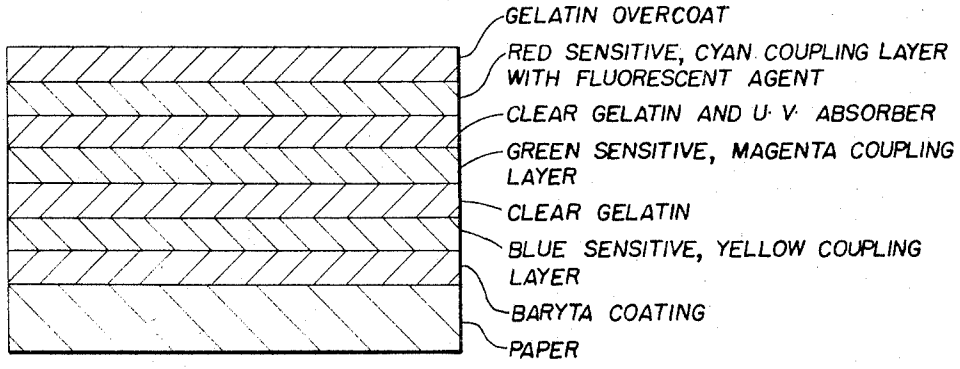
March 25, 1969 E. B. KNOTT ET AL 3,434,837

PHOTOGRAPHIC ELEMENT

Filed June 5, 1964



EDWARD B· KNOTT
MIROSLOV V· MIJOVIC
DAVID G· SAUNDERS
INVENTORS

BY R. Frank Smith
Clyde H. Webster

ATTORNEYS

United States Patent Office 3,434,837
Patented Mar. 25, 1969

3,434,837

PHOTOGRAPHIC ELEMENT

Edward B. Knott, Miroslav V. Mijovic, and David George Saunders, Harrow, Middlesex, England, assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

Continuation-in-part of application Ser. No. 275,370, Apr. 24, 1963. This application June 5, 1964, Ser. No. 373,020

Int. Cl. G03c 1/84, 7/26, 1/92

U.S. Cl. 96—74 10 Claims

This invention relates to color print material, and more particularly to color prints having incorporated therein fluorescent brightening agents.

This application is a continuation-in-part of our application Ser. No. 275,370, filed Apr. 24, 1963, now abandoned.

Photographic color print material generally comprises a white reflecting support, for example, baryta-coated paper, having separate blue, green and red sensitive layers over the white surface. Generally, the red sensitive layer, containing cyan coupler, is the uppermost light sensitive coating. Clear gelatin layers may be provided between the light sensitive layers, and a gelatin layer may be coated over the top red sensitive layer for protection. Previously, fluorescent brightening agents have been incorporated in the baryta coating of color print material. Such photographic elements have frequently been objectionable due to an unpleasant bluish bloom which may be present in dark areas of the print. In addition, it is difficult to provide satisfactory protection against ultraviolet radiation for the dyes in the color print while still retaining the desired fluorescence of the brightening agent. For example, if ultraviolet inhibitors are incorporated in the light sensitive layers, ultraviolet light will be absorbed by such agents and prevented from reaching and activating the fluorescent brightening agent.

One object of our invention is to provide color print material having optical brightening agents incorporated therein. Another object of our invention is to provide photographic prints which contain optical brightening agents, are free from bluish bloom in dark areas of the print and are stable to ultraviolet light. A further object of our invention is to provide a method of incorporating fluorescent agents in color print materials. Other objects of our invention will appear herein.

In accordance with one embodiment of our invention, we provide an improvement in color print materials of the type comprising a white reflecting support having coated thereover a plurality of separate contiguous layers, at least two of said layers containing a silver halide emulsion and couplers capable of forming dye images with the oxidation products produced in color development, which comprises incorporating in a layer of the color print material a fluorescent agent which absorbs radiation in the ultraviolet region of the spectrum, has high fluorescent emission in the blue region of the spectrum and is substantially insoluble in water.

