methanol and ethanol. The water soluble inorganic halides, e. g., sodium bromide, potassium bromide, ammonia bromide and the corresponding chlorides and iodides may be simply dissolved in water. Similarly, water-soluble silver salts such as silver nitrate, silver sulfamate, silver citrate, silver acetate can also be added from water solution. The silver halides are prepared in the hydrophilic protein color former whereby a light-sensitive colloid composition is formed. It can be further treated to improve its photographic properties by the procedures employed with gelatino silver halide emulsions. For instance, the hydrophilic protein color former can be coagulated, washed, ripened, free from excess soluble salts adjusted to the desired pH, digested and then coated. As desired the compositions may be set and shredded for later use in coating solutions.

Various types of sensitizing dyes which modify the spectral sensitivity of the resulting emulsion can be added if desired. Suitable dyes include the cyanines, carbo-pseudo cyanines, merocyanines or rhodanines, etc., which are useful in sensitizing gelatin silver halide emulsions. Similarly, emulsion sensitizers, e. g., sodium thiosulfate and sodium hyposulfite; allyl thiourea, allyl isothiocyanate and anti-fogging agents, e. g., benzimidazole, nitrobenzimidazole, benzotriazole, and methyl thiouracil; preservatives, e. g., thymol, menthol, and alcohol; hardeners, e. g., chrome alum, potassium alum, formalin, and dimethylolurea; and other emulsion constituents can be used if desired at various stages preferably prior to coating.

The final coating compositions can be applied to a support or to a water-permeable colloidal layer on a support in the same manner that gelatino silver halide emulsions are coated. After drying the resulting elements can be exposed and processed in various manners to form colored images.

Multilayer films other than those described in the above examples may be prepared according to this invention. Thus, the layer for recording red light and producing the blue-green part image may be sensitized to green and red light both and protected by a green absorbing red filter layer between it and the exposure, or the sensitive layers may be coated in a different order, or one of these layers may on the other side of the support. In addition, the present invention can be applied to a two-color process by suitable selection of dye intermediate nuclei and sensitizing compounds. Further, the invention can be combined with other processes for producing colored photographic images. For example, in the case of a three-color film, two-color images may be produced on one side of the support by the process of this invention, whereas the remaining color image may be produced, for example, on the other side of the support by toning or on the same side by an imbibition process. The term hydrophilic as used in this application when referring to the color formers or dye intermediates is intended to denote vegetable protein color formers which include in their molecular structure nuclei which are capable of forming aquinoneimine (including indophenol, indoamine, and indoamine) dye or an azomethine in color coupling development of silver salt images and

which in the form of thin layers, e. g., one to ten or more microns in thickness are insoluble in water at 20° C., but are freely water-permeable. They should moreover be soluble to the extent of 5 parts by weight in 100 parts of a boiling aqueous solution containing less than 50 and preferably less than 25 per cent of ethanol.

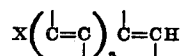
An advantage of the new film elements of this invention resides in the increased ability of the dye images formed. Another advantage resides in the toughness and flexibility of the light-sensitive layers. A further advantage resides in the fact that the color yielding layers produce the maximum color density obtainable from the amount of silver salt reduced by the color coupling development. This admits of a saving of silver and silver halides. The lower amount of silver halides permitted by the use of these elements is of major importance in multilayer color films because the intermost layers receive light passing through layers intervening the source of light. The less silver halides the upper layers contain, the more light passes through to the lower layers and less scattering and absorption of light occurs. This results in faster films having a greater degree of definition and resolution than is obtainable by the use of immobile color formers in gelatin silver halide layers.

The products of this invention have wide utility in color photography. They can be utilized as a direct taking stock or in duplicating or copying and in making color prints on paper. Any number of color positives can be produced from a single color negative made and treated in accordance with the above procedures. The color negatives or positives can be used for preparing color separation negatives or positives by varying the printing light. The new film elements have broad utility in processes of color photography involving the formation of azo dye images. Thus, they may be used in the procedures described in United States Patent No. 2,297,732 and 2,342,620. In addition they are useful in other azo processes such as the hydrazine processes described in United States Patent No. 2,220,929 and 2,339,213 wherein azo dyes are produced on color development with aromatic hydrazine reduced agents. They are also useful in catalytic bleach processes employing silver or silver salts images and in the formation of silver anti-diazotates followed by coupling to form azo dye images.

It is to be understood that this invention is not limited to the specific embodiments described above as many apparent widely different embodiments of the invention may be made without departing from the spirit and scope thereof.

What is claimed is:

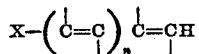
1. A color yielding element comprising a support bearing at least one layer composed of a hydrophilic vegetable protein color former, said compound having a plurality of color former groups, each being linked by a carbon to carbon linkage to a $-\text{CH}_2-$ group to an amino nitrogen atom of the protein molecule, each color former group containing in one of its tautomeric forms a composition of the structure



where X is taken from the group of primary amino, secondary amino and hydroxyl groups and n is a number from the group consisting of 0 and 1, said layer having light-sensitive silver halides dispersed therethrough.

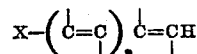
2. An element as defined in claim 1 wherein the protein is zein.

3. A color yielding element comprising a support bearing at least one layer composed of a hydrophilic vegetable protein color former, said compound having a plurality of color former groups, each being linked by a carbon to carbon linkage to a $-\text{CH}_2-$ group to an amino nitrogen atom of the protein molecule, each color former group containing in one of its tautomeric forms a composition of the structure



where X is taken from the group of primary amino, secondary amino and hydroxyl groups and n is a number from the group consisting of 0 and 1, said layer having light-sensitive silver halides and a sulfur sensitizer dispersed there-through.

4. A color yielding element comprising a support bearing at least one layer composed of a hydrophilic vegetable protein color former, said compound having a plurality of color former groups, each being linked by a carbon to carbon linkage to a $-\text{CH}_2-$ group to an amino nitrogen atom of the protein molecule, each color former group containing in one of its tautomeric forms a composition of the structure



where X is taken from the group of primary amino, secondary amino and hydroxyl groups and n is a number from the group consisting of 0 and 1, said layer having light-sensitive silver halides and a color sensitizing agent dispersed therethrough.

ANDREW B. JENNINGS.