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2,937,997

DETERGENT COMPOSITIONS CONTAINING CARBOXY-ESTERS OF HYDROXYBENZIMIDAZOLYL-STILBENES

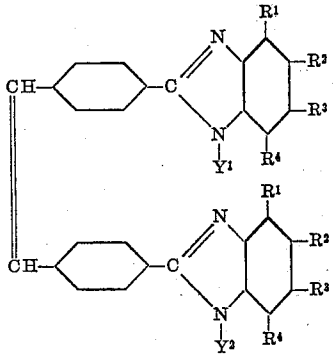
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12 Claims. (Cl. 252—117)

This invention relates to novel fluorescent carboxy-esters of the benzimidazolylstilbene series useful as whitening and brightening agents and to the preparation of the same.

In my U.S. patent application Serial No. 503,015, filed April 21, 1955, now U.S. Patent 2,838,504, issued June 10, 1958, there are described benzimidazolylstilbenes having the structural formula



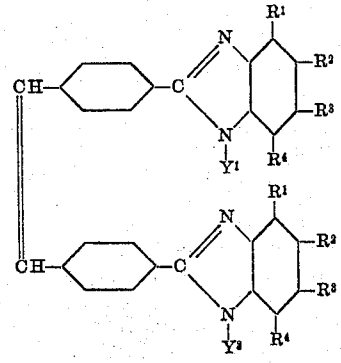
FORMULA I

where R^1, R^2, R^3, and R^4 are radicals of the class consisting of hydrogen, lower alkyl containing 1–4 carbon atoms, lower alkoxy containing 1–4 carbon atoms, and halo, and Y^1 and Y^2 are radicals of the class consisting of hydrogen, lower alkyl containing 1–6 carbon atoms, hydroxy-lower alkyl containing 2–6 carbon atoms, 2-hydroxy-3-sulfopropyl, hydroxy-oxaalkyl containing 3–15 carbon atoms, carboxy-lower alkyl containing 2–6 carbon atoms, cyano-lower alkyl containing 3–6 carbon atoms, allyl, methallyl, and monocyclic aralkyl containing 7–11 carbon atoms. The benzimidazolylstilbenes of the above formula are water-insoluble compounds which are highly useful as whitening and brightening agents, for instance in the form of dispersions in aqueous media, such as in soap and synthetic detergent compositions, for the treatment of white and colored textiles.

I have now discovered that certain of the benzimidazolylstilbenes described in my said prior application, namely those containing one or more alcoholic hydroxyl groups in the radicals Y^1 and Y^2, can be converted to novel carboxy-esters affording for some purposes valuable advantages as whitening and brightening agents in

the treatment of threads, sheets, films, filaments, textile fabrics and the like, as well as in the manufacture of paper, varnishes, inks, coatings, and plastics.

Broadly speaking, the new compounds of the instant invention are carboxy-esters of dicarboxylic acids with hydroxy-benzimidazolylstilbenes having the structural formula



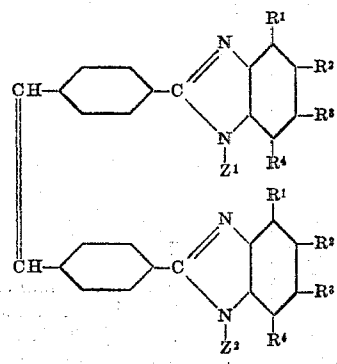
FORMULA II

where R^1, R^2, R^3, and R^4 are radicals of the class consisting of hydrogen, lower alkyl containing 1–4 carbon atoms, lower alkoxy containing 1–4 carbon atoms, and halo, Y^1 is a radical of the class consisting of hydrogen, lower alkyl containing 1–6 carbon atoms, hydroxy-lower alkyl containing 2–6 carbon atoms, 2-hydroxy-3-sulfopropyl, hydroxy-oxaalkyl containing 3–15 carbon atoms, carboxy-lower alkyl containing 2–6 carbon atoms, cyano-lower alkyl containing 3–6 carbon atoms, allyl, methallyl, and mono-cyclic aralkyl containing 7–11 carbon atoms, and Y^3 is a member of the class consisting of hydroxy-lower alkyl containing 2–6 carbon atoms, 2-hydroxy-3-sulfopropyl, and hydroxy-oxaalkyl containing 3–15 carbon atoms. It will be appreciated that the radicals R^1, R^2, R^3, R^4, and Y^1 are identical respectively with the corresponding radicals as defined in U.S. Patent 2,838,504, issued June 10, 1958, and that Y^3 represents the hydroxyl-containing radicals within the definition of Y^2 in the said co-pending application. More particularly, the carboxy-esters of my invention are those which can be prepared by interaction of cyclic anhydrides of aromatic, aliphatic, and cycloaliphatic 1,2-dicarboxylic acids with the hydroxy-benzimidazolylstilbenes of Formula II; in this reaction the alcoholic hydrogen of the hydroxy-benzimidazolylstilbene is replaced by a carboxy-carboxylic acyl radical of the structure