In another embodiment of our invention, a fluorescent agent which absorbs radiation in the ultraviolet region of the spectrum, has high fluorescent emission in the blue region of the spectrum and is substantially insoluble in water, is dissolved in a low-molecular weight, organic, crystalloidal material having a boiling point above 175° C., which material has high solvent action for the fluorescent agent, and the solution is incorporated in a hydrophilic colloid, which may contain silver halide and a dye-forming coupler, and is coated on a support having a white reflecting surface. We have found that globules of fluorescent agent dissolved in such solvents, when incorporated in photographic print materials, do not migrate from the layer in which they are incorporated and

are not leached from the print material during development and processing.

In accordance with another embodiment of our invention, a color print material having separate blue, green and red sensitive silver halide coatings thereon which contain couplers capable of forming, respectively, yellow, magenta and cyan dyes, has incorporated in at least one of said layers a fluorescent agent which absorbs ultraviolet radiation, has high fluorescent emission in the blue region of the spectrum and is substantially insoluble in water. Advantageously, the fluorescent agent is incorporated in the layer by mixing a solvent solution of the fluorescent agent in a high boiling solvent of the type defined herein. Preferably, the layer containing fluorescent agent is incorporated in the outermost color-coupler containing layer, and the coupler in the layer forms a dye on color development, which dye coacts with the fluorescent agent to extinguish the fluorescence of the fluorescent agent in areas where the dye is developed. We have found that color print materials of this type do not have an objectionable bluish bloom in dark areas of the print, which has been present in prior art print materials where the fluorescent agent was incorporated in the support or baryta coating. In addition, the fluorescent agent by its absorption of ultraviolet radiation serves to protect the dyes in lower layers of the color print material. Further protection of dyes in the lower layers may be provided by incorporating an ultraviolet absorber in one or more layers of the color print material. Preferably, the ultraviolet absorber is incorporated in a layer of the color print material below the layer containing the fluorescent agent so that the fluorescence thereof is not diminished due to absorption of ultraviolet radiation by the ultraviolet absorber.

In accordance with a preferred embodiment of our invention, we provide color print material having a white reflecting support, blue and green sensitive coatings thereon, and a red sensitive layer thereover containing phenolic cyan dye forming coupler and a fluorescent brightening agent.

A typical photographic element in accordance with our invention is illustrated in the accompanying drawing which shows a baryeta coated paper having thereon a blue sensitive, yellow coupling layer; a clear gelatin layer, green sensitive, magenta coupling layer; a clear gelatin layer with an ultraviolet absorber; red sensitive, cyan coupling layer and a protective gelatin overcoat. The fluorescent agent is incorporated in the upper, red sensitive, cyan coupling layer.

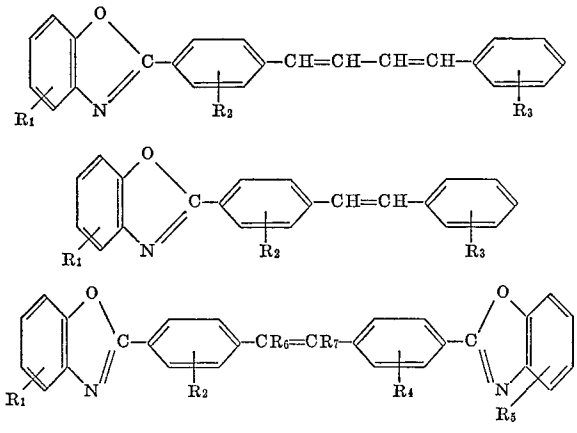
The fluorescent agents which we employ in accordance with our invention absorb radiation in the ultraviolet region of the spectrum, have high fluorescent emission in the blue region of the spectrum, and are substantially insoluble in water. Any fluorescent brightening agent having these general properties may be incorporated in color print material in accordance with our invention. Among such fluorescent agents are the following:

