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FLUORESCENT COATING COMPOSITION

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This invention relates to fluorescent coating compositions. More particularly, this invention relates to substantially colorless fluorescent coating compositions especially adapted to overprinting.

It is well known that objects coated or printed with colored, fluorescent organic dyes quickly acquire an undesirable appearance by daylight because of the poor light fastness of the fluorescent dyes. Thus, for example, when cards, sheets or the like articles are printed with colored, fluorescent dyes for the purpose of display under ultraviolet light at night, in a short time the articles lose their distinctive appearance and become unattractive for display by daylight, due to fading or virtual disappearance of the colors printed thereon. Therefore, it is usually necessary either to discard the display article, to replace it frequently, or to cover it during the daylight hours to protect it from light and thus prolong the period of useful fluorescence.

It is a purpose of the present invention to provide fluorescent coating compositions which are substantially colorless by daylight and which can be applied over the surface of white, monochromatic, or multi-colored objects coated or printed with relatively light-stable non-fluorescent pigments or dyes, thereby to obtain objects which display substantially the same colors both by daylight and under ultraviolet light in the respective coated areas.

It is feasible that an object, such as a display article, having printed thereon a given color be coated with a colorless dye which fluoresces under ultraviolet light in approximately the same color as the non-fluorescent pigment or dye. In this way, there could be produced a colored area which retains its color well in daylight, since relatively light-stable non-fluorescent pigments or dyes are readily available and can be employed. However useful this procedure might prove in the coating of monochromatic objects, the serious drawbacks involved in applying it to multi-colored objects are immediately apparent. Each area of different color to be overcoated with a compound fluorescing in the same color would require a separate process of overcoating and, as will be readily appreciated, this would in many cases be tedious and impractical if not impossible, particularly when intricate designs were involved. It is highly desirable, therefore, to have a single fluorescent coating composition which can be applied in one operation to all areas, regardless of color or design, on which a fluorescent coating is desired while at the same time each respective area retains substantially its same characteristic color under ultraviolet light as by daylight.

The novel coating compositions of the instant invention comprise a substantially colorless varnish having therein minor proportions by weight of a compound which fluoresces red under ultraviolet light, a compound which fluoresces blue under ultraviolet light, and a compound which fluoresces yellow under ultraviolet light, each of said compounds being substantially colorless in dilute solution (e.g. at concentrations of 0.01–1% by weight) by daylight and the three compounds being in such proportion to each other that the mixture fluoresces white or bluish-white over a white surface under ultraviolet light. These new coating compositions have substantially no effect on the color of prints coated therewith when the prints are viewed by daylight, and under ultraviolet light the coating fluoresces in approximately the same color as the daylight color of the print the coating overlies. Thus, for example, the coating fluoresces red over red, blue over blue, yellow over yellow, green over green, orange over orange, and so forth.

The only presently available red-fluorescent dye which is substantially colorless in dilute solution in colorless solvents by daylight apparently is 2-(3-hydroxy-2-naphthyl)benzimidazole and it is this compound which has been employed in preparing the compositions of this invention. It will be apparent to those skilled in the art, however, that any dye which fluoresces red under ultraviolet light and which is soluble in the varnish to the extent of 0.01–1% to yield a solution substantially colorless by daylight would be suitable for use in these novel varnishes.

As the blue-fluorescent compound, substantially colorless by daylight in dilute solution, in the new coating composition, it has been preferred to employ 4-methyl-7-dimethylaminocoumarin. Other members of the well-known 4-lower alkyl-7-substituted aminocoumarin class of blue-fluorescent dyes, particularly the 4-methyl-7-di-(lower alkyl)aminocoumarins, such as 4-methyl-7-diethylaminocoumarin, can be employed, if desired, or alternatively a chemically-different type of dye having the desired properties, for example acridone, can be employed.

The yellow-fluorescent compound substantially colorless by daylight in dilute solution preferably used in the coating compositions of this invention is 3,7-bis(phenylcarbamylamino)dibenzothiophene-5,5-dioxide. As will be readily appreciated, however, other yellow-fluorescent dyes having the requisite solubility in the varnish and yielding a substantially colorless dilute solution can be employed instead.

The varnishes suitable for use in the practice of this invention are the substantially colorless varnishes of the type commonly used in the printing and coating art which comprise a natural or synthetic resin and a solvent. These well-known compositions include, for example, rotogravure varnishes, steam-set varnishes, overprint varnishes, aniline ink varnishes, and letter press varnishes. A preferred type of varnish comprises a rosin or modified rosin in a glycol solvent, for example a rosin modified with an alpha, beta-unsaturated acid such as maleic acid or fumaric acid in diethylene glycol. Other very useful varnishes are, for example: ethyl cellulose in xylene; butylated melamine in a mixture of xylene and butanol; long chain fatty acid-modified phthalic-glycerol alkyd resin in a hydrocarbon solvent; and a liquid drying oil-modified phthalic alkyl resin such as Aroplaz 1278 (U.S. Industrial Chemicals, Inc.).

It has been found that the linseed oil varnishes do not afford good results in the practice of this invention.

The incorporation of the three fluorescent compounds into the colorless varnish is carried out by any of the usual procedures for formulating pigmented varnishes. The ingredients are mixed together, each in appropriate respective amount, until a uniform mixture is obtained. The resulting coating composition is applied as a varnish in conventional fashion.

Each of the fluorescent compounds is used in minor proportion by weight in the coating composition. The amount of each fluorescent compound is about 0.01–1% by weight of the coating composition, and it is generally preferred to employ approximately 0.1% of each. The exact relative amounts of the fluorescent compounds is determined of course by the requisite that they form

a mixture which is substantially colorless under ultraviolet light. For a given set of three compounds, the red to blue to yellow proportion is readily determined by mixing equal amounts of the three components into the colorless varnish, observing the color of the fluorescent coating composition thus obtained over a white background under ultraviolet light, and adding in small increments further amounts of any of the three dyes required to arrive at the proper red to blue to yellow proportion to produce a mixture fluorescing white or bluish white over the white background under ultraviolet light. For example, if the 1:1:1 mixture initially prepared fluoresces slightly red over white, more colorless, blue-fluorescing dye or more yellow-fluorescing dye or both are added; or if it fluoresces too blue over white, more colorless, red-fluorescing dye or more yellow-fluorescing dye, or both are added; and so forth. When using the preferred combination of 4-methyl-7-dimethylaminocoumarin, 2 - (3 - hydroxy - 2 - napthyl) benzimidazole, and 3,7-bis(phenylcarbamylamine)dibenzothiophene-5,5-dioxide, the use of approximately equal weights of each fluorescent compound is satisfactory, the 1:1:1 proportion being fairly good and optimum results being obtained by adding a small further quantity of 3,1 - bis(phenylcarbamylamino)dibenzothiophene - 5,5-dioxide to yield a red-blue-yellow proportion by weight of 1:1:1.2.

This invention is illustrated by the following examples without, however, being limited thereto.

Example 1

One-tenth percent solutions of each of 4-methyl-7-dimethylaminocoumarin, 2 - (3 - hydroxy - 2 - naphthyl) benzimidazole, and 3,7 - bis(phenylcarbamylamino)dibenzothiophene-5,5-dioxide (prepared as described in Example 22 of U.S. Patent 2,563,493), which are all compounds substantially colorless in dilute solution by daylight and which fluoresce blue, red, and yellow, respectively, under untraviolet light, were prepared in a varnish consisting of equal weights of diethylene glycol and fumaric acid-modified rosin having an acid number of approximately 350 (Teglac 127, American Cyanamid). Equal weights of these three solutions were mixed thoroughly to form a uniform mixture. The resulting fluorescent coating composition was used to coat a carton, printed blue with phthalocyanine blue ink and having non-fluorescent white letters thereon, by applying the composition with a roller over the whole surface of the carton. The appearance of the carton when thus coated was virtually unchanged when viewed by daylight; and under ultraviolet light, the blue area fluoresced blue and the white letters fluoresced bluish-white. While this result was fairly satisfactory in that a pleasing effect was obtained, it appeared that more fluorescent yellow in the mixture was desirable and by gradual addition of a further quantity of a 0.1% solution of 3,7 bis(phenylcarbamylamino)dibenzothiophene-5,5-dioxide to the composition there was obtained an optimum weight proportion of blue-red-yellow of 1:1:1.2. On exposure to daylight, the coated carton retained its normal appearance, showing no discoloration even after the fluorescence of the carton under ultraviolet light had diminished substantially.

Example 2

Following the same operative procedure as described above in Example 1, except that as the varnish there was used a 10% solution of ethyl cellulose (high viscosity; Hercules N–22) by weight in xylene. The fluorescent coating compositions (red-blue-yellow proportions of 1:1:1 and 1:1:1.2) obtained in this manner were each coated over cartons printed with non-fluorescent red, green, and blue inks on a non-fluorescent white background. The appearance of the coated cartons in both instances was virtually unchanged by daylight, and under ultraviolet light the red fluoresced red, the green fluoresced green, the blue fluoresced blue and the white fluoresced white.

Example 3

The same general procedure described above in Example 1 was followed but there were used 10% solutions of each of the three fluorescent dyes in a varnish composed of 50% by weight of butylated melamine (Resimene 875, Monsanto), in a mixture consisting of equal parts by weight of xylene and butanol. The fluorescent coating compositions (red-blue-yellow proportions of 1:1:1 and 1:1:1.2) thus obtained were each coated over cartons printed with non-fluorescent blue and yellow inks on a non-fluorescent white background. The appearance of the cartons in both instances was unchanged by daylight and under ultraviolet light the blue fluoresced blue, the yellow fluoresced yellow, and the white fluoresced white.

What is claimed is:

1. A fluorescent coating composition comprising a substantially colorless varnish having incorporated therein minor proportions by weight of a compound which fluoresces red under ultraviolet light, a compound which fluoresces blue under ultraviolet light, and a compound which fluoresces yellow under ultraviolet light, each of said compounds being substantially colorless in dilute solution by daylight and being in such proportion to each other that the mixture fluoresces white over a white surface under ultraviolet light.

2. A fluorescent coating composition comprising a substantially colorless varnish having incorporated therein minor proportions by weight of 3,7-bis(phenylcarbamylamino)dibenzothiophene - 5,5 - dioxide, a 4 - methyl - 7-di(lower alkyl)aminocoumarin, and 2 - (3 - hydroxy - 2-naphthyl)benzimidazole, each of said compounds being substantially colorless in dilute solution by daylight and being in such proportion to each other that the mixture fluoresces white over a white surface under ultraviolet light.

3. A fluorescent coating composition comprising a substantially colorless varnish consisting essentially of a resin and a solvent for said resin, and approximately equal minor proportions by weight of 2-(3-hydroxy-2-naphthyl)benzimidazole, a 4-methyl-7-di(lower alkyl)-aminocoumarin, and 3,7-bis(phenylcarbamylamino)dibenzothiophene-5,5-dioxide.

4. A fluorescent coating composition comprising a substantially colorless varnish consisting essentially of a resin and a solvent for said resin, and approximately equal minor proportions by weight of 2-(3-hydroxy-2-naphthyl)benzimidazole, 4 - methyl - 7 - dimethylaminocoumarin, and 3,7 - bis(phenylcarbamylamino)dibenzothiophene-5,5-dioxide.

5. A fluorescent coating composition comprising a substantially colorless varnish consisting essentially of a fumaric acid-modified rosin and a diethylene glycol and incorporated in said varnish a minor weight proportion of a mixture of one part by weight of 2-(3-hydroxy-2-naphthyl)benzimidadzole, one part by weight of 4-mthyl-7-dimethylaminocoumarin, and one and two-tenths parts by weight of 3,7-bis(phenylcarbamylamino)dibenzothiophene-5,5-dioxide.

6. A fluorescent coating composition comprising a substantially colorless varnish consisting essentially of a solution of ethyl cellulose in xylene and incorporated in said varnish a minor weight proportion of a mixture of one part by weight of 4-methyl-7-dimethylaminocoumarin, one part by weight of 2-(3-hydroxy-2-naphthyl)benzimidazole and one and two-tenths parts by weight of 3,7 - bis(phenylcarbamylamino)dibenzothiophene-5,5-dioxide.

7. A fluorescent coating composition comprising a substantially colorless varnish consisting essentially of a solution of butylated melamine in a mixture of xylene and butanol and incorporated in said varnish a minor weight

proportion of a mixture of one part by weight of 4-methyl-7-dimethylaminocoumarin, one part by weight of 2-(3-hydroxy-2-naphthyl)benzimidazole and one and two-tenths parts by weight of 3,7-bis(phenylcarbamylamino)dibenzothiophene-5,5-dioxide.

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