HOOC—A—CO—

where A is the residue of the 1,2-dicarboxylic acid. When two or more alcoholic hydroxyl groups are present in the hydroxybenzimidazole (Formula II), an appropriate amount of acid anhydride can be employed to afford one mole of acid anhydride per mole of alcoholic hydroxyl; ordinarily, however, I prefer to esterify no more than two of the hydroxyl groups in polyhydroxy-benzimidazolylstilbenes. Thus, in a preferred aspect, the

present invention relates to the new carboxy-esters having the structural formula



FORMULA III

where R^1, R^2, R^3, and R^4 are radicals of the class consisting of hydrogen, lower alkyl containing 1–4 carbon atoms, lower alkoxy containing 1–4 carbon atoms, and halo, Z^1 is a radical of the class consisting of hydrogen, lower alkyl containing 1–6 carbon atoms, carboxy-lower alkyl containing 2–6 carbon atoms, cyano-lower alkyl containing 3–6 carbon atoms, allyl, methallyl, monocyclic aralkyl containing 7–11 carbon atoms, acyloxy-lower alkyl wherein lower alkyl contains 2–6 carbon atoms, 2-acyloxy-3-sulfopropyl, and acyloxy-oxaalkyl wherein oxaalkyl contains 3–15 carbon atoms, and Z^2 is a radical of the class consisting of acyloxy-lower alkyl wherein lower alkyl contains 2–6 carbon atoms, 2-acyloxy-3-sulfopropyl, and acyloxy-oxaalkyl wherein oxaalkyl contains 3–15 carbon atoms, said acyloxy being defined in each instance in the definitions of Z^1 and Z^2 by the formula HOOC—A—COO—, where A is the residue of an acid of the group consisting of aromatic 1,2-dicarboxylic acids containing 8–20 carbon atoms, aliphatic 1,2-dicarboxylic acids containing 4–22 carbon atoms, and cycloaliphatic 1,2-dicarboxylic acids containing 7–8 carbon atoms.

The preparation and properties of the hydroxy-benzimidazolylstilbenes (Formula II) employed as starting materials in the instant invention are described in detail in my U.S. Patent 2,838,504, issued June 10, 1958. If desired, a pure hydroxy-benzimidazolylstilbene can be used; however, I have found that is frequently advantageous, especially from an economic standpoint, to employ a mixture of benzimidazolylstilbenes as the starting material. Thus, there can be used either a mixture of two or more hydroxy-benzimidazolylstilbenes (Formula II), or a mixture consisting chiefly of one or more hydroxy-benzimidazolylstilbenes (Formula II) with a minor proportion of one or more hydroxyl-free benzimidazolylstilbenes within the general Formula I above.

The acid anhydride starting materials employed in the preparation of my carboxy-esters are the cyclic anhydrides of aromatic, aliphatic, and cycloaliphatic dicarboxylic acids having the two carboxylic acid radicals attached to adjacent carbon atoms. These acid anhydrides are well-known as a class and many members are readily available commercially; illustrative compounds include: phthalic anhydride; halophthalic anhydrides such as chloro- and bromo-phthalic anhydrides, for instance 3-chlorophthalic anhydride, 3-fluorophthalic anhydride, 4-chlorophthalic anhydride, and tetrachlorophthalic anhydride; phenylphthalic anhydrides, such as 3,4-diphenylphthalic anhydride; 1,2-cyclohexanedicarboxylic anhydride; 1,2-cyclopentanedicarboxylic anhydride; 4-cyclohexene-1,2-dicarboxylic anhydride; succinic anhydride; alkylsuccinic anhydrides, such as methylsuccinic anhydride, dimethylsuccinic anhydride, dodecylsuccinic anhydride, and octadecylsuccinic anhydride; alkenylsuccinic anhydride, such as allylsuccinic anhydride, decenylsuccinic anhydrides, dodecenylsuccinic anhydrides, and octadecenylsuccinic anhydrides; aralkylsuccinic anhydrides, such as benzylsuccinic anhydride; maleic anhydride; alkylmaleic anhydrides, such as methylmaleic anhydride; and aralkylmaleic anhydrides, such as benzylmaleic anhydride. Phthalic anhydrides are the preferred acid anhydride starting materials.