(1) 2-(4′-stilbenyl)-1,4,5-triphenylimidazole
(2) 4-dimethylamino-4′-lauroylamidostilbene
(3) 1-[4-(2,4-di-t-amylphenoxyacetamido)phenyl]-4-phenylbuta-1,3-diene
(4) 7-diethylamino-4-methylcoumarin
(5) 3-ethoxycarbonyl-5,6-benzocoumarin
(6) Diethyl succinylsuccinate
(7) 1,4-bis-(2-benzoxazolyl)benzene
(8) Cis-1,2-bis-(2-benzoxazolyl)ethylene
(9) Trans-1,2-bis-(2-benzoxazolyl)ethylene
(10) Cis-1,2-bis(2-benzimidazolyl)ethylene
(11) 3-(5-hydroxy-2-phenyloxazol-4-ylmethylene)isochroman-1,4-dione

(12) 3-phenyl-7-(2-[dimethylaminoethyl]ureido)coumarin.

The substituted stilbene and substituted coumarin (such as those described in British Patent 786,234) fluorescent agents are particularly useful.

Other useful fluorescent brightening agents include those having one of the following structural formulas:



in which R_1, R_2, R_3, R_4 and R_5 are substituents which may be aryl, aralkyl, alkyl, alkoxy, aryloxy, hydroxyl, amino, substituted amino, cyano, carboxylic acid, amide, ester, CH_3CO—, CH_3SO_2—, $(CH_3)_2NSO_2$—, CF_3, halogen or hydrogen atoms; R_6 and R_7 are hydrogen, alkyl groups such as methyl or ethyl, or cyano.

Typical examples of specific compounds having one of the above structural formulas include the following:

1-[4-(benzoxazol-2-yl)phenyl]-4-phenylbuta-1,3-diene
4-(benzoxazol-2-yl)stilbene
4,4'-di-(benzoxazol-2-yl)stilbene
4,4'-di-(benzoxazol-2-yl)-2-methyl stilbene
4,4'-di-(benzoxazol-2-yl)-α-cyanostilbene
4,4'-di-(benzoxazol-2-yl)-2,2'-dimethylstilbene
4,4'-di-(6-methoxybenzoxazol-2-yl)stilbene
4,4'-di-(benzoxazol-2-yl)-2-aminostilbene
4,4'-di-(benzoxazol-2-yl)-2-hydroxystilbene
4,4'-di-(benzoxazol-2-yl)-2-chlorostilbene
4,4'-di-(benzoxazol-2-yl)-2-cyanostilbene.

The above compounds may be prepared in accordance with the method described in British provisional application No. 47,527/62, filed Dec. 17, 1962.

Our invention will be further illustrated by the following examples.

EXAMPLE 1

0.5 gram of 2-(4'-stilbenyl)-1,4,5-triphenylimidazole (fluorescent agent) was dissolved in 13 ml. of dibutyl phthalate at about 90–100° C., together with 0.3 ml. of a 7.5% aqueous solution of tri-isopropylnaphthalenesulfonic acid, sodium salt. This solution was poured into 30 ml. of 9% gelatin solution at 40° C., and homogenized with rapid stirring for 2 minutes. The dispersion was added to 150 ml. of a silver chlorobromide photographic emulsion containing 1.2 g. of silver (approximately 80% chloride, 20% bromide) cyan color coupler dispersion and gelatin. After the addition of gelatin hardener and surface active coating aid, the mixture was coated onto baryta-coated paper base to give 0.0336 g. silver and 0.028 g. of the fluorescent agent per square foot. After setting and drying, the coating was exposed to a step wedge and developed with a developer containing 4-amino-N-ethyl-N-[β-methanesulfonamidoethyl] - m - toluidine sesquisulfate monohydrate as the active agent, and stopped, fixed, bleached and hardened in the usual manner. The print thus obtained showed strong fluorescence in the areas where there was no image dye formation, but no fluorescence, or very weak fluorescence, in areas where the dye density was high. Under normal daylight viewing conditions the fluorescent agent had the effect of enhancing the appearance of whiteness in the areas of minimum densities without apparent reduction in the areas of high density. The print was free from bluish bloom in areas of dye development.

