

PATENT SPECIFICATION

1,110,015

NO DRAWINGS.

1,110,015



Date of Application and filing Complete Specification:

4 June, 1965.

No. 23941/65.

Application made in United States of America (No. 373,020) on 5 June, 1964.

(Patent of Addition to No. 1,072,915 dated 17 Dec., 1963).

Complete Specification Published: 18 April, 1968.

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Index at Acceptance:—G2 C(C5, D15B).

Int. Cl.:—G 03 c 7/26.

COMPLETE SPECIFICATION.

Photographic Colour Print Materials.

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, (Assignees of EDWARD BOWES KNOTT, MIROSLAV VASA MIJOVIC and DAVID GEORGE SAUNDERS), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to photographic materials, and more particularly to a photographic colour print material having incorporated therein fluorescent brightening agents.

Photographic colour print materials generally comprise a white reflecting support, for example, baryta-coated paper, having separate blue, green and red sensitive silver halide emulsion layers over the white surface. Generally, the red sensitive layer, containing a 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. Fluorescent brightening agents have been incorporated in the baryta coating of such colour print materials but the effect is greatly reduced by the dye image in the superposed layers. When the fluorescent brightening agents have been incorporated in the upper emulsion layers an unpleasant bluish bloom often occurs in the dark areas of the print. In addition, it is difficult to provide satisfactory protection against ultraviolet radiation for the dyes in the colour print while still retaining the desired fluorescence of the brightening agent. For example, if ultraviolet inhibitors are incorporated in the light sensitive layers ultra-

violet light will be absorbed by such agents and prevented from reaching and activating the fluorescent brightening agent. In Specification No. 1,072,915 there is described and claimed a photographic colour print material comprising a white reflecting support carrying three light sensitive silver halide emulsion layers, one of each sensitive or sensitized respectively to the red, green and blue regions of the spectrum, in which the top silver halide emulsion layer contains a dispersion of an organic solvent in which is dissolved or dispersed a fluorescent brightening agent compound which is insoluble in water.

According to the present invention there is provided a photographic colour print material comprising a white reflecting support carrying three light sensitive silver halide emulsion layers, one of each sensitive respectively to the red, green and blue regions of the spectrum, in which at least one emulsion layer below the top emulsion layer contains a dispersion of a water insoluble fluorescent brightening agent dissolved or dispersed in a water insoluble liquid which has a boiling point greater than 175°C and which is a solvent for the fluorescent brightening agent.

The photographic colour print material preferably contains a coupler capable of dye formation with the oxidation products of a colour developing agent in each light sensitive emulsion layer. The coupler is preferably dissolved or dispersed in a water insoluble liquid. The liquid in which the fluorescent brightening agent is dissolved or dispersed may be the same as that in which the coupler is dissolved or dispersed.

The water insoluble liquids employed in preparing solutions of fluorescent brightening agents for incorporation into hydrophilic colloid materials for the photographic colour

[Price 4s. 6d.]

print materials of the invention are the low-molecular weight, organic, water-insoluble, crystalloidal materials having a boiling point above 175°C and good solvent action for the fluorescent brightening agent. Typical useful solvents include:

- Acids*
- 10 p-Sec.amylbenzoic acid
β-Phenylpropionic acid
Dibenzyl acetic acid
Phenyl ethyl acetic acid
Mono-n-amylphthalate (acid ester)
Undecylenic acid
Benzyl hydrogen succinate (acid ester)
- Alcohols*
- 15 n-Hexylphenylcarbinol
β-(p-Tert. butyl phenoxy)-ethyl alcohol
- Amides*
- 20 N-Acetyl N-n-butyl aniline
N-Acetyl N-methyl p-toluidine
N-Benzoyl piperidine
- Amide Derivatives*
- 25 N-n-amylphthalimide
N-n-amyl succinimide
N-2-cyanobutylphthalimide
- Carbamates*
- Ethyl N,N-di-n-butyl carbamate
Ethyl N-phenyl carbamate
- Esters*
- 30 Tetrahydrofurfuryl benzoate
Ditetrahydrofurfuryl succinate
Ethyl benzyl malonate
Dimethyl phthalate
Ethyl phthalate
35 Propyl phthalate
n-Butyl phthalate
n-Amyl phthalate
Iso-amyl phthalate
Benzyl phthalate
40 β-Methoxyethyl phthalate
β-Ethoxyethyl phthalate
β-Butoxyethyl phthalate
Ethyl α-naphthoate
Methyl o-methoxybenzoate
45 Butyl o-methoxybenzoate
α-Naphthyl acetate
Methyl p-toluenesulphonate
Ethyl o-anisate
Methyl phthalylethyl glycollate
50 Butyl phthalylbutyl glycollate
Resorcinol diacetate
n-Hexyl benzoate
- Ketone Derivatives*
- 55 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

60

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

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Sulphonamides

N - p - Toluenesulphonyl N - methyl o-toluidine
N - p - Toluenesulphonyl N,N - dimethylamine
p,p'-Di-n-amylbenzenesulphonanilide
p-Toluenesulphonyl N,N-di-n-butyl amine

80

Sulphones

n-Butyl sulphone
Iso-amyl sulphone

85

Ureas

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

Solutions of fluorescent brightening 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.

