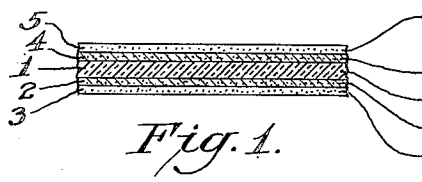
March 27, 1951 O. W. MURRAY 2,546,400

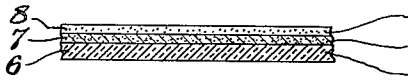
COLOR YIELDING ELEMENT FOR COLOR PHOTOGRAPHY

Filed Dec. 11, 1945



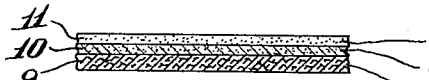
Polyvinyl-o-Benzaldehyde Sulfonic Acid Acetal and Blue Green Color Former
Silver Halide
Transparent Support
Silver Halide Emulsion
Polyvinyl-o-Benzaldehyde Sulfonic Acid Acetal and Magenta Color Former

Fig. 1.



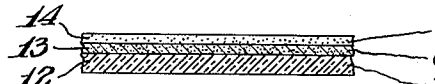
Methyl Cellulose and Magenta Color Former
Gelatin-Silver Halide
Transparent Support

Fig. 2.



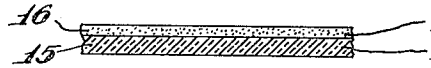
Sodium Alginate - alpha-Naphthol
Gelatin-Silver Halide
Baryta Coated Paper

Fig. 3.



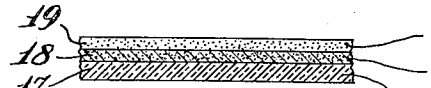
Cellulose Acetate Phthalate-Blue Green Color Former
Gelatin Silver Halide
Transparent Support

Fig. 4.



Polyvinyl Acetal Magenta Color Former
Hydrolyzed Vinyl Acetate/Ethylene Film

Fig. 5.



Gelatin-Sodium Caseinate-Yellow Color Former
Gelatin Silver Halide
Transparent Support

Fig. 6.

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2,546,400

UNITED STATES PATENT OFFICE

2,546,400

COLOR YIELDING ELEMENTS FOR COLOR PHOTOGRAPHY

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Application December 11, 1945, Serial No. 634,256

11 Claims. (Cl. 95—2)

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This invention relates to photography and more particularly to color-yielding elements for color photography. Still more particularly it relates to multilayer films for color photography. Still more particularly it relates to photographic films which have two differentially sensitized silver halide emulsion layers and two respectively coactive adjacent layers containing color formers, said layers being removable in aqueous baths. The invention also relates to the preparation of such elements and to processes for the production of dye images therefrom.

A relatively large number of processes for producing multicolor images which involve the use of color formers have been proposed. The color formers couple with the oxidation products of primary aromatic amino color developing agents, e. g., diethylparaphenylene diamine hydrochloride and 2-amino-5-diethylamino toluene hydrochloride, formed during the development of silver salt images and produce quinoneimine or azomethine dye images in situ with the silver salt images. After removal of the latter, a dye image remains. Films for three-color photography, for example, have been proposed which contain a plurality of silver halide emulsion layers and filter layers which contain immobile color formers and are so arranged and sensitized that each will record about one-third of the visible spectrum.

Another type has been proposed which instead of having the color formers in the silver halide emulsion layers have them in adjacent water-permeable colloid emulsion layers.

Each of the above types suffer from some disadvantages. When color formers are placed in emulsion layers they often reduce the overall sensitivity, reduce or destroy the color sensitized characteristics, and/or produce general emulsion fog. This is particularly true of the high molecular weight, non-migratory type. Others wander in emulsion layers and cause dilution and contamination of color. These disadvantages are overcome when color formers are placed in adjacent layers. The resulting films, however, sometime do not have an adequate density of dye image or dye image contrast when immobile color formers are used. When the mobile types are used in continuous processing systems, e. g., of cine film, an accumulation of leached color former obtains in the developing solution which gives rise to color contamination in the layers.