EXAMPLE 2

The same procedure was followed as in Example 1 except that the fluorescent agent employed was 3-ethoxycarbonyl-5,6-benzocoumarin. The results obtained were similar to the results obtained in Example 1.

EXAMPLE 3

A baryta-coated paper was coated with, respectively, blue sensitive-yellow coupling emulsion layer, plain gelatin layer, green sensitive-magenta coupling layer, plain gelatin layer and then with the emulsion of Example 1, which was also sensitized to red light by means of a dye. The print was exposed to a step wedge and developed with a developer containing 4-amino-N-ethyl-N-[β-methane-sulfonamidoethyl]-m-toluidine sesquisulfate monohydrate as the active agent, and stopped, fixed, bleached and hardened in the usual manner. The color print showed good whiteness in the areas where there was no dye formation due to the fluorescence of the fluorescent agent. There was no fluorescence, or bluish bloom, in the areas where the dye density was high. In addition, the fluorescent agent provided ultraviolet protection for the dyes contained in the lower layers of the emulsion.

EXAMPLE 4

The same procedure was followed as in Example 3 except that the fluorescent agent employed was 3-ethoxycarbonyl-5,6-benzocoumarin. The same results were obtained as in Example 3.

EXAMPLE 5

The same procedure was followed as in Example 1 except that the fluorescent agent employed was 3-phenyl-7-[2-(dimethylaminoethyl)ureido]coumarin. The results obtained were similar to the results obtained in Example 1.

EXAMPLE 6

The procedure of Example 1 was followed except that 0.5 gram cyan coupler was included with the 0.5 gram 2-(4'-stilbenyl)-1,4,5-triphenylimidazole in the dibutyl phthalate solution, and dispersed in gelatin as in Example 1. The dispersion was then added to the silver chlorobromide emulsion which did not, in this example, contain any cyan coupler. The emulsion containing the cyan coupler and fluorescent agent were coated and tested as in Example 1, and similar results were obtained.

The substantially water insoluble fluorescent agents which we employ in our invention are non-migratory. Hence, these fluorescent agents remain in the red sensitive, cyan-coupling layer during coating and processing. These fluorescent agents are also highly useful brighteners in black-and-white print materials due to their non-migratory characteristics. When water-soluble fluorescent agents are incorporated in either color or black-and-white print material, the fluorescent agent tends to migrate to other layers of the print, causing bluish bloom, or the fluorescent agent may be leached out of the print during processing.

The amount of fluorescent agent incorporated into the red sensitive cyan coupler containing layer should be greater than 1 milligram per square foot, and preferably is within about 5 to 35 milligrams per square foot. No advantage is obtained by incorporating more than 100 milligrams per square foot in the layer and at higher levels the fluorescence will be reduced by the autoquenching effect.

The solvents which we employ to prepare solutions of fluorescent agent for incorporation into hydrophilic colloid materials for photographic elements are the low-molecular weight, organic, water-insoluble, crystalloidal

materials having a boiling point above 175° C. and good solvent action for the fluorescent agent. Typical useful solvents include:

Acids

p-Sec.amylbenzoic acid, β-phenylpropionic acid, dibenzyl acetic acid, phenyl ethyl acetic acid, mono-n-amyl phthalate (acid ester), undecylenic acid, benzyl hydrogen succinate (acid ester).

Alcohols

n-Hexylphenylcarbinol, β-(p-tert. butyl phenoxy)-ethyl alcohol.

Amides

Acetyl n-butyl aniline, acetyl methyl p-toluidine, benzoyl piperidine.

Amide derivatives

N-n-amylphthalimide, N-n-amyl succinimide, N-2-cyanobutylphthalimide.

Carbamates

Ethyl N,N-di-n-butyl carbamate, ethyl N-phenyl carbamate.

Esters

Tetrahydrofurfuryl benzoate, tetrahydrofurfuryl succinate, ethyl benzyl malonate, methyl phthalate, ethyl phthalate, propyl phthalate, n-butyl phthalate, n-amyl phthalate, iso-amyl phthalate, benzyl phthalate, β-methoxyethyl phthalate, β-ethoxyethyl phthalate, β-butoxyethyl phthalate, ethyl-α-naphthoate, methyl o-methoxybenzoate, butyl o-methoxybenzoate, α-naphthyl acetate, methyl p-toluenesulfonate, ethyl o-anisate, methyl phthalylethyl glycollate, butyl phthalylbutyl glycollate, resorcinol diacetate, n-hexyl benzoate.

Ketone derivatives

Benzophenone, 2,4'-dichlorobenzophenone, α-methoxy acetophenone, acetophenone, 2,4-dihydroxy valerophenone, p-sec.-amylbenzophenone.

Phenol ethers

Veratrole (1,2-dimethoxybenzene), eugenol methyl ether, hydroquinone dimethyl ether.

Phosphate esters

Triphenyl phosphate, tricresyl phosphate, diphenyl mono-p-tert. butyl phenyl phosphate, monophenyl di-p-tert. butyl phenyl phosphate, diphenyl mono-o-chlorophenyl phosphate, monophenyl di-o-chlorophenyl phosphate, tri-p-tert. butyl phenyl phosphate, tri-o-phenylphenyl phosphate, di-p-tert. butyl phenyl mono (5-tert. butyl-2-phenylphenyl)-phosphate.

Sulfonamides

p-Toluenesulfonyl methyl o-toluidine, p-toluenesulfonyl dimethylamide.

Sulfonamide derivatives

p,p'-Di-n-amylbenzenesulfonanilide, p-toluenesulfonyl di-n-butyl amide.

Sulfones

n-Butyl sulfone, iso-amyl sulfone.

Ureas

N,N'-diethyl-N,N'-diphenyl urea, N,N-di-n-butyl urea.

Solutions of fluorescent agent in these solvents are dispersed as globules which are water immiscible. The globules are dispersed in the layer in which they are incorporated, and are not washed out by aqueous processing baths.

As noted above, the fluorescent agents are preferably incorporated in color print material in the outermost layer containing coupler capable of forming a dye which co-acts with the fluorescent agent to extinguish fluorescence in those areas, and only those areas, where the dye is produced by color development. The manner in which a dye functions to extinguish fluorescence is not known, and whether a dye possesses this function cannot be predicted. However, many couplers are known to produce dyes which possess this function. Particularly useful couplers which form dyes that extinguish fluorescense are the cyan-forming phenolic couplers. (As used herein and in the appended claims, the term "phenolic couplers" is used broadly as inclusive of both phenolic and naphtholic couplers.) Typical useful phenolic couplers include those described in U.S. Patent 2,423,730 and the following:

Couplers producing cyan images

5-(p-amylphenoxybenzenesulfonamino)-1-naphthol
5-(N-benzyl-N-naphthalenesulfonamino)-1-naphthol
5-(n-benzyl-N-n-valerylamino)-1-naphthol
5-caproylamino-1-naphthol
2-chloro-5-(N-n-valeryl-N-p-isopropylbenzylamino)-1-naphthol
2,4-dichloro-5-(p-nitrobenzoyl-β-o-hydroxyethylamino)-1-naphthol
2,4-dichloro-5-palmitylamino-1-naphthol
5-diphenylethersulfonamido-1-naphthol
1-hydroxy-2-(N-isoamyl-N-phenyl)-naphthamide
1-hydroxy-2-(N-p-sec. amylphenyl)-naphthamide
8-hydroxy-1-α-naphthoyl-1,2,3,4-tetrahydroquinoline
2-lauryl-1-chlorophenol
1-naphthol-2-carboxylic-α-naphthalide
1-naphthol-5-sulfo-cyclohexylamide
5-phenoxyacetamino-1-naphthol
5-β-phenylpropionylamino-1-naphthol
Monochlor-5-(N-γ-phenylpropyl-N-p-sec. amyl-benzoyl-amino-1-naphthol.