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The fluorescent brightening agents are preferably incorporated in the colour print material in a 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 colour 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 fluorescence 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 No. 2,423,730 and the following.

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Couplers Producing Cyan Images

5 - (p - amylphenoxybenzenesulphonamido)-1 - naphthol

- 5 - (N - benzyl - naphthalenesulphonamido) - 1 - naphthol
- 5 - (N - benzyl - N - n - valeryl amino) - 1 - naphthol
- 5 - caproyl amino - 1 - naphthol
- 2 - chloro - 5 - (N - n - valeryl - N - p - isopropylbenzyl amino) - 1 - naphthol
- 2,4 - dichloro - 5 - (N - p - nitrobenzoyl - N - β - hydroxyethyl amino) - 1 - naphthol
- 10 2,4 - dichloro - 5 - palmityl amino - 1 - naphthol
- 5 - diphenylethersulphonamido - 1 - naphthol
- 1 - hydroxy - 2 - (N - isoamyl - N - phenyl) - naphthamide
- 15 1 - hydroxy - 2 - (N - p - sec. amylphenyl) - naphthamide
- β - hydroxy - 1 - α - naphthoyl - 1,2,3,4 - tetrahydroquinoline
- 2 - lauryl - 1 - chlorophenol
- 20 1 - naphthol - 2 - carboxylic - α - naphthyl - amide
- 1 - naphthol - 5 - sulpho - cyclohexylamide
- 5 - phenoxyacetamido - 1 - naphthol
- 5 - β - phenylpropionyl amino - 1 - naphthol
- 25 Monochlor - 5 - (N - γ - phenylpropyl - N - p - sec. amyl - benzoyl amino) - 1 - naphthol
- 4 - Dimethylamino - 4¹ - lauroylamido - stilbene
- 1 - [4 - (2,4 - Di - t - amylphenoxy - acetamido)phenyl] - 4 - phenylbutal - 1,3 - diene
- 7 - Diethylamino - 4 - methylcoumarin
- 3 - Ethoxycarbonyl - 5,6 - benzo - coumarin
- Diethyl succinylsuccinate
- 1,4 - bis - (2 - Benzoxazolyl)benzene
- cis - 1,2 - Bis - (2 - benzoxazolyl) - ethylene
- trans - 1,2 - Bis - (2 - benzoxazolyl) - ethylene
- cis - 1,2 - Bis - (2 - benzimidazolyl) - ethylene
- 3 - (5 - Hydroxy - 2 - phenyloxazol - 4 - ylmethylene)isochroman - 1,4 - dione
- 3 - phenyl - 7 - (2 - [dimethylamino - ethyl]ureido)coumarin

The substituted stilbene and substituted coumarin (such as those described in British Patent No. 786,234) fluorescent brightening agents are particularly useful. Further fluorescent brightening agents which may be used in the materials of the invention are described in Specification Nos. 1,072,914 and 1,072,915.

The following example illustrates the preparation of a photographic colour print material according to the invention.

Example

0.5 gm of 3-phenyl-7-[2-dimethylamino-ethyl]ureido]coumarin, a fluorescent brightening agent, was dissolved in 13 ml of dibutyl phthalate at about 90—100°C together with 0.5 gm of α -pivalyl-2-chloro-5-[γ -(2,4-di-tert-amylphenoxy)butyramido] acetanilide, a yellow coupler. The solution was passed into 30 ml of 9% by weight 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 gm of silver (approximately 80% chloride and 20% bromide). The mixture was coated on a baryta coated paper base to give 0.0336 gm of silver and 0.028 gm of the fluorescent compound per square foot. After setting and drying a plain gelatin layer, a green sensitive silver halide emulsion layer containing a magenta coupler, a further gelatin layer, a red sensitive silver halide emulsion layer containing a cyan coupler were coated on top of the blue sensitive layer in succession.

The coated material was exposed to a step-wedge and developed in a developer containing 4-amino-N-ethyl-N-[β -methane sulphonamidoethyl]-m-toluidine sesqui sulphate monohydrate as the active agent after which it was treated successively with a stop bath, fixing bath, bleaching bath and hardened in the usual manner. The colour

The amount of the fluorescent brightening agent incorporated into the silver halide emulsion layer should be greater than 5 milligrams per square foot, and preferably between 15 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 auto-quenching effect.

The fluorescent brightening agent by its absorption of ultraviolet radiation serves to protect the dyes in lower layers of the colour 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 colour print material. In this case, the ultraviolet absorber is incorporated in a layer of the colour print material below the layer containing the fluorescent brightening agent so that the fluorescence thereof is not diminished due to absorption of ultraviolet radiation by the ultraviolet absorber.

The fluorescent brightening agents which are used in accordance with the 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 a colour print material in accordance with our invention. Among such fluorescent brightening agents are the following:

1. 2 - (4¹ - Stilbenyl) - 1,4,5 - triphenyl - imidazole

print obtained showed good whiteness in the areas where there was no dye formation due to the fluorescence of the fluorescent brightening agent. There was no fluorescence or bloom in the high density areas.

