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COLOR PHOTOGRAPHY

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FIG. 1

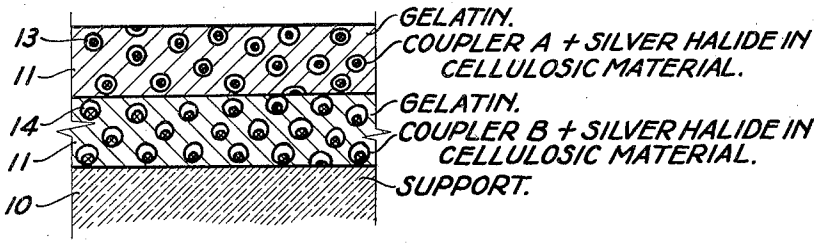


FIG. 2

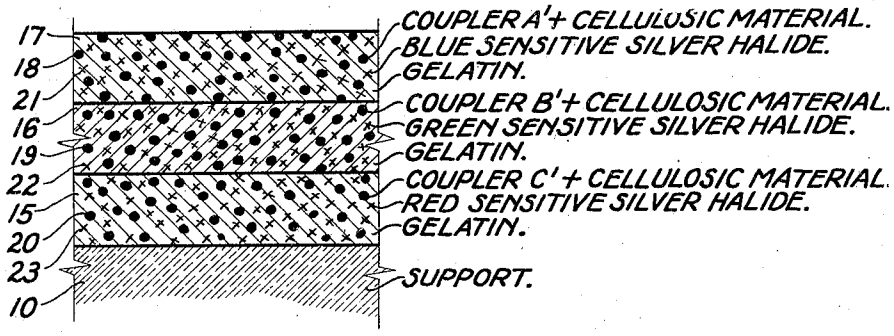
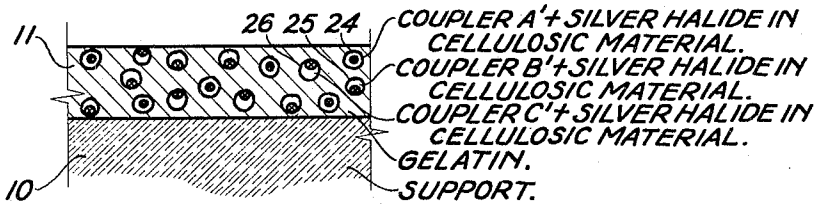


FIG. 3



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COLOR PHOTOGRAPHY

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14 Claims. (Cl. 95—2)

This invention relates to color photography and particularly to a method for incorporating coloring materials such as coupling compounds in a photographic layer.

Processes of color photography in which coloring materials are incorporated in a sensitive photographic layer are well known. A process of this type which is widely used commercially involves the coupling of a color forming compound with a primary aromatic amino developing agent to form a colored image. The coupling compounds used in this process are those having a reactive methylene group or a reactive phenolic group which couples with the oxidation product of the primary aromatic amino developing agent on photographic development. Suggestions have been made for incorporating these coupling compounds either in the developing solution or in the sensitive layer before exposure.

When the coupling compounds are incorporated in the developing solution, it is desirable that they be as soluble as possible in the developing solution so that upon photographic development they will penetrate the gelatin or other colloidal material of the sensitive layer and thereby permit the formation of a dye image in any exposed portion of the layer. However, when the coupling compounds are to be incorporated in the sensitive layer prior to exposure, they should be insoluble in order that they do not wander out of the layer during coating of a multi-layer material or during photographic development. Methods have been proposed for keeping the coupler compounds in the photographic layer, most of these involving the use of large molecules of coupler to prevent diffusion.

In U. S. Patent 1,055,155, March 4, 1913, Fischer describes a multi-color process using coupling compounds incorporated in the photographic layers. However, it has since been found that the coupling compounds known to Fischer could not be kept in the respective layers of a multi-layer material by merely mixing them with the gelatin of the emulsion. All of the compounds disclosed by Fischer diffuse from the layer and no color separation can be obtained in Fischer's process.

We have discovered a method for incorporating coloring materials such as coupling compounds in a photographic layer or layers so that they do not diffuse from the layer or layers but may be made to react with the oxidation product of an aromatic amino developing agent to form a colored image or colored images on photographic development. Our method does not involve the use of large coupler molecules, since the couplers which we propose to use, if merely mixed with a gelatine-silver halide emulsion, would diffuse from the emulsion when used in a multi-layer coating.