Any suitable ultraviolet absorber may be incorporated in the photographic print materials of the invention to provide protection for dyes which deteriorate when subjected to ultraviolet radiation. These agents may be incorporated in emulsion or hydrophilic colloid spacing layers. Typical useful ultraviolet absorbers are the thiazolidone derivatives disclosed in U.S. Patents 2,739,888, 2,739,971 and 2,808,330.

The fluorescent agent of our invention may be incorporated in any of the hydrophilic colloids useful in photography, such as those described in U.S. Patent 3,039,873, column 13, lines 40–67.

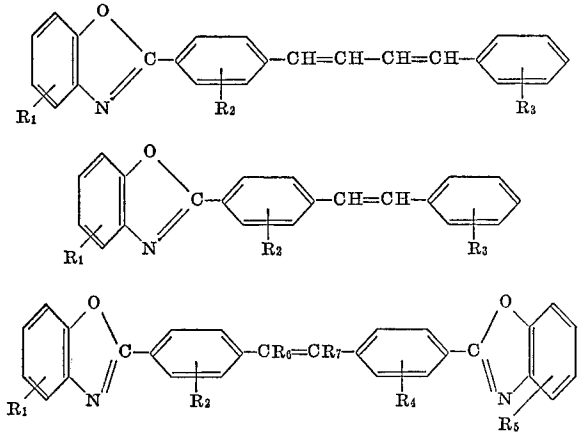
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. Photographic print material comprising a support having a white surface, a plurality of coatings over said white surface which coatings includes light sensitive coatings individually sensitive to blue, green and red regions of the spectrum, the red sensitive coating being the outermost light sensitive coating, said red sensitive coating containing a fluorescent agent which has strong absorption of radiation in the ultraviolet region of the spectrum, high fluorescent emission in the blue region of the spectrum and which is substantially insoluble in water and, a photographic coupler in said outermost coating which forms a dye which extinguishes the fluorescence of the fluorescent agent in those areas in which the dye is produced.

2. Photographic print material comprising a support having a white surface, a plurality of coatings over said white surface which coatings include light sensitive coatings individually sensitive to blue, green and red regions of the spectrum, the red sensitive coating being the outermost light sensitive coating, said red sensitive coating

containing a fluorescent agent selected from the group consisting of:



wherein R_1, R_2, R_3, R_4 and R_5 are substituents selected from the group consisting of aryl, aralkyl, alkyl, alkoxy, aryloxy, hydroxyl, amino, substituted amino, cyano, carboxyl, amide, ester,

CH_3CO—, CH_3SO_2—, $(CH_3)_2NSO_2$—, CF_3—

halogen and hydrogen, and R_6 and R_7 are selected from the group consisting of hydrogen, cyano and alkyl groups, 2 - (4' - stilbenyl) - 1,4,5 - triphenylimidazole, 4-dimethylamino - 4' - lauroylamidostilbene, 1-[4-(2,4-di-t-amylphenoxyacetamido) - phenyl] - 4 - phenylbuta-1,3-diene, 7-diethylamino-4-methylcoumarin, 3-ethoxycarbonyl-5,6-benzocoumarin, diethyl succinylsuccinate, 1,4-bis-(2-benzoxazolyl)ethylene, trans-1,2-bis - (2-benzoxazolyl)-ethylene, cis-1,2-bis-(2-benzimidazolyl)ethylene and 3-(5-hydroxy-2-phenyloxazol-4-ylmethylene)isochroman-1,4-dione and, a photographic coupler in said outermost coating which forms a dye which extinguishes the fluorescence of the fluorescent agent in those areas in which the dye is produced.