WHAT WE CLAIM IS:—

1. A photographic colour print material comprising a white reflecting support carrying three light sensitive silver halide emulsion layers, one of each sensitive respectively to the red, green and blue regions of the spectrum, in which at least one emulsion layer below the top emulsion layer contains a dispersion of a water insoluble fluorescent brightening agent dissolved or dispersed in a water insoluble liquid which has a boiling point greater than 175°C and which is a solvent for the fluorescent brightening agent.
2. A photographic colour print material as claimed in claim 1 in which each light sensitive silver halide emulsion layer contains a coupler capable of dye formation with the oxidation products of a colour developing agent.
3. A photographic colour print material as claimed in claim 2 in which the coupler is dissolved or dispersed in a water insoluble liquid.
4. A photographic colour print material as claimed in claim 3 in which the fluorescent compound is dissolved or dispersed in the same liquid as the coupler in one of the light sensitive layers.
5. A photographic colour print material as claimed in any of the preceding claims in which the fluorescent compound is a fluorescent coumarin derivative.
6. A photographic colour print material as claimed in claim 5 in which the fluorescent compound is 3-phenyl-7-(2-[dimethylamino-ethyl]ureido) coumarin.

7. A photographic colour print material as claimed in any of the preceding claims 4 to 6 in which the fluorescent compound is dissolved in the same liquid as a phenolic coupler.

8. A photographic colour print material as claimed in any of the preceding claims in which the amount of fluorescent compound lies between 5 and 100 milligrams per square foot.

9. A photographic colour print material as claimed in claim 8 in which the amount of the fluorescent compound lies between 15 and 35 milligrams per square foot.

10. Photographic colour print materials as claimed in claim 1 and as herein described.

11. A photographic colour print material as claimed in claim 1 and as herein described with reference to the example.

12. Method of making a photographic colour print comprising exposing a material according to claim 1 to a pattern of red, green and blue light and processing the exposed material so as to obtain a cyan, magenta and yellow dye image in the red, green and blue sensitive layers respectively.

13. Photographic colour prints whenever made by the method of claim 12.

14. A photographic colour print comprising a white reflecting support carrying three layers containing cyan, magenta and yellow dye images respectively in which at least one dye image-containing layer below the top dye image-containing layer contains a dispersion of a water insoluble fluorescent brightening agent dissolved or dispersed in a water insoluble liquid which has a boiling point greater than 175°C and which is a solvent for the fluorescent brightening agent.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1968.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
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WHAT WE CLAIM IS:—

1. A photographic colour print material comprising a white reflecting support carrying three light sensitive silver halide emulsion layers, one of each sensitive respectively to the red, green and blue regions of the spectrum, in which at least one emulsion layer below the top emulsion layer contains a dispersion of a water insoluble fluorescent brightening agent dissolved or dispersed in a water insoluble liquid which has a boiling point greater than 175°C and which is a solvent for the fluorescent brightening agent.
2. A photographic colour print material as claimed in claim 1 in which each light sensitive silver halide emulsion layer contains a coupler capable of dye formation with the oxidation products of a colour developing agent.
3. A photographic colour print material as claimed in claim 2 in which the coupler is dissolved or dispersed in a water insoluble liquid.
4. A photographic colour print material as claimed in claim 3 in which the fluorescent compound is dissolved or dispersed in the same liquid as the coupler in one of the light sensitive layers.
5. A photographic colour print material as claimed in any of the preceding claims in which the fluorescent compound is a fluorescent coumarin derivative.
6. A photographic colour print material as claimed in claim 5 in which the fluorescent compound is 3-phenyl-7-(2-[dimethylamino-ethyl]ureido) coumarin.
7. A photographic colour print material as claimed in any of the preceding claims 4 to 6 in which the fluorescent compound is dissolved in the same liquid as a phenolic coupler.
8. A photographic colour print material as claimed in any of the preceding claims in which the amount of fluorescent compound lies between 5 and 100 milligrams per square foot.
9. A photographic colour print material as claimed in claim 8 in which the amount of the fluorescent compound lies between 15 and 35 milligrams per square foot.
10. Photographic colour print materials as claimed in claim 1 and as herein described.
11. A photographic colour print material as claimed in claim 1 and as herein described with reference to the example.
12. Method of making a photographic colour print comprising exposing a material according to claim 1 to a pattern of red, green and blue light and processing the exposed material so as to obtain a cyan, magenta and yellow dye image in the red, green and blue sensitive layers respectively.
13. Photographic colour prints whenever made by the method of claim 12.
14. A photographic colour print comprising a white reflecting support carrying three layers containing cyan, magenta and yellow dye images respectively in which at least one dye image-containing layer below the top dye image-containing layer contains a dispersion of a water insoluble fluorescent brightening agent dissolved or dispersed in a water insoluble liquid which has a boiling point greater than 175°C and which is a solvent for the fluorescent brightening agent.

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