Our method consists in surrounding or mixing the coloring material, such as a coupling compound, with a water-insoluble but water permeable cellulosic binder and then dispersing this material in a colloidal material such as gelatin. For example if the coupler is mixed with a cellulose ester such as cellulose nitrate and this mixture is then dispersed in gelatin, there is little or no tendency for the coupler to diffuse from the cellulosic material into the gelatin. This is true even when the coupler is quite alkali-soluble and couplers can, therefore, be employed which have hitherto been regarded as unsuitable for incorporation in photographic layers either because of the readiness of their diffusion or because of the readiness of diffusion of dyes formed from them on photographic development. The coupling compounds with the cellulosic binder can best be suspended in the gelatin or other water permeable material by means of an organic solvent which is immiscible with water and, therefore, it is possible to use couplers which are extremely insoluble in aqueous alkaline solution and whose very insolubility in aqueous solutions hitherto made it difficult to incorporate them in materials such as gelatin. In some cases the use of a water-miscible solvent, such as alcohol, induces crystallization or wandering of the coupler, and for this reason it is frequently desirable to use water-immiscible solvents in dissolving the coupler.

In the accompanying drawing the figures represent enlarged sections of photographic film made according to various modifications of our invention.

According to the present invention, there is provided a photographic element having a plurality of differentially color sensitive photographic emulsions on a single support, at least one such photographic emulsion containing a coupling compound dispersed in a water-insoluble but water-permeable material. The element may have a plurality of layers of differentially color-sensitive emulsions on a single support, one at least of which layers consists of a dispersion of a water-insoluble but water-permeable binder containing a coupling compound in a gelatino-silver halide emulsion.

In the preferred modification of our invention, the photographic element may have an emulsion consisting of silver halide in gelatin, the gelatin having distributed therein finely dispersed parti-

cles of water-insoluble, water-permeable binder containing the coupling compound. A plurality of layers may be coated in this way each containing in the water-insoluble, water-permeable, cellulosic binder a coupling compound corresponding in a suitable manner to the sensitivity of the layer. For example, for the usual three-layer photographic element a red sensitive photographic emulsion would be chosen containing a blue-green coupling compound, a green-sensitive emulsion containing a magenta coupling compound and a blue-sensitive emulsion containing a yellow coupling compound.

In another modification of our invention the cellulosic particles themselves may contain the silver halide as well as the coupling compound. In this modification of our invention particles of cellulosic binder may be prepared each containing the appropriate coupling compound and properly sensitized silver halide grains and these may be separately dispersed in a plain gelatin layer so that a single layer element is obtained in which three differently colored images may be formed. Obviously the color sensitizer, where one is employed, is included with the silver halide in any case.

The water-insoluble, water-permeable cellulosic binder used to surround the particles of coupler may be a cellulose ester, such as cellulose nitrate or cellulose acetate, or a mixed organic ester of cellulose, such as cellulose acetate phthalate. Cellulose ethers may also be used. Collodion solutions, well known in the photographic art, may also be employed.

We have found that the cellulosic binders, although they prevent the diffusion of the coupler into adjacent water soluble layers, that is into the gelatin, are sufficiently accessible to the developing and other processing baths to enable the usual methods of color processing to be applied. By our method, therefore, known coupler compounds may be incorporated in photographic layers and the layers may be processed in the ordinary way. If desired, the color processing baths may contain ingredients such as organic solvents or wetting agents to facilitate the penetration into the water soluble binder.

We have found that different coloring materials and coupler compounds are respectively more suitable for use with different cellulosic binders and that with some combinations of coupling compound and cellulosic binder there is difficulty in obtaining satisfactory dye densities. This, we believe to be due to the difficulty of penetration of some of the cellulosic binders by the processing solutions. We have found that the structure or character of the cellulosic particles may be altered by incorporating in the cellulosic solution before dispersion substances which we shall call porosity modifiers. These materials change the porosity or consistency of the cellulosic material in the final state which it attains in the dried coating and enable better penetration of the photographic processing baths without inducing diffusion of the coupler. The following materials have been found suitable for this purpose:

Ethers

Ethylene glycol monobenzyl ether
Diethylene glycol monobutyl ether
Diethylene glycol monobutyl ether monoacetate
Diethylene glycol monoethyl ether
Diethylene glycol diethyl ether
Ethylene glycol monophenyl ether.