3. Photographic print material comprising a support having a white surface, a plurality of coatings over said white surface which coatings include light sensitive coatings individually sensitive to blue, green and red regions of the spectrum, the red sensitive coating being the outermost light sensitive coating, said red sensitive coating containing 2-(4'-stilbenyl) - 1,4,5 - triphenylimidazole and, a photographic coupler in said outermost coating which forms a dye which extinguishes the fluorescence of the fluorescent agent in those areas in which the dye is produced.

4. Photographic print material comprising a support having a white surface, a plurality of coatings over said white surface which coatings include light sensitive coatings individually sensitive to blue, green and red regions of the spectrum, the red sensitive coating being the outermost light sensitive coating, said red sensitive coating containing 3-ethoxycarbonyl-5,6-benzocoumarin and, a photographic coupler in said outermost coating which forms a dye which extinguishes the fluorescence of the fluorescent agent in those areas in which the dye is produced.

5. In a photographic element having a support with a white surface and a plurality of coatings thereon including light sensitive coatings individually sensitive to blue, green and red regions of the spectrum, the red sensitive coating being the uppermost light sensitive coating, the improvement for brightening the white areas of the print which comprises incorporating in said red sensitive coating a fluorescent agent which has strong absorption of radiation in the ultraviolet region of the spectrum, high fluorescent emission in the blue region of the spectrum and which is substantially insoluble in water and a photographic coupler in said red sensitive coating which forms a cyan dye which extinguishes the fluorescence of the fluorescent agent in those areas in which the cyan dye is produced.

6. The photographic print material of claim 2 wherein the support is baryta-coated paper.

7. A photographic color print material comprising a support having separate blue, green and red sensitive coatings thereon containing couplers capable of forming, respectively, yellow, magenta and cyan dyes, the outermost of said coupler containing layers having incorporated therein a fluorescent agent which absorbs ultraviolet radiation, has high fluorescent emission in the blue region of the spectrum and is substantially insoluble in water, and the coupler in said outermost layer forms, on color development, a dye which extinguishes the fluorescence of the fluorescent agent in those areas in which the dye is produced.

8. Photographic print material comprising a support having a white surface, a plurality of coatings over said white surface which coatings include light sensitive coatings individually sensitive to blue, green and red regions of the spectrum, the red sensitive coating being the outermost light sensitive coating, said red sensitive coating containing a substituted stilbene fluorescent agent and a photographic coupler which forms a cyan dye which extinguishes the fluorescence of the fluorescent agent in those areas in which the cyan dye is produced.

9. Photographic print material comprising a support having a white surface, a plurality of coatings over said white surface which coatings include light sensitive coatings individually sensitive to blue, green and red regions of the spectrum, the red sensitive coating being the outermost light sensitive coating, said red sensitive coating containing a substituted coumarin fluorescent agent and a photographic coupler which forms a cyan dye which extinguishes the fluorescence of the fluorescent agent in those areas in which the cyan dye is produced.

10. A photographic color print material comprising a support having separate blue, green and red sensitive photographic silver halide emulsion layers thereon which contain couplers capable of forming, respectively, yellow, magenta and cyan dyes, said red sensitive layer having dispersed therein globules of a water-insoluble fluorescent agent, which has a strong absorption of ultraviolet radiation, dissolved in a substantially water-insoluble, low molecular weight, organic, crystalloidal material having a boiling point above 175° C., said material having good solvent action for the fluorescent agent, said red sensitive layer containing a phenolic coupler which forms cyan dye which extinguishes the fluorescence of said fluorescent agent in those areas in which the cyan dye is produced.

References Cited

UNITED STATES PATENTS

2,322,027	6/1943	Jelley et al.	96—74
2,639,990	5/1953	Kendall et al.	96—82
2,956,879	10/1960	Van Campen	96—84
3,047,390	7/1962	Koerber et al.	96—82
3,244,524	4/1966	Trucker	96—84

FOREIGN PATENTS

1,150,274	6/1963	Germany.

NORMAN G. TORCHIN, *Primary Examiner.*

RONALD H. SMITH, *Assistant Examiner.*

U.S. Cl. X.R.

96—69, 82, 84