

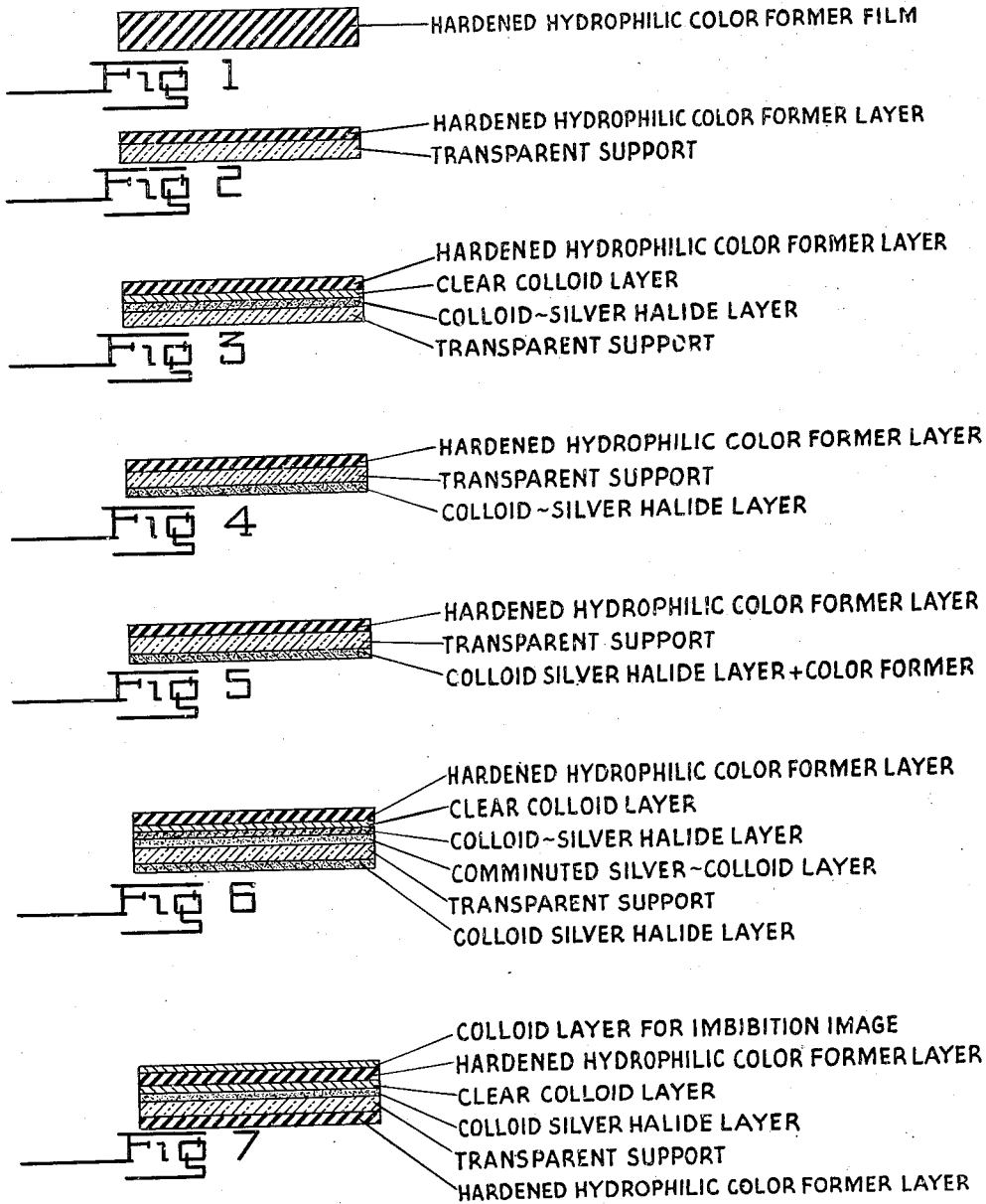
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COLOR YIELDING PHOTOGRAPHIC ELEMENTS

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COLOR YIELDING PHOTOGRAPHIC ELEMENTS

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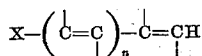
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This invention pertains to photography. More particularly, it pertains to improved color yielding elements for the recording of photographic colored images which have at least one stratum composed of a hardened hydrophilic synthetic color former. It also relates to processes of making such elements.