The above objects may be accomplished and the above disadvantages obviated by the novel color-yielding elements and processes of this invention. It has been found that if color formers which migrate in gelatino-silver halide emulsions are incorporated in a water-soluble, dilute alkali-insoluble colloid and coated on a gelatino-silver halide emulsion layer, useful color-yielding elements are obtained. The colloids should be substantially insoluble in aqueous alkaline developer solutions containing 2% or more by weight of dissolved inorganic salts. All of the advantages gained by the use of color formers in adjacent layers are obtained. In addition, the elements have other decided advantages. During color coupling development the color formers migrate to the adjacent silver halide grains and form dye images in situ with the developed silver images instead of in the adjacent colloid layers. Any color former which is not utilized during color coupling development can readily be removed from the film by washing the layer of water-soluble, dilute alkali-insoluble colloid from the element. This can be accomplished by washing with water immediately after development. The removal of the layer improves the quality and clarity of the final elements.

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A satisfactory element for printing two-color components can be made by coating one side of a transparent film base with a gelatino-silver halide emulsion layer which is sensitive to one portion of the visible spectrum, e. g., blue, green. On such layer is coated an aqueous solution of a mobile orange-red color former and a water-soluble, dilute alkali-insoluble colloid. The other side of the base is coated with a gelatino-silver halide emulsion layer which is sensitive to a different portion of the visible spectrum, e. g., orange-red. On this layer there is coated an aqueous solution of a water-soluble, dilute alkali-insoluble colloid containing a blue-green, mobile color former. Appropriate color separation records are printed onto the respective records and the element is color developed. The outer layers are removed by washing in water. The silver and silver salts can then be removed by appropriate treatment, e. g., bleaching with Farmer's reducer. The resulting element contains dye images in the original silver halide layers. The elements have good clarity, dye density, and contrast. There was no evidence of significant leaching of the color former into the developer solution on inspection of the developer solutions. Such results indicate and a uni-directional travel of the intermediate.

When gelatin layers containing immobile or non-diffusing color formers are placed adjacent to gelatino-silver halide emulsion layers in like manner, quite different results are obtained. The

dye image is formed in the color former layer only. The images, moreover, have very low dye contrast. The gelatin layer could not be removed by a simple washing procedure.

Likewise when gelatin layers containing mobile or diffusing color formers were coated on gelatino-silver halide emulsion layers and exposed and color processed in like manner different results were obtained. Dye images were formed in the silver halide emulsion layer and in the adjacent gelatin layer. The images were extremely flat and the developer solution evidenced considerable contamination by color former which had leached from the film.

In the preferred aspect of the invention the adjacent layers are composed of polyvinyl acetals of aromatic monoaldehydes having sulfonic acid or carboxylic acid groups, and mobile color formers. Suitable acetals of this type can be prepared from polyvinyl alcohols and substantially completely hydrolyzed polyvinyl esters and aldehyde carboxylic or sulfonic acids such as ortho-, meta-, and para-benzaldehyde sulfonic acid, acetaldehyde disulfonic acid, naphthaldehyde sulfonic acids, e. g., 1-naphthaldehyde-2-sulfonic acid, 1-naphthaldehyde-4-sulfonic acid, 2-naphthaldehyde-5-sulfonic acid, and the corresponding carboxylic acids, by condensation in the presence of mineral acids or acid salts after the manner described in German Patent No. 643,650. Such acetals are insoluble in aqueous alkaline photographic developer solutions containing 2% or more by weight of dissolved inorganic salts. The condensation should be carried out until the vinyl alcohol groups have been acetalized.

Further the particular acetals just described possess high resistivity to alkaline developer solutions and appear to acquire an extremely hard surface when treated with them. Mobile or diffusing color formers which have been incorporated in this material and coated over a gelatin silver halide emulsion layer exhibit uni-directional diffusion into the emulsion layer. Only an insignificant quantity tends to diffuse into the alkaline developing solution. A cross-sectional study of the film shows that dye images are formed in the gelatin emulsion alone with no image formation in the adjacent resin-dye intermediate layer. This rapid uni-directional diffusion gives rise to strong contrasting dye images in the light-sensitive gelatin layer which is extremely important in color printing films.

The invention will be further illustrated but is not intended to be limited by the following examples. The parts are by weight.

Example I

A photographic element as illustrated in Fig. 1 of the drawing was made by coating onto the respective sides of a cellulose acetate film base 1 a gelatino-silver bromide iodide emulsion containing 15 grams of tartrazine per liter to form layer 2 having a coating weight of 80 mg./sq. decimeter, and to form similar layer 4. On layer 2 there was then coated a 5% aqueous dispersion containing the sodium salt of the polyvinyl alcohol acetal of ortho-benzaldehyde sulfonic acid containing 1 part of 3-methyl-1-(meta-aminophenyl)-5-pyrazolone per 5 parts of acetal to form thin layer 3. Similarly onto layer 4 there was coated layer 5 from a 5% aqueous solution of the aforesaid acetal containing 1 part of 2,4-dichloro-1-naphthol per 5 parts of acetal.