Phthalate esters

Dimethyl phthalate
Dibutyl phthalate
Benzyl phthalate
β-Ethoxyethyl phthalate

Alcohols

Heptadecanol
N-hexanol
Octyl alcohol

Miscellaneous esters

Benzyl benzoate
Triphenyl phosphate
Tricresyl phosphate
Ethyl palmitate
Methyl abietate
β-Ethoxyethyl sebacate
β-Ethoxyethyl maleate
β-Ethoxyethyl adipate
Ethylene glycol dilaurate

Miscellaneous compounds

p-Toluenesulfonanilide
Tripropionin
Trivalerin
Monoacetin
Triacetin

These modifiers may be used in amounts ranging from 5% to 50% of the amount of cellulosic material.

Porosity may be effectively decreased by hardening with chromium salts, particularly where cellulose acetate is used as the water-insoluble, water-permeable binder.

The following examples which are illustrative only, indicate various methods of forming sensitive photographic layers for color photography according to our invention.

Example 1

An emulsion is made by preparing a solution of the following ingredients:

N-butyl acetate	cc	1000
1-hydroxy-2-N-methyl-naphthanilide	g	10
Cellulose nitrate	g	20
Ethylene glycol monobenzyl ether	g	5

This solution is mixed with the following:

Gardinal (fatty alcohol sulfate)	g	2½
Water	cc	1250

The whole mixture is heated on a steam bath at 100° C. with constant stirring to evaporate all of the butyl acetate and some of the water. At the end of the evaporation process the volume has been reduced to about 300 cc. This dispersion of cellulose nitrate particles containing the coupler is added to 1000 cc. of a red-sensitive gelatino-silver halide emulsion. The resulting emulsion is coated on a suitable support. A yellow filter layer is then coated on the emulsion, consisting of tartrazine in gelatin.

The top layer consists of a green-sensitive silver halide gelatin emulsion to which has been added a cellulose nitrate dispersion made as described in the preceding paragraph, but using as the coupler a mixture yielding an orange-red dye upon development. Suitable couplers for this purpose are n-propyl-p-benzoyl acetamino benzene sulfonate and 2-cyanoacetylnaphthalene-sulfon-N-methyl anilide. These couplers are used in the amount of 5 grams each and producing an orange red dye upon development in a coupling developer. This emulsion is coated

as the top layer to produce a two-layer sensitive material.

In place of the tartrazine filter dye, the film may contain a yellow dye throughout the emulsions which is removable during processing either by virtue of its solubility or its susceptibility to a chemical action of one of the processing baths.

Example 2

A three-layer sensitive film is made as follows: The bottom layer consists of a red-sensitive gelatino-silver halide emulsion to which has been added a dispersion of cellulose nitrate containing, as a blue-green coupler, 5-phenoxy acetamino-1-naphthol, made as described in Example 1. The middle layer is a green-sensitive gelatino-silver halide emulsion with a cellulose nitrate dispersion containing as a magenta coupler 2-cyanoacetylnaphthalene-sulfon-N-methylanilide. Over the green sensitive layer is coated a thin intermediate layer containing a yellow filter material which is removed during processing, such as colloidal silver in gelatin. The top layer is unsensitized silver halide emulsion containing as a yellow coupler ω-benzoylacet-o-chloranilide and cellulose nitrate dispersion made as in Example 1.

The amount of coupler used in these dispersions may vary over wide limits. It is found necessary to adjust the coupler concentration in each particular case depending upon the dye density to be produced the thickness of the layers and other factors. In general the coupler concentrations may range from about 2½ grams to about 15 grams of coupler per liter of emulsion. The cellulose nitrate and other ingredients of the emulsion may also be varied over a wide range, depending upon properties of the particular combination being used.