An object of this invention is to provide new materials for use in color photography. A further object is to provide improved elements for recording photographic images in color. A more specific object is to provide improved color yielding elements useful in the procedures of United States Patent 2,328,034. Still another object is to provide strong, stable, flexible, light-insensitive color yielding elements which are capable of forming quinoneimine or azomethine dyes.

The above objects may be accomplished by the invention hereinafter described and illustrated in the accompanying drawing.

The novel color-yielding elements of this invention have at least one stratum composed of a hardened hydrophilic synthetic color former. These color formers are hydrophilic synthetic colloids having as a part of their chemical structure color former nuclei which have been hardened by reaction with a protein hardening agent. Such nuclei or color former components 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, betachlorethyl, beta-hydroxyethyl, benzyl, etc., and n is 0 or 1. Thus X may be a primary or secondary amine group. Such active coupling groups are found in reactive methylene dye intermediates and in aromatic hydroxyl and amino compounds and include reactive ethenol, aminoethenyl, 4-hydroxy- and 4-amino-1,3-butadienyl groups. These groups are found in phenols, naphthols, anilines, naphthylamines, acylacetamides, cyanoacetamides, beta-ketoesters, pyrazolones, N-homophthylamines, coumaranones, indoxyls, thioindoxyls, etc.

The hydrophilic synthetic colloid color formers can be hardened prior to being cast into layers or films or after formation by reaction with a protein hardening agent. Suitable agents include aldehydes and ketones and aldehyde-yielding materials, such as formaldehyde, acetaldehyde, glyoxal, acrolein, methylol ureas, e. g., methylolurea and dimethylolurea. The amount

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of hardening agent per part of color former can be varied over a fairly wide range, e. g., 0.5+1.0 part per part of color former. The hardening treatment should be carried out to such an extent that a layer 15 microns in thickness will not show any solubility in a 5% solution of Na₂CO₃ at 68° F. in 5 minutes.

Various types of color yielding elements embodying the novel strata are comprehended by the invention. One practical type consists of a film or foil composed solely of the hardened hydrophilic colloid color former which is of sufficient thickness to permit handling by the technician without rupture or disintegration. A thickness of at least 5 to 10 microns is generally necessary for adequate film strength but thicknesses of 3 to 50 microns represents a practical range.

Another type consists of a support which may be composed of paper, metal, cellulose derivatives, high polymers, e. g., nylon, etc., which has imposed thereon at least one layer composed solely of a hardened color former.

Still another type consists of a support which may be composed of paper, metal, cellulose derivatives, high polymers, e. g., nylon, etc., which has imposed thereon at least one layer composed solely of a hardened hydrophilic color former, and at least one light-sensitive silver salt layer; the hardened hydrophilic color former layers being outer-most and physically separated by a stratum which prevents color coupling coaction with any silver salt layer of the element. In some instances the stratum may be a water impermeable membrane or a film base. In others it may be somewhat water-permeable but of such thickness that color coupling cannot take place through the stratum.

The supports for certain of the elements of this invention may be transparent and quite thin so long as they possess sufficient mechanical strength for processing and handling, or they may be adhesively joined to a paper or transparent support of greater strength and/or thickness or to a thin transparent membrane or support.

In the accompanying drawing which forms a part of this specification there are shown several representative types of color yielding elements.

Fig. 1 is an enlarged cross-sectional view of a color yielding element comprising a film composed of a hardened hydrophilic color former.

Fig. 2 is an enlarged cross-sectional view of another color-yielding element comprising a support and a layer of a hardened hydrophilic color former.

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Fig. 3 is an enlarged cross-sectional view of another element comprising a support, a colloid silver halide layer, a clear colloid layer, and a layer of a hardened hydrophilic color former.

Fig. 4 is an enlarged cross-sectional view of another element comprising a support, a colloid silver halide layer on one side thereof and a layer of a hardened hydrophilic color former on the other side.

Fig. 5 is an enlarged cross-sectional view of an element similar to that of Fig. 4 wherein the silver halide layer contains a color former.

Fig. 6 is an enlarged cross-sectional view of an element similar to that of Fig. 3 which contains a gelatin-comminuted silver layer on the support and a hardened hydrophilic color former layer on the other side of the support.

Fig. 7 is an enlarged cross-sectional view of an element comprising a support, a colloid silver halide layer and a clear gelatin layer on one side thereof and a colloid color layer on the other side.

The above figures will be further explained in the following examples.