The film thus prepared was appropriately exposed to the green and red separation negatives of a set of three primary color separation negatives. The exposed element was then developed in

N-diethylparaphenylenediamine.HCl	grams	2.0
Na_2CO_3	do	30.0
KBr	do	0.5
Na_2SO_3	do	7.0
Water to	liter	1

and then washed, bleached in potassium ferricyanide and fixed in plain hypo. The outer polyvinyl acetal layers dissolved from the film during the wash and left a two component element. The film evidenced high speed and contrast, good color density and low stain. A satisfactory yellow component was applied by using a conventional imbibition matrix containing a yellow dye.

A similar film can be made by substituting a yellow color former such as acetoacetanilide for either the blue-green or magenta color former.

In addition to serving as a temporary binder for the color former, the acetal layers of the films operated as a very satisfactory anti-abrasion layer. All abrasions on the resin surface were, of course, removed in washing the layer off.

Example II

A photographic element is shown in Fig. 2 is made by coating a gelatino-silver bromide iodide emulsion onto a cellulose acetate film base 6 to form layer 7 having a coating weight of 80 mg. of silver halide per square decimeter. A layer 8 was coated onto the latter layer from a 3% aqueous methyl cellulose (containing less than 10% methyl groups) solution containing 0.8 part of 3-methyl-1-(metaaminophenyl) - 5 - pyrazolone per 5 parts of methyl cellulose. The film when exposed to an image and color developed in a solution like that of Example I had a magenta image in layer 7. The film had good anti-abrasion properties but was not as efficient as that of Example I.

Example III

The film illustrated in Fig. 3 is made by coating onto a baryta coated paper 9 a gelatino-silver bromide iodide emulsion layer 10 having a coating weight of 40 mg./sq. decimeter. Onto this layer is coated a 1½ aqueous solution of sodium alginate containing one gram of alpha-naphthol per 10 grams of sodium alginate to form layer 11. The film was exposed to a negative and developed in a color developer solution of the type disclosed in Example I containing 1 part of aluminum chloride per liter of developer. A dye image remainder in layer 10 after removal of the silver and silver salts by bleaching in 3.5% potassium ferricyanide and fixing in plain hypo. The sodium alginate layer 11 is readily removed by washing in water at any time after development. A source of strontium, barium or calcium ions, e. g., strontium nitrate, calcium chloride, calcium nitrate, can be substituted for the aluminum compound.

Example IV

The film element shown in Fig. 4 is made in like manner by coating a cellulose acetate film base 12 with a fine grain gelatino-silver bromide iodide emulsion to a weight of 60 mg. of silver halide per square decimeter forming layer 13. On this layer is coated a 3% aqueous mixture of 5 parts of cellulose acetate-acid phthalate sodium salt and one part of gelatin, having incorporated

thereon one part of 2,4-dichloro-1-naphthol per 7 parts of mixed binder to form layer 14 about .00008 inch in thickness.

Exposure to a negative and subsequent development in:

2-amino-5-diethyl amino toluene		
HCl	grams	3.0
Na_2CO_3 (anhydrous)	do	30.0
KBr	do	.25
Na_2SO_3 (anhydrous)	do	10.0
Water to	liter	1

yielded a blue-green image in layer 13. Layer 14 was removed readily in the wash after development.

Contamination tests run on the developing solution showed an extremely low concentration of leached color former.

Example V

A film element as illustrated in Fig. 5 of the drawing was made by preparing an aqueous emulsion of silver halide in a completely hydrolyzed vinyl acetate/ethylene interpolymer, as described in Example I of McQueen United States application Serial No. 528,945, filed March 31, 1944, now United States Patent 2,397,866, hardening it by treatment with formaldehyde or dimethylolurea. Hardening may be effected by heating a solution containing 5 parts of the polymer with one part of dimethylolurea at 80° C. for three hours. The resulting dispersion or emulsion was then coated on a casting wheel to a thickness of 0.0005 inch thick. A film element 15 composed of the hardened polymer emulsion was formed. A 40 mg./sq. decimeter layer 16 composed of the polyvinyl acetal of Example I having dispersed therein 1 gram of 1-phenyl-3-methyl-5-pyrazolone per 10 grams of acetal was deposited on film 15. The element was exposed, color developed and processed, after the manner described in Example I, and yielded a magenta image in the film 15. Layer 16 was easily removed during a water washing step following development.