The process of interacting the hydroxy-benzimidazolylstilbene with the cyclic dicarboxylic anhydride is conveniently carried out by employing approximately one mole of the acid anhydride per equivalent of hydroxyl desired to be esterified in the hydroxy-benzimidazolylstilbene, preferably, approximately one mole of acid anhydride is employed per mole of monohydroxy-benzimidazolylstilbene and two moles of acid anhydride per mole of dihydroxy- and polyhydroxy-benzimidazolylstilbenes. The esterification proceeds readily when the two reactants are heated together, advantageously in a solvent and in the presence of an organic base; it is usually sufficient to heat the mixture at 100–120° C. for about thirty minutes to one hour. The reaction mixture is then poured into acidified water, and the precipitate thus formed, which is the desired carboxy-ester of the hydroxy-benzimidazolylstilbene, is collected on a filter and washed. Sometimes, it is convenient to employ an excess of the acid anhydride as the reaction solvent, for example when esterifying a monohydroxy-benzimidazolylstilbene or when diesterifying a dihydroxy-benzimidazolylstilbene. In these cases, the mixture of the two reactants is heated to fusion to facilitate complete reaction.

Instead of employing a single acid anhydride in the reaction, there can be used a mixture of cyclic dicarboxylic acid anhydrides, in appropriate total quantity. Also, when more than one hydroxyl group in the hydroxy-benzimidazolylstilbene is to be esterified, the reaction can be carried out step-wise, one molecular equivalent of acid anhydride at a time, and the acid anhydride can be the same or different in each step, so that mixed carboxy-esters can be readily prepared if desired.

In general, my new carboxy-esters are yellow or greenish-yellow crystalline solids which are slightly soluble in dimethyl sulfoxide, 2-methoxyethanol, and 2-ethoxyethanol, and are insoluble in hydrocarbon solvents. The compounds form salts when mixed with organic or inorganic bases, and many of these salts are either readily soluble in water or more soluble in water than the free acid form of the carboxy-ester. Thus, the solubility of the carboxy-esters in solvent media such as water or aqueous lower alkanols is considerably enhanced by the presence of bases, for instance sodium hydroxide, potassium hydroxide, ammonia, pyridine, triethanolamine, 2,2-bis(hydroxymethyl)-2-aminoethanol, and the like. Many of the carboxy-esters are easily soluble in dilute aqueous ammonia solution.

When the new compounds of my invention are dissolved in aqueous media, they fluoresce blue-white under ultraviolet light and show a wide range of absorption in the ultraviolet region. Increasing the water-solubility of whitening and brightening agents ordinarily has an adverse effect on their substantivity to many synthetic fibers. Surprisingly, however, my new carboxy-esters, which have enhanced solubility in aqueous media as compared with the corresponding hydroxy-benzimidazolylstilbene starting materials (Formula II), are substantive to a wide variety of natural and synthetic fibers, for example, cotton, cellulose acetate, viscose rayon, nylon, and silk, and are absorbed by such fibers even from very low concentrations in aqueous solutions. The compounds have relatively high stability to sunlight, soap, synthetic detergents and chlorine-containing bleaching agents. The substantivity properties of the carboxy-esters are in fact closely similar to those of the hydroxy-benzimidazolylstilbenes (Formula II), which are substantially water-insoluble.

The above-described properties of my new compounds adapt them especially to use in aqueous solutions as whitening and brightening agents in treating fabrics to neutralize the yellowness in white textiles or to enhance the brilliance of colored textiles. In such utilization, the relatively high resistance of my compounds to chlorine bleaching and to light are valuable advantages.

The treatment of textile fabrics with my compounds is readily carried out by conventional procedures. Thus, for example, an aqueous solution containing about 0.0001 to 0.5% by weight of the carboxy-ester, or a salt thereof such as an ammonium salt, is applied to the fabric, which absorbs the fluorescent compound and is whitened or brightened beneficially thereby. This application of the compound can be conveniently carried out in conjunction with a washing or rinsing operation.

The solutions are readily formed, for example, by dissolving the compound in water alone or, if the water-solubility is not sufficiently high, in water containing a small amount of an organic or inorganic base. In some cases, a non-aqueous solvent such as 2-methoxyethanol or 2-ethoxyethanol, optionally containing a small amount of an organic base such as triethanolamine, can be employed. The solutions thus obtained can be mixed in desired quantity with a solid or liquid soap or synthetic detergent.

A preferred mode of using and marketing the compounds of my invention is by incorporating them into solid or liquid soaps and synthetic detergents in an appropriate concentration, for example 0.02 to 0.5% of the whitening and brightening agent by weight. The synthetic detergents used are water-soluble synthetic organic anionic and non-ionic detergents (for example, see McCutcheon's "Synthetic Detergents," McNair-Dorland Company, New York, N.Y., 1950, pages 120–174) such as organic sulfates and sulfonates, for instance sodium lorol sulfate, and sodium (higher alkyl) benzenesulfonates, and tert-dodecylmercaptopolyethoxyethanol (Nonic 218). Soaps and anionic detergents are of course frequently available in admixture with each other or with smaller amounts of inorganic detergents or builders such as tetrasodium pyrophosphate, sodium tripolyphosphate, sodium metasilicate, sodium borate and sodium perborate, and these mixtures can also be employed in utilizing my invention.