Example 3

A high speed photographic multi-layer material is made by coating three gelatino-silver halide emulsion sensitive respectively to the red, green and blue regions of the spectrum on a single support, each emulsion containing finely dispersed particles of collodion or another cellulose derivative containing no silver halide but merely the coupling compound required for that layer. For the red sensitive layer the coupling compound (1-naphthol-2-carboxylic-α-naphthylide) may be used, for the green-sensitive layer the coupling compound 2-cyanoacetyl naphthalene sulfon-N-methyl anilide may be used and for the blue sensitive layer the coupling compound benzoyl acet-2,5-dichloroanilide may be used. These couplers produce respectively blue-green, magenta and yellow images upon photographic development.

The processing of this film may be carried out either to produce a negative image by immediate immersion in a color-forming developer or it may be developed initially in an ordinary MQ developer or a positive image may be formed by exposing the film to white light after the ordinary first development and then developing the residual halide in a color forming developer. In either case the coupling compound remains within the cellulose particle into which, however, the oxidized coupling developer penetrates freely in those localities where it has been oxidized by developing the sensitive silver halide grains. A dye image is thus built up in those cellulose particles most nearly adjacent to the exposed silver halide grains.

Example 4

A sensitive photographic layer containing a coupler together with silver halide in a cellulosic binder the whole being dispersed in gelatin was made as follows:

20 cc. of a commercial collodion emulsion were diluted with 20 cc. of N-butyl acetate and this solution was then added to 100 cc. of a 0.1% solution of a higher fatty alcohol sulfate in water. This latter compound which is sold under the trade name Gardinol is a well known dispersing agent. To this solution there was added 0.25 gram of 5-phenoxyacetamino-1-naphthol and the mixture was then run through a small homogenizer and was recirculated for five minutes. Subsequently it was vacuum distilled to remove solvents employed in the preparation of the collodion emulsion and the butyl acetate which was added as noted above. Prior to the removal of the solvent by vacuum, small amounts of N-octyl alcohol were added to prevent foaming. After the volatile solvents were removed, the suspension of fine particles in the Gardinol solution was added to 50 cc. of a 6% gelatin solution and these were coated on a support. The particles of cellulosic binder thus produced were below 1 mμ in diameter. Upon exposure of this layer and development in an aromatic amino developing agent, a blue-green image was produced.

Example 5

A collodion silver halide emulsion is made in the usual manner and divided into three parts A, B and C. To A and B are added respectively suitable quantities of non-water-soluble red and green sensitizers, for example, pinacyanol or the neothiazolocarbocyanine derived from 2,4-dimethyl thiazole ethiodide for the red, and erythrosin for the green. To A, B and C, respectively, are added suitable quantities of coupling compounds which, with a developer such as diethyl-p-phenylene-diamine, will yield blue-green, magenta and yellow dye images. Suitable compounds are 5,7-dibromo-8-hydroxyquinoline for blue-green, p-phenylbenzoyl acetonitrile for the magenta and β-naphthoyl acetone for the yellow. At this stage there are three batches of collodion, silver halide emulsion differentially light-sensitive and capable of forming differently colored images. Sensitizers and couplers are contained in true solution in the organic solvents used for the collodion.

An aqueous gelatin solution is then prepared and maintained at a pH low enough to prevent dissolving the coupling components. To this gelatin are added in substantially equal quantities minute dried particles of the three collodion emulsions which have been spray dried or otherwise dispersed. These particles will be about the size of ordinary negative emulsion grains but each will contain a number of exceedingly fine silver halide particles suspended in the collodion and in intimate contact with the sensitizing dye and coupling compound.

After suitable mixture of the dispersed particles, the gelatin carrier containing them is coated as a single layer on a photographic support. On exposure and development in a single developer such as diethyl-p-phenylenediamine this layer forms three differently colored images.

Example 6

The following example illustrates the dispersion of an originally colored material in a cellu-

losic compound, in a gelatino-silver halide emulsion.

A solution is prepared containing 20 grams of cellulose nitrate, 10 grams of ethylene glycol monobenzyl ester, 10 grams of benzene azo cresol and 750 cc. of butyl acetate. This solution is emulsified, for example, by homogenization with 1000 cc. of a 0.2% aqueous solution of a higher fatty alcohol sulfate. The emulsion is heated with stirring to expel the butyl acetate and the remaining fine suspension of dyed cellulose nitrate particles are added to 1000 cc. of a gelatino silver halide emulsion containing 6.5% gelatin.