Example I

A solution was prepared by admixing 25 grams of salicylaldehyde-ortho-sulfobenzaldehyde polyvinyl acetal with 5 cc. of 5N NaOH and 500 cc. of water. To this was added 5 grams of dimethylolurea and 50 cc. of water. The resulting solution was heated to 80° C. for 30 minutes. It was cast onto a polished metal support in the form of a thin film and allowed to dry. The resulting film was stripped from the support and was found to be insoluble in water and alkaline photographic developer solutions. It had a structure like that illustrated in Fig. 1 of the drawing.

A color separation negative was printed onto a positive film bearing a gelatino-silver halide layer and the film was developed and fixed using standard solutions. The positive silver images were then bleached in an aqueous solution of potassium ferricyanide to silver ferrocyanide images and the film was then washed thoroughly and soaked in 10% sodium carbonate. The color yielding film element described in the preceding paragraph was soaked in a solution of the following composition:

Diethyl-p-phenylenediamine	grams	10
Na ₂ SO ₃	do	2
N-methyl-p-aminophenol sulfate	do	0.6
Water to	cc	1000

The two films were pressed together and held in intimate contact until a blue-green color image formed in the latter element and they were then separated. The resulting element can then be mounted on a support with similar elements prepared from different color separation positives and similar elements yielding different colors, e. g., magenta and yellow which are mounted on each other in register to form a three-color picture as described in United States Patent 2,328,034.

Example II

A solution was prepared by mixing 5 grams of 3-allyl salicyl acetal of polyvinyl alcohol with phthalaldehydic acid, 15 cc. of dimethyl formamide, 1.5 cc. of 5N NaOH and 250 cc. of water. To the solution were added 3 grams of dimethylolurea and 50 cc. of water. The resulting solution was then coated onto a cellulose acetate film base to form an element of the type shown in Fig. 2 of the drawing.

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The element can be used for the formation of the blue-green color of three-color prints after the manner disclosed in Example I of United States Patent 2,328,034.

Instead of coating the film onto a permanent support, it can be cast as described in Example I hereof; or the element can be used as the base element on which two different colored image bearing elements free from supports can be mounted in register.

Example III

A solution was prepared by mixing 10 grams of the polyvinyl acetal of N(m-formylphenyl)-1-acetoxy-2-naphthalenesulfonamide, 2 cc. of 5N NaOH, 40 cc. of ethanol and 160 cc. of water. To the solution were added 3 grams of dimethylolurea and 25 cc. of water.

The resulting solution was cast onto a paper support forming an element of the type shown in Fig. 2 of the drawing. Upon color coupling development by imbibition contact with a bleached color separation positive containing silver ferrocyanide images and impregnated with 10% sodium carbonate as described in United States Patent 2,328,034 blue-green images formed in like manner.

Example IV

The reaction product of polyvinyl alcohol and m-benzoylacetamidobenzaldehyde ethylene glycol acetal may be substituted for the polymer in Example III resulting in elements containing a yellow color yielding layer or stratum.

Example V

A color yielding element of the type shown in Fig. 3 was prepared by coating a gelatino-silver halide emulsion layer onto a cellulose acetate film base having a gelatin-phenol substratum. On the latter layer was coated the solution described in Example I to form an outer hardened color forming polyvinyl acetal color former layer.

The silver halide layer is then exposed by printing a color separation negative onto it and developed in an ordinary positive type metolhydroquinone developer and washed. The outer layer is then converted into a colored image bearing layer by imbibition contact development with a bleached color separation positive prepared from another color separation negative. The inner layer is then developed in a color coupling developer solution containing N-diethylaminoaniline and an orange-red color former consisting of a mixture of phenylmethylpyrazolone and acetoacetaniline in a 5 to 4 ratio and having the following composition:

1-phenyl-3-methylpyrazolone-5	grams	10
Acetoacetanilide	do	8
Diethylparaphenylenediamine	do	3
Na ₂ CO ₃	do	30
H ₂ O	liter	1

The silver and silver salts are then removed by means of Farmer's reducer, washed and dried.

In Murray United States application Serial No. 500,198 filed August 27, 1943, now abandoned, there are described several alternative ways of developing elements similar to the multilayer elements described above. The present elements differ only in having a hardened hydrophilic color former layer instead of a non-hardened layer and can be processed to colored pictures by any of the procedures described in said application.

The color yielding elements may contain light-sensitive layers composed of simple or mixed silver halides which may contain the usual sensitizers, desensitizers, stabilizers, fog inhibitors, emulsion hardeners, etc. Suitable types include silver chloride, silver bromide, silver chlorobromide, silver chloride-bromide-iodide, silver bromide-iodide, etc., which may contain cyanine, cyazine, merocyanine, styryl and related sensitizing dyes. The silver halide layers are anchored to the supports by means of the usual subbing solutions. Such solutions are also useful for anchoring dye component layers to bases.

While the above description has been restricted for the most part to the formation of dye images in non-photographic layers by bringing a separate element containing reducible silver salt images into contact with the dye yielding layer in the presence of the constituents of a color coupling developer, it is also possible to form such dye images in separate elements containing images other than silver salt images.

The dye components or color formers are in general selected so that they together form a composite dye image which reproduces a color scene or object. Thus the dye components used in the layer which is treated by contact development in general should form dyes complementary in color to that which exposed the color separation negative record employed therewith. Likewise, the dye components or color formers used in the inner layer or the developing solution used for processing thereof should form a dye which is complementary in color to that which exposed the color separation record. When reproduction of an original color object field is not a desideratum, a dye which forms any desired color can be used.

As examples of suitable orange-red color formers which can be used in emulsion layers or in developing solutions upon being dispersed therein if necessary by means of alkali and/or alcohol are the diacetylacetamino-1,2,4,5-benzobisthiazoles of United States Patent 2,140,540 of which difuroylacetamino-1,2,4,5-benzobisthiazole and diacetoacetamino-1,2,4,5-benzobisthiazole are especially useful. Additional yellow color formers include 2-hydroxy-3-naphthoylaminobenzoylacetanilide, sodium stearoylaminobenzoylacetanilide-p-carboxylate, furoylacet-p-amino phenylamyl ether (described in U. S. Patent 2,184,303) and di-picolinoylacetbenzidine.

Suitable non-migratory magenta color formers which are especially useful are 1-(3'-sulfo-phenyl)-3-(4''-stearoylamino-phenyl)-3-(4''-dodecoylamino-phenyl)-5-pyrazolone, 4,4'-bis(3''-methyl pyrazolonyl-1'')-diphenyl (described in U. S. Patent 2,200,924), 4,4'-methylene-bis(m-stearoylaminophenyl)-methyl pyrazolone (described in U. S. Patent 2,294,909), and 4,4'-o-sulfobenzylidene-bis-(phenyl methyl pyrazolone) (described in U. S. Patent 2,294,909).

Suitable non-migratory blue-green color formers of especial utility include 4,4'-di-(1-hydroxy-2-naphthoyl-amino) diphenyl, 1-hydroxy-2-carboxy-5-dodecoylamino naphthalene, 1-N-stearoyl-4-N-(1'-oxy-2'-naphthoyl)-phenylene-diamine sodium sulfonate, resorcinol mono-n-dodecyl ether (described in U. S. Patent 2,166,181), product of p-hydroxy-benzoic acid and formaldehyde (described in U. S. Patent 2,323,481), product of polyvinyl alcohol and salicyl-aldehyde (described in U. S. Patent 2,310,943).

In the multilayer elements described in Figs. 6 and 7 the colloid-silver halide layers are selectively sensitized to different regions of the spectrum

and the color formers are chosen so that they form dyes complementary in color to the utilized sensitivity of the silver halide layers. Thus for blue, green and red sensitive layers there should be used color formers which form yellow, magenta and blue-green dyes respectively. These elements are similar to those described in U. S. Patent 2,369,171 but utilize hardened hydrophilic color formers.

Additional color formers which are useful not only with aryene diamino developing agents, but also the aryl hydrazines are described in U. S. Patents 2,154,918, 2,166,181, 2,178,612, 2,179,228, 2,179,238, 2,179,239, 2,213,986, 2,179,244, 2,186,045, 2,186,719, 2,186,734, 2,186,735, 2,186,736, 2,186,849, 2,140,540, 2,133,937, and 2,200,924.

The preferred developing agents which may be used in the dye coupling development steps hereof are derivatives of p-phenylenediamine and particularly the asymmetric dialkyl p-phenylenediamines of 1 to 4 carbon atoms, e. g., p-aminodimethyl-aniline, p-aminodiethylaniline, p-aminobutylaniline, etc. Other developing agents which may be used include p-phenylenediamine itself, p-methylaminoaniline, p-ethylaminoaniline, p-aminophenol, N,N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 1,2,5-toluylenediamine, 2-amino-5-diethylamino-toluene, p-amino-N-phenylmorpholine, N-p-aminophenyl-piperidine, N-methyl-N-hydroxyethyl-p-phenylenediamine, N-butyl-N-hydroxyethyl-p-phenylene-diamine, 2-amino-5-(N-butyl-N-hydroxyethyl) aminotoluene, beta-gamma-dihydroxy-propyl-p-phenylenediamine, etc. These aromatic amino developing agents in the form of their organic or inorganic acid salts may be used in the preparation of the developing solutions. The salts are in general more stable than the free bases. As examples of suitable salts, mention is made of the hydrochlorides, sulfates, acetates, etc.