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

EXAMPLE 1

(A) 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene

A mixture of 4,4'-bis(benzimidazol-2-yl) stilbene, 180 ml. of 2-methoxyethanol, and 14.2 g. of a 50% aqueous solution of sodium hydroxide was heated at 76–86° C. and 30 g. of ethylene oxide was passed into the resulting solution over a period of one hour. During this period, a solid precipitated from the solution. To the reaction mixture there was then added dropwise 1500 ml. of warm (50° C.) water. The mixture was then filtered and the solid thus collected was washed with water to free it of alkali. There was thus obtained 39 g. of product which consisted chiefly of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl] - 4' - {1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl} stilbene (Formula II: Y^1=$HOCH_2CH_2$—; Y^3=$HOCH_2CH_2$—O—CH_2CH_2—; R^1, R^2, R^3, and R^4=H). It was found that this component could be separated from the mixture in pure form by repeated recrystallization of the product from 95% ethanol. The yield of the pure compound, a lemon-yellow crystalline solid melting at 280–285° C., from the mixture in this manner was about 30%.

Analysis.—Calcd.: N, 10.28%; C, 74.8%; H, 5.93%. Found: N, 10.47%; C, 74.25%; H, 5.90%.

(B) Bis(acid maleate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene

5.0 g. of the mixture of hydroxyethylated products obtained as described in part A above, 2.0 g. of maleic anhydride, 50 ml. of dimethyl sulfoxide, and 5 ml. of pyridine were heated together at 100–120° C. for thirty minutes. The reaction mixture was mixed with 500 ml. of water and made barely acid to Congo red paper by addition of hydrochloric acid. The mixture was filtered and the solid thus collected was washed free of hydrochloric acid with water. There was obtained in this manner 7.0 g. of product which melted at 155–157° C. It consisted chiefly of the bis(acid maleate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl] - 4' - {1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene (Formula III:

Z^1=HOOC—CH=CH—COO—CH_2CH_2—;

Z^2=HOOC—CH=CH—COO—CH_2CH_2—O—CH_2CH_2—;

R^1, R^2, R^3, and R^4=H). The product was readily soluble in 2-methoxyethanol containing a small amount of triethanolamine.

EXAMPLE 2

Bis(acid phthalate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene

10.92 g. of crude 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene obtained as described above in Example 1(A), 7.0 g. of phthalic anhydride, 40 ml. of dimethyl sulfoxide, and 5 ml. of pyridine were heated together at 100–120° C. for thirty minutes. The reaction mixture was stirred with 500 ml. of water having dissolved therein 7 ml. of concentrated (about 37%) hydrochloric acid. The insoluble product was collected on a filter paper, washed free of hydrochloric acid with water, and dried. There was thus obtained 15.9 g. of product which melted at 131–132° C. It consisted chiefly of the bis(acid phthalate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4' - {1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene (Formula III:

Z^1=ortho—HOOC—C_6H_4—COO—CH_2CH_2—;

Z^2=ortho—HOOC—C_6H_4—COO—CH_2CH_2—O—CH_2CH_2—;

R^1, R^2, R^3, and R^4=H). The product was soluble in dilute aqueous ammonia solution, dilute aqueous triethanolamine solution, and 2-methoxyethanol.

By neutralizing the product with two equivalents of 2,2-bis(hydroxymethyl)-2-aminoethanol, there was obtained the corresponding bis-amine salt.

Analysis.—Calcd. C, 64.3%; H, 5.76%; N, 7.75%; O, 22.2%. Found: C, 63.27%; H, 6.28%; N, 7.85%; O (by difference), 22.6%.

The above bis(acid phthalate) was also obtained in substantially the same yield when 40 cc. of N,N-dimethylaniline was used as the reaction solvent instead of the mixture of dimethyl sulfoxide and pyridine.

The same bis(acid phthalate) was also obtained when an excess of phthalic anhydride was used as a solvent and the reaction was carried out by fusing a mixture of the two reactants.

EXAMPLE 3

Acid phthalates of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl] - 4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene

A mixture of 54.2 g. of crude 4-[1-(2-hydroxyethyl) benzimidazol - 2 - yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl] benzimidazol-2-yl}stilbene, 15.5 g. of phthalic anhydride, 200 ml. of dimethyl sulfoxide, and 20 ml. of pyridine was

heated at 100–120° C. for thirty minutes. The reaction mixture was stirred in a solution of 35 ml. of concentrated hydrochloric acid in 2000 ml. of water. The insoluble product was collected on a filter, washed free of hydