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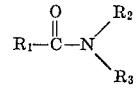
AMIDE DISPERSANT FOR FLUORESCENT AGENTS IN PHOTOGRAPHIC ELEMENTS

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ABSTRACT OF THE DISCLOSURE

Photographic elements are provided which contain a water-insoluble, organic fluorescent agent dispersed in amide solvent having the formula:



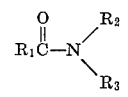
wherin R, is alkyl, aryl or aralkyl and R_2 and R_3 each are independently selected from group consisting of hydrogen, alkyl, aryl and aralkyl, the sum of the carbon atoms in R_1, R_2, and R_3 being at least 6.

This invention relates to photographic elements, and more particularly to photographic print materials having incorporated therein a dispersion of fluorescent agent. It also relates to dispersions of fluorescent agents in certain solvents.

It is desirable to provide photographic print materials having optical brightening agents or fluorescent agents therein to provide improved appearance of the white and highlight areas of the print. Previously, it has been suggested to provide dispersions of optical brightening agents in various high boiling solvents, such as dibutyl phthalate, and to incorporate such dispersions in photographic print materials. We have now found that improved brightening may be achieved with a given fluorescent agent when the fluorescent agent is dispersed in certain solvents in a high ratio of solvent to fluorescent agent.

One object of our invention is to provide novel dispersions of optical brightening agents. Another object of our invention is to provide photographic print materials having incorporated therein dispersions of fluorescent agent in certain solvents. Other objects of our invention will appear herein.

These and other objects of our invention are accomplished by providing a dispersion of fluorescent agent in a substantially water-insoluble, low-molecular weight, organic, crystalloidal amide having a boiling point above about 165° C., said amide having good solvent action for the fluorescent agent. Advantageously, the amides used in the invention have the following formula:



wherein R_1 is selected from the group consisting of alkyl, aryl and aralkyl, and R_2 and R_3 each are independently selected from the group consisting of H, alkyl, aryl and aralkyl, the sum of the carbon atoms in R_1, R_2 and R_3 being at least 6 and preferably at least 14. Good results are obtained when the sum of the carbon atoms in R_1, R_2 and R_3 are as high as 25 or 30, although higher numbers of carbon atoms in these groups may be used if desired. We have found that the dispersions in accordance with the invention provide substantially greater brightness to photographic elements than corresponding dispersions of the same fluorescent agents in the solvents which have previously been employed for this purpose. Photographic print materials having incorporated therein dispersions of fluorescent agent in accordance with the invention exhibit excellent rendition of the white and highlight areas and have the further advantage the dispersion of fluorescent agent is not leached from the print material during processing, and the dispersions do not migrate from the layer in which the are incorporated when the photographic print material contains a plurality of layers.

The improved results obtained with solvent dispersions in accordance with the invention over those of the prior art are demonstrated in the following examples. In these examples, a three color paper print material was prepared. The print material was identical in each example except for the cyan coupler dispersion included in the red sensitive emulsion layer. The color print materials had the following composition:

Layer 6—gelatin
Layer 5—red sensitive silver halide emulsion and a phenolic cyan coupler
Layer 4—gelatin
Layer 3—green sensitive silver halide emulsion containing a pyrazolone magenta coupler
Layer 2—gelatin
Layer 1—blue sensitive silver halide emulsion containing an acyl acetanilide yellow coupler
Paper support

Example 1

A solution of 2.52 grams of a phenolic cyan coupler such as, for example, Couplers Nos. 3, 4, 5, or 6 of U.S Patent 2,801,171, in 5.04 ml. diethylauramide was dispersed in an aqueous solution containing 5.58 grams gelatin and about 0.1 gram wetting agent (Alkanol B) The mixture was passed five times through a Manton-Gaulin colloid mill, and the final weight was adjusted with water to 126 grams. This was used as the cyan coupler dispersion in the red sensitive layer (Layer 5) to give a coverage of 35 mg. of the cyan coupler per square foot.

Example 2

Example 1 was repeated except that dibutylphthalate was used in place of diethylauramide.

Example 3

Example 1 was repeated except that 0.36 gram 3-(phenyl)-7-(2 - [dimethylaminoethyl]ureido) coumarin was dissolved in the diethylauramide along with the cyan coupler, giving a coverage of 5 mg. of the fluorescent agent per square foot.

Example 4

The procedure of Example 3 was repeated except that 10.08 ml. of diethylauramide was used in place of the 5.04 ml. quantity.

Example 5

The procedure of Example 3 was repeated except that dibutyl phthalate was used instead of diethylauramide.

Example 6

The procedure of Example 4 was repeated except that dibutyl phthalate was used in place of diethylauramide.

The photographic print materials prepared in accordance with the above examples each were exposed on an intensity scale sensitometer and processed in the same manner by a standard color development process for color print materials of the type having incorporated color forming couplers. The results obtained are tabulated in the following table:

TABLE I

Solvent	Ratio of solvent to brightener	Relative spectral radiance	Relative spectral fluorescence
Diethyl Lauramide	(1)	69.0	2.0
Do	14:1	69.6	23.8
Do	28:1	72.3	38.2
Dibutyl phthalate	(1)	69.0	2.0
Do	14:1	69.6	9.8
Do	28:1	69.4	13.0

[1] No brightener.

In the above table, relative spectral radiance was determinated by measuring the energy emitted and reflected from the sample when irradiated with undispersed white light. Relative spectral fluorescence was determined by irradiating the samples with ultraviolet energy (365 mercury line) and the emitted energy was measured monochromatically in the visible region of the spectrum. (The fluorescent agent absorbs ultraviolet energy and re-emits it in the blue region of the spectrum.) The relative spectral radiance is a highly sensitive measurement and increases of 1 to 2 units are readily apparent to an observer on the greatly improved brightness in white and highlight areas.

As may be observed in the information set out in the above table, the combination of diethylauramide and optical brightening agent, at a high solvent to brightener ratio, produced an increase of three units in the relative spectral radiance scale, thus showing a highly unexpected increase in the brightness of this paper print material over samples containing dispersions of the same brightening agent but using the dibutyl phthalate solvent of the prior art. In addition, the information shows that a very substantial improvement is obtained in the relative spectral fluorescence when diethylauramide is employed as solvent over that obtained when dibutyl phthalate is used.

A large number of amides in addition to diethylauramide coact with fluorescent agents to produce an unexpected increase in relative radiance in compositions containing such dispersions. Typical useful amides include caprylamide, capramide, lauramide, myristamide, palmitamide and stearamide. We have also found that the N-monoalkyl and N,N-dialkyl substituted amides are highly useful, such as N-butyl caprylamide, N,N-dipropyl capramide, N-methyl lauramide, N,N-dibutyl myristamide, N,N-dipropyl palmitamide and N,N-dimethyl stearamide. Particularly useful results are obtained when, in the general formula given above, R_1 is an alkyl group of from 6–20 carbon atoms, and R_2 and R_3 are H or alkyl groups of 1–4 carbon atoms. Other useful amides may contain aryl groups, such as phenyl.

The solvents which we employ in accordance with our invention are useful in dispersing any water insoluble, organic fluorescent agent with an improvement in the relative radiance or brightness of photographic prints containing such dispersion. Typical useful fluorescent agents include benzidines, coumarins, stilbenes, benzimidazoles, benzoxazoles and pyrazolidones. Especially useful dispersions in accordance with the invention are obtained with the 7-amino coumarin compounds, preferably the 7-ureido coumarin brightening agents of the type described in British Patent 786,234.

In order to obtain substantially improved relative radiance with dispersions in accordance with the invention, it is desirable to employ a solvent to fluorescent agent ratio of at least 10:1, and preferably of at least 20 to 25:1. Considerably higher ratios of solvent to fluorescent agent may be employed if desired, such as 50:1, 100:1 or higher. (As used herein and in the appended claims, the ratio of solvent to fluorescent agent is in parts by weight.)

Dispersions of optical brightening agents in the solvents employed in the invention may be advantageously incorporated in black-and-white photographic materials, either in the emulsion layer or in a layer separate from the emulsion layer. The dispersions of the invention are highly useful in photographic color print materials, and may be dispersed in any suitable layer. For example, in color print materials of the type having separate red, green and blue sensitive emulsion layers containing couplers capable of forming, respectively, cyan, magenta, and yellow dye, the dispersions of the invention may be incorporated in any layer thereof, or, preferably in the outermost color coupler-containing layer. Advantageously, the dispersions are incorporated in a layer of color print material which contains color-forming couplers which, upon development, form a dye which coacts with the fluorescent agent in the dispersions of the invention to extinguish fluorescence in just those areas where the dye has been developed. Elements of this type are highly advantageous in that they provide extremely good whiteness in areas of the print where no dye is developed, and produce good brightness in highlight areas of the print, while at the same time avoiding any objectionable bluish bloom which is sometimes present in color print materials of the type having optical brightening agents incorporated in the support. The phenolic (including naphtholic) cyan forming couplers are typical of the couplers which form dyes that coact with fluorescent agents to selectively extinguish fluorescence in just those areas where the dye is developed. Typical useful phenolic cyan couplers are described in U.S. Patents 2,423,730 and 2,801,171.

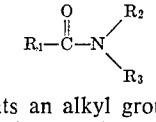
The dispersions of optical brightening agent in accordance with the invention may be incorporated in photographic elements in various hydrophilic colloid layers (which, as noted above, may contain silver halide). Typical useful hydrophilic colloids are all those described in Col. 13, lines 41–67 of U.S. Patent 3,039,873.

The dispersions of the invention may also be incorporated in hydrophilic coatings to be used as scintillating layers in direct electron recording films. Such coatings may be applied over or under a silver halide emulsion layer, or on the opposite side of the support from the emulsion.

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:

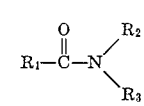
1. A photographic element comprising a support having coated thereon a light sensitive silver halide emulsion layer and a separate hydrophilic colloid layer, at least one of said layers having incorporated therein a dispersion of water-insoluble organic fluorescent agent in a solvent having the following formula:



wherein R_1 represents an alkyl group having from 6 to 20 carbon atoms; and, R_2 and R_3 each is selected from the group consisting of hydrogen and an alkyl group containing from 1 to 4 carbon atoms.

2 A photographic element as defined in claim 1 wherein the sum of the carbon atoms in the alkyl groups in R_1, R_2 and R_3 is from 14 to 25.

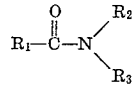
3. A photographic element comprising a support having coated thereon a light sensitive silver halide emulsion layer containing a dispersion of water-insoluble organic fluorescent agent in a solvent having the following formula:



wherein R_1 represents an alkyl group having from 6 to 20 carbon atoms; and, R_2 and R_3 each is selected from the group consisting of hydrogen and an alkyl group containing from 1 to 4 carbon atoms.

4. A photographic element as defined in claim 3 wherein the sum or the carbon atoms in the alkyl groups in R_1, R_2 and R_3 is from 14 to 25.

5. A photographic element comprising a white reflecting support having coated thereon separate blue, green and red light sensitive silver halide emulsion layers, said layers containing color couplers which form, respectively, yellow, magenta, and cyan dyes on color development; the red sensitive layer containing cyan-forming coupler being the outermost light sensitive layer, said red sensitive layer having incorporated therein a dispersion of water-insoluble organic fluorescent agent in a solvent having the following formula:



wherein R_1 represents an alkyl group having from 6 to 20 carbon atoms; and, R_2 and R_3 each is selected from the group consisting of hydrogen and an alkyl group containing from 1 to 4 carbon atoms.

6. A photographic element as defined in claim 5 wherein the sum of the carbon atoms in the alkyl groups in R_1, R_2 and R_3 is from 14 to 25.

7. A photographic element as defined in claim 6 wherein said water insoluble organic fluorescent agent is a 7-ureido coumarin derivative and said solvent is diethyl lauramide.

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