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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Fluorescent Brightening Agents in Colour Print Materials

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2. 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. Frequently, 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 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 ultraviolet light will be absorbed by such agents and prevented from reaching and activating the fluorescent brightening agent.

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 or sensitised respectively to 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 compound which is insoluble in water.

Preferably the top silver halide emulsion layer also contains a dispersion of an organic solvent in which is dissolved or dispersed a cyan forming colour coupler. It is frequently convenient for such a cyan forming colour coupler and the fluorescent compound to be contained in a single dispersion in the organic solvent.

Colour prints containing fluorescent agents in the upper red sensitive, cyan coupling layer in accordance with a preferred form of the invention effectively make the white areas of such prints appear whiter. In addition, these fluorescent agents when incorporated in colour prints in accordance with the invention provide good protection against the deleterious effects of ultraviolet light on the lower dye areas of the print. If desired, additional ultraviolet absorbing agents may be incorporated in the lower dye layers of the colour print to afford additional protection for these dyes against ultraviolet radiation without decreasing the brightening activity of the fluorescent agents in the colour prints. When the fluorescent brightening agents are incorporated in the top, cyan coupler containing layer of the colour print, the fluorescence of the brightening agent is not visible in areas where the cyan dye develops. Hence, objectionable

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SPECIFICATION AMENDED - SEE ATTACHED SLIP

bluish bloom, present in the colour prints containing fluorescent agents on top of the cyan layer is overcome by the present invention.

The substantially water insoluble fluorescent agents which are used in the materials of the invention are non-migratory. Hence, these fluorescent agents remain in the red sensitive, cyan-coupling layer during coating and processing. When water-soluble fluorescent agents are incorporated in colour 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 5 milligrams per square foot, and preferably is within about 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 agents which are incorporated in the photographic materials of 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 is suitable for incorporation in colour print materials in accordance with the invention. Among such fluorescent agents are the following:

1. 2 - (4' - Stilbenyl) - 1,4,5 - triphenylimidazole
2. 4 - Dimethylamino - 4' - lauroylamido-stilbene
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. vis - 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

Other useful fluorescent brightening agents include 4-benzoxazole stilbenes, 4,4'-bis benzoxazole stilbenes and 1[4-(benzoxazole-2-yl)phenyl]-4-phenylbuta-1,3-dienes. These compounds are described in applications Nos. 47527/62 (Serial No. 1072914) and 49689/63 (Serial No. 1072916) and specification No. 941,048.

Typical examples of specific compounds of this type are listed in Table 1 below:

TABLE 1

1 - [4 - (Benzoxazol - 2 - yl)phenyl] - 4-phenylbuta - 1,3 - diene	5
4 - (Benzoxazol - 2 - yl)stilbene	
4,4' - di - (Benzoxazol - 2 - yl) stilbene	70
4,4' - di - (Benzoxazol - 2 - yl) - 2-methyl stilbene	
4,4' - di - (Benzoxazol - 2 - yl) - α -cyanostilbene	10
4,4' - di - (Benzoxazol - 2 - yl) - 2,2'-dimethylstilbene	75
4,4' - di - (6 - Methoxybenzoxazol - 2 - yl) stilbene	
4,4' - di - (Benzoxazol - 2 - yl) - 2-aminostilbene	80
4,4' - di - (Benzoxazol - 2 - yl) - 2-hydroxystilbene	
4,4' - di - (Benzoxazol - 2 - yl) - 2-chlorostilbene	20
4,4' - di - (Benzoxazol - 2 - yl) - 2-cyanostilbene	85

The above compounds may be prepared in accordance with the methods described in the above mentioned applications and specification.

The following examples illustrate the preparation of photographic colour print material according to the invention.

EXAMPLE 1

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 an emulsion containing a fluorescent compound as described below 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 - sulphonamidoethyl] - m - toluidine sesquisulphate monohydrate as the active agent, and stopped, fixed, bleached and hardened in the usual manner. The colour 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.

0.5 grams 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-isopropylphthalenesulphonic 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

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photographic emulsion containing 1.2 gram of silver (approximately 80% chloride, 20% bromide) cyan colour coupler dispersion and gelatin.

5 EXAMPLE 2

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

75 WHAT WE CLAIM IS:—

1. A photographic colour print material comprising a white reflecting support carrying three light-sensitive silver halide emul-
15 sion 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 dis-
20 persed a fluorescent compound which is insoluble in water.

2. A photographic colour print material according to claim 1 in which the top silver halide emulsion layer also contains a dis-
25 persion of an organic solvent in which is dissolved or dispersed a cyan forming colour coupler.

3. A photographic colour print material according to claim 2 in which the cyan form-
30 ing colour coupler and the fluorescent com-

pound are contained in a single dispersion of the organic solvent.

4. A photographic colour print material according to any of the preceding claims in which the amount of the fluorescent compound
35 dispersed in the top layer lies between 5 and 100 milligrams per square foot.

5. A photographic colour print material according to claim 4 in which the amount of the fluorescent compound dispersed in the top
40 layer lies between 15 and 35 milligrams per square foot.

6. A photographic colour print material according to any of the preceding claims in which the fluorescent compound is one of those
45 listed in Table I herein.

7. A photographic colour print material according to any of the preceding claims in which the white reflecting support is baryta-
50 coated paper.

8. Photographic colour print materials as hereinbefore described.

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

10. Photographic colour prints whenever made by the method of claim 9.

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PATENTS ACT, 1949

SPECIFICATION NO. 1,072,915

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated 13th November 1969 this Specification has been amended
105 under Section 14 in the following manner:—

Page 1, line 51, page 3, line 21, after "water" insert "and not a colour forming coupler"

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photographic emulsion containing 1.2 gram of silver (approximately 80% chloride, 20% bromide) cyan colour coupler dispersion and gelatin.

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EXAMPLE 2

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

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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 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 compound which is insoluble in water.

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2. A photographic colour print material according to claim 1 in which the top silver halide emulsion layer also contains a dispersion of an organic solvent in which is dissolved or dispersed a cyan forming colour coupler.

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3. A photographic colour print material according to claim 2 in which the cyan forming colour coupler and the fluorescent com-

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pound are contained in a single dispersion of the organic solvent.

4. A photographic colour print material according to any of the preceding claims in which the amount of the fluorescent compound dispersed in the top layer lies between 5 and 100 milligrams per square foot.

5. A photographic colour print material according to claim 4 in which the amount of the fluorescent compound dispersed in the top layer lies between 15 and 35 milligrams per square foot.

6. A photographic colour print material according to any of the preceding claims in which the fluorescent compound is one of those listed in Table I herein.

7. A photographic colour print material according to any of the preceding claims in which the white reflecting support is baryta-coated paper.

8. Photographic colour print materials as hereinbefore described.

9. 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 or yellow dye image in each of the layers.

10. Photographic colour prints whenever made by the method of claim 9.

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