Numerous coupler compounds are suitable for use in our invention where the photographic layer is designed to be developed with an aromatic amino developing agent. As stated above, couplers may be used which would not be suitable for incorporating in a gelatin emulsion without the use of some special means to prevent diffusion. The couplers which we may use have a molecular size and shape such that, although capable of diffusing through gelatin, they are readily rendered non-diffusing by physically combining them with a dispersed cellulosic material.

The following couplers are suitable for use in our invention. It is to be understood that this list is not intended to be exhaustive, but merely to typify compounds which may be used.

Couplers producing cyan images

2,2'-dihydroxy-5,5'-dibromostilbene
p,p'-Di-(2 - hydroxybenzamido) - diphenylmethane
Sebacic acid di-(2-hydroxyanilide)
8-hydroxy - 1 - α - naphthoyl -1,2,3,4-tetrahydroquinoline
1-naphthol-5-sulfo-cyclohexylamine
1-naphthol-2-carboxylic-α-naphthalide
5-diamylnaphthalenesulfonamido-1-naphthol
5 - [N-(p-toluenesulfonyl)]-[N'-β-hydroxyethyl] amino-1-naphthol
5-diphenylethersulfonamido-1-naphthol
5-phenoxyacetamino-1-naphthol
5 - [N - benzoyl - N - β - hydroxyethyl] -amino-1-naphthol
5-amyldiphenylethersulfonamido-1-naphthol
2,4 - dichloro- 4-[p-nitrobenzoyl-β-hydroxyethylamino]-1-naphthol

Couplers producing magenta images

1,4-phenylene bis-3(1-phenyl-5-pyrazolone)
2-cyanoacetylnaphthalenesulfon - N - methylanilide
2-cyanoacetylcoumarone - 5-sulfon-N-methylanilide
2-cyanoacetylcoumarone-5-sulfondimethylamide
2-cyanoacetyl-5-benzoylaminocoumarone
2-cyanoacetyl-β-naphthofuran
Cyanoacet-β-naphthalide

Couplers producing yellow images

N-phenyl-N'-(p-acetoacetaminophenyl) urea
p,p'Diacetoacetaminodiphenylmethane
Benzoylacet-2,5-dichloranilide
N,N'-di-(ω-benzoylacetyl) -p-phenylenediamine
N,N'-di-(p-benzoylacetaminophenyl) - naphthalene-1,5-disulfonamide
p,p'-Di(acetoacetamino)diphenyl
4,4'-di(acetoacetamino)-3,3'-dimethyldiphenyl

Our invention will now be described with particular reference to the accompanying drawing. As shown in Fig. 1, a support 10 of any suitable material such as cellulose nitrate or cellulose acetate, synthetic resin, or paper, is coated with a plain gelatin layer 11 and a plain gelatin layer 12 each containing dispersed particles of a suitable water permeable but water insoluble cellulosic binder. Emulsion layer 12 contains the cellulosic particles 13 containing coupler A and silver halide. Gelatin layer 11 contains dispersed particles 14 of cellulosic material containing coupler B and silver halide. It is to be understood that the silver halide is dispersed in the cellulosic particle and that the coupler is dissolved in it, and that the drawing is not intended to indicate that the silver halide and the coupler occupy concentric portions in the cellulosic particle.

As shown in Fig. 2, the support 10 is coated with gelatino silver halide emulsion layers 15, 16 and 17 sensitive respectively to the red, green and blue regions of the spectrum. Emulsion layer 17 contains cellulosic particles 18 containing coupler A', emulsion layer 16 contains cellulosic particles 19 containing coupler B' and emulsion layer 15 has dispersed therein cellulosic particles 20 containing coupler C'. The blue, green and red sensitive silver halide particles in the respective emulsion layers are represented by numerals 21, 22 and 23.

Fig. 3 shows a support 10 containing a gelatin layer 11 containing differentially sensitized particles of cellulosic binder. 24 is a particle of cellulosic binder containing coupler A' and silver halide grains, 25 is a particle of cellulosic binder containing coupler B' and silver halide grains sensitized to another region of the spectrum and 26 is a particle of cellulosic binder containing couplers C' and silver halide grains sensitized to a third region of the spectrum.

The method of preparing, exposing and developing these various types of photographic element will be understood from referring to the specific examples above.

Our invention is susceptible of numerous variations not herein specifically described and it is to be understood that our invention is limited only by the scope of the appended claims.