In place of the particular hydrophilic color formers described in the working examples, there are many others which can be hardened in like manner. Thus any of the specific polyvinyl-acetal color formers described in U. S. Patent 2,310,943, the acetals of hydroxyl polymers described in U. S. Patent 2,320,422 and the condensation products of phenols and naphthols or hydroxy aromatic carboxylic or sulfonic acids with difunctional resin-forming reagents such as aldehydes and ketones, etc. described in U. S. Patent 2,323,481 can be hardened and cast into layers in like manner. Still other hydrophilic color formers which can be similarly hardened are described in U. S. Patents 2,178,612, 2,186,734, 2,307,399 and in application Serial No. 528,943, filed March 31, 1944, now U. S. Patent 2,397,865.

A number of different bleaching procedures can be used for the elements which are used for contact development. Films or plates containing a positive or negative silver image can be bleached to redevelopable silver salts, as for example with potassium ferricyanide, copper chloride, or copper bromide in the presence of an oxidizing agent such as chromic acid, potassium ferricyanide in the presence of alkali carbonate or ammonia, etc.

In place of the sodium carbonate solutions may be used potassium carbonate, potassium hydroxide, lithium carbonate, and other aqueous solutions for soaking the bleached photographic elements. The concentrations may range somewhat depending on the pH of the particular agent, the bleaching agent used, the dye intermediate used and the concentration of the developing

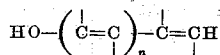
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agent, and the amount of sulfite present. In general, amounts of 2 to 15% are practical.

The novel elements of this invention have the advantage that the layers composed of the hardened color formers have greater dimensional stability than the previously proposed elements. The elements of the type described in Fig. 1 of the drawing have greater strength and can be made thinner than unhardened layers. The hardened layers permit the use of many hydrophilic color formers which are too sensitive to water for successful use. The hardened layers moreover are better able to withstand machine processing.

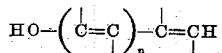
What is claimed is:

1. A photographic element comprising a support in sheet form bearing an outermost light-insensitive layer composed of a polyvinyl acetal color former containing an active dye coupling structure of the formula



where n is a number taken from the class consisting of 0 and 1 which color former has been hardened by treatment with a protein hardening agent taken from the class consisting of aldehydes, ketones, and aldehyde yielding compounds, and at least one light-sensitive colloid silver halide emulsion layer separated from said color former layer by a water-permeable layer of such thickness that no color coupling action takes place between the color former and silver halide.

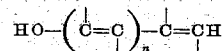
2. A photographic element comprising a transparent water-impermeable film base, a light-sensitive colloid silver halide emulsion layer on one surface of said base and on the other surface of said base a light-insensitive layer composed of a polyvinyl acetal color former containing an active dye coupling structure of the formula



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where n is a number taken from the class consisting of 0 and 1 which color former has been hardened by treatment with a protein hardening agent taken from the class consisting of aldehydes, ketones and aldehyde yielding compounds.

3. A photographic element comprising a transparent water-impermeable film base, a light-sensitive colloid silver halide emulsion layer on one surface of said base and on the other surface of said base a light-insensitive layer composed of a polyvinyl acetal color former containing an active dye coupling structure of the formula



where n is a number taken from the class consisting of 0 and 1 which color former has been hardened by treatment with a methylolurea.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,169,250	Izard	Aug. 15, 1939
2,211,323	Fordyce	Aug. 13, 1940
2,245,218	Murray et al.	June 10, 1941
2,253,078	Lowe	Aug. 19, 1941
2,279,411	Peterson	Apr. 14, 1942
2,282,001	Russell et al.	May 5, 1942
2,310,943	Dorough et al.	Feb. 16, 1943
2,320,422	Frohlich	June 1, 1943

FOREIGN PATENTS

Number	Country	Date
503,752	Great Britain	Apr. 11, 1939
537,256	Great Britain	June 16, 1941