Example VI

A cellulose acetate film base 17 as shown in Fig. 6 of the drawing was provided with an 80 mg. per sq. decimeter coating of a panchromatic gelatino-silver iodobromide emulsion layer 18. On this layer was deposited a 30 mg. per sq. decimeter coating 19 of a mixture of 20 parts of sodium caseinate to one part of gelatin containing one gram of acetoacetanilide per five grams of mixed binder from an aqueous solution thereof. Exposure and color development of the resulting film, after the manner described in Example I, resulted after removal of the silver and silver salts of a yellow image being formed in layer 18. The film was not as efficient as those described above using synthetic hydroxyl polymer and cellulose derivative dispersions but was still useful for preparing dye images.

In place of the specific color formers described in the above examples, there may be used a large number of other mobile color formers. The utility of a particular color former of this type can be readily determined by incorporating a conventional amount of the intermediate in a gelatin silver halide emulsion layer on a film base in ordinary illumination. One half of a strip of the film is immersed for ten minutes in a 5% sodium carbonate solution. After a short rinse, the complete strip is developed in a normal color developer. If the leached end is lighter in intensity than the unleached end then the color former is mobile and will be operable in the process. Generally those which show considerable mobility are more satisfactory than those of only slight mobility for this type of process.

The expression "color former" as used herein has the well-established meaning in the art and references to organic compounds which are capable of coupling with oxidized primary aromatic developing agents to form quinoneimine or azomethine dyes. Such compounds are also capable of condensation or coupling with diazotized aromatic amines to form azo dyes.

Color formers usually contain as the active group a structure which may be represented by the formula:

$$X-(C=C)_n-C=CH-$$

where X is HO— or RHN— or an aliphatic or substituted aliphatic group, and n is 0 or 1. The "free" or "dangling" valences may be, of course, satisfied by any of a large number of atoms or groups, e. g, hydrogen, halogen, carboxylic or sulfonic acid groups and their derivatives, fused rings, alkyl, aryl, alkoxy, aryloxy, etc. The hydrogen atom in the formula may be replaced by groups readily displaced in the coupling reaction, e. g., halogen atoms, carboxylic or sulfonic acid groups. This group is found in the reactive methylene dye intermediates and in aromatic hydroxyl and amino compounds and includes the reactive ethenol, aminoethenyl, 4-hydroxy- and 4-amino-1,3-butadienyl groups. These groups occur in phenols, naphthols, aromatic amines, acylacetamides, beta-ketoesters, pyrazolones, homophthalimides, cyanoacetyl compounds, etc. A large number of suitable mobile color formers are described in the British Journal of Photography, pages 647 and 648, for October 14, 1938. This article also discloses a large number of primary aromatic amino color developing agents which can be used in processing the elements described herein.

The reactive ethenol group as represented by

$$HO-C=CH-$$

occurs in phenols and naphthols which couple in the ortho position 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 $-NO_2$,

$$-C=O, \quad -C=N-, \quad -C\equiv N$$

and others. The CH_2 group is usually present between two such groups, for example, $-COCH_2CO-$, $-COCH_2CN$, $-COCH_2C=N-$, in a cyclic or acyclic system. The enol forms of these examples are

$$HOC=CH-CO-, \quad HO-C=CH-CN$$

and

$$HOC=CH-C=N-$$

respectively.

The reactive amino ethenyl group RHN—C=CH— occurs in aromatic amino compounds which couple in the ortho position.

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

$$HO-C=C-C=CH-$$

and

$$RHN-C=C-C=CH-$$

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

In place of the gelatin which is used as a binding agent for the light-sensitive silver salts, there may be substituted other water-permeable or hydrophilic colloids which are insoluble in photographic developing and fixing, etc. solutions. Suitable colloids include agar-agar, polyglycuronic acid, hydrophilic polymers, hydrophilic cellulose derivatives, e. g., ethyl cellulose, cellulose acetate containing 20 to 25% of solubilizing groups, such as acid phthalate groups, etc.

The colloid silver halide emulsion layers may contain in addition to the light-sensitive silver halide, e. g., silver chlorides, silver-chloride-bromide, silver-iodobromide, etc., various sensitizing dyes and other materials which are common in emulsion layers. Such additional materials include fog inhibiting agents, emulsion hardeners, emulsion perservatives, etc.