We claim:

1. A light-sensitive layer for producing a colored image, comprising a gelatino-silver halide emulsion containing finely divided particles of a water-insoluble but water-permeable cellulose ester containing a color former in physical mixture therewith, dispersed in the gelatin.

2. A light-sensitive layer for producing a colored image, comprising an emulsion of silver halide in a water-soluble, water-permeable colloidal medium, said emulsion containing finely divided particles of a water-insoluble but water-permeable cellulose ester containing a color former in physical mixture therewith, dispersed in the water-soluble, water-permeable colloidal medium.

3. A light-sensitive element for producing a colored image, comprising a layer of a water-permeable silver halide-colloidal medium having dispersed therein finely-divided particles of a water-insoluble but water-permeable cellulose ester containing a color-former in physical mixture therewith.

4. The method of producing a color-forming photographic layer, which comprises mixing a water-insoluble but water permeable cellulose compound in an organic solvent with a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development, dispersing the mixture of cellulose compound and color-forming

compound in a gelatino-silver halide emulsion, and coating said dispersion on a support.

5. The method of producing a color-forming photographic layer, which comprises mixing a water-insoluble but water permeable cellulose nitrate with a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development, dispersing the mixture of cellulose nitrate and color-forming compound in a gelatino-silver halide emulsion, and coating said dispersion on a support.

6. The method of producing a color-forming photographic layer, which comprises mixing a water-insoluble but water-permeable cellulose acetate with a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development, dispersing the mixture of cellulose acetate and color-forming compound in a gelatino-silver halide emulsion, and coating said dispersion on a support.

7. The method of producing a color-forming photographic layer, which comprises mixing with a water-insoluble but water-permeable cellulose compound a porosity modifier for the material and a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development, dispersing the mixture of cellulose compound and color-forming compound in a gelatino-silver halide emulsion, and coating said dispersion on a support.

8. The method of producing a color-forming photographic layer, which comprises mixing with a water-insoluble but water-permeable cellulose nitrate a porosity modifier for the cellulose nitrate and a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development, dispersing the mixture of cellulose nitrate and color-forming compound in a gelatino-silver halide emulsion, and coating said dispersion on a support.

9. The method of producing a color-forming photographic layer, which comprises mixing with a water-insoluble but water-permeable cellulose acetate a porosity modifier for the cellulose acetate and a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development, dispersing the mixture of cellulose acetate and color-forming compound in a gelatino-silver halide emulsion, and coating said dispersion on a support.

10. In the method of producing a sensitive photographic element capable of being developed to form a colored image, the steps which comprise dissolving in a water-insoluble but water permeable cellulose compound a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development, and a porosity modifier for the cellulose compound which increases the permeability of the cellulose compound to developing solutions when incorporated in a gelatin emulsion layer, and dispersing the cellulose compound containing the color-forming compound and porosity modifier in a gelatin layer.

11. In the method of producing a sensitive photographic element capable of being developed to form a colored image, the steps which comprise dissolving in a water-insoluble but water-permeable cellulose nitrate a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development, and a porosity modifier for the cellulose nitrate which increases the permeability of the cellulose nitrate to developing solutions when incorporated in a gelatin emulsion layer, and dispersing the cellulose nitrate containing the color-forming compound and porosity modifier in a gelatin layer.

12. A photographic element for producing multi-color photographic images, comprising gelatin having dispersed therein a water-insoluble but water permeable cellulose compound containing in separate particles different color formers in physical mixture therewith and differently-sensitized silver halides.

13. A photographic element for producing multi-color photographic images, comprising a gelatin layer having dispersed therein a water-insoluble but water-permeable cellulose ester containing in separate particles different color-formers in physical mixture therewith and differently-sensitized silver halides.

14. The method of incorporating a coupling compound in a light-sensitive gelatino-silver halide emulsion, which comprises dissolving it in a water-immiscible solvent and a water-insoluble but water-permeable cellulose ester, and dispersing the cellulose ester containing the coupling compound, in the gelatino-silver halide emulsion.

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CERTIFICATE OF CORRECTION.

Patent No. 2,304,940. December 15, 1942.

LEOPOLD D. MANNES, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 63-64, after "developer" insert --, fixed, rehalogenized and redeveloped in a color forming developer--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of February, A. D. 1943.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)