An advantage of this invention resides in the fact that it provides new elements for color photography which utilize mobile color formers. Color formers of this type do not give satisfactory results in gelatin layers espectially in multilayer photographic elements because such color formers migrate from layer to layer and into the processing solutions.

An additional advantage of the novel elements resides in the fact that the silver halide layers are protected during exposure and processing. The outer protective layer can be effectively removed by a simple washing operation. The color former-resin layer forms an effective antiabrasion surface for the emulsion layer which is also meritorious.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A photographic element comprising a support, a light-sensitive colloid-silver halide emulsion layer superposed thereon bearing on its entire surface a dry outer layer of a water-soluble colloid which is insoluble in aqueous alkaline developer solutions containing at least 2% by weight of dissolved inorganic salts, said outer layer containing a mobile color former which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

2. A photographic element comprising a support, a light-sensitive gelatino-silver halide emulsion layer superposed thereon bearing on its entire surface a dry outer layer of a water-soluble colloid which is insoluble in aqueous alkaline developer solutions containing at least 2% by weight of dissolved inorganic salts, said outer layer containing a mobile color former which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

3. A photographic element comprising a transparent support, a light-sensitive hydrophilic colloid-silver halide emulsion layer superposed thereon bearing on its entire surface a dry outer layer of a water-soluble colloid which is insoluble in aqueous alkaline developer solutions containing at least 2% by weight of dissolved inorganic salts, said outer layer containing a mobile color former which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

4. A photographic element comprising a transparent support, a light-sensitive gelatino-silver halide emulsion layer superposed thereon bearing on its entire surface a dry outer layer of a water-soluble colloid which is insoluble in aqueous alkaline developer solutions containing at least 2% by weight of dissolved inorganic salts, said outer layer containing a mobile color former which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

5. A photographic element comprising a support, a light-sensitive hydrophilic colloid-silver halide emulsion layer superposed thereon bearing on its entire surface a dry outer layer composed of a polyvinyl acetal of an aromatic aldehyde containing an acid group taken from the class consisting of carboxylic acid and sulfonic acid groups, said acetal having intimately dispersed therethrough a mobile color former which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

6. A photographic element comprising a transparent support, a light-sensitive gelatino-silver halide emulsion layer superposed thereon bearing on its entire surface a dry outer layer composed of a polyvinyl acetal of an aromatic aldehyde containing a sulfonic acid group, said acetal having intimiately dispersed therethrough a mobile color former which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

7. A photographic element comprising a transparent support having on each side thereof a light-sensitive colloid-silver halide emulsion layer superposed thereon bearing on its entire surface a dry outer layer of a water-soluble colloid which is insoluble in aqueous alkaline developer solutions containing at least 2% by weight of dissolved inorganic salts, said outer layer containing a mobile color former which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

8. A photographic element comprising a transparent support having on each side thereof a light-sensitive gelatino-silver emulsion layer superposed thereon bearing on its entire surface a dry outer layer of a water-soluble colloid which is insoluble in aqueous alkaline developer solutions containing at least 2% by weight of dissolved inorganic salts, said outer layer containing a mobile color former which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

9. A photographic element comprising a transparent support having on each side thereof a light-sensitive gelatino-silver halide emulsion layer superimposed thereon bearing on its entire surface a dry outer layer composed of a polyvinyl acetal of an aromatic aldehyde containing a sulfonic acid group, said acetal having dispersed therethrough a mobile color former

which is capable of coupling with oxidized primary aromatic amino developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

10. The process which comprises exposed a photographic element of the type defined in claim 1 to an object field, developing said element in a developer solution containing a primary aromatic amino developing agent, removing the silver and silver salts and washing the outer layer from the element at some stage after development.

11. A photographic element comprising a transparent support having a light-sensitive hydrophilic colloid-silver halide emulsion layer superposed on at least one surface a layer composed of sodium-o-sulfobenzaldehyde acetal of polyvinyl alcohol coated on the entire surface of at least one of said emulsion layers, said acetal having intimately dispersed therethrough a

mobile color former which is capable of coupling with oxidized primary aromatic amino color developing agents to form a dye taken from the group consisting of quinoneimine and azomethine dyes.

OTIS WILLARD MURRAY.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,905,438	Capstaff	Apr. 25, 1933
1,954,337	Staud	Apr. 10, 1934
1,966,330	Burwell	July 10, 1934
2,159,600	Murray et al.	May 23, 1939
2,196,226	Murray et al.	Apr. 9, 1940
2,323,246	Schneider et al.	June 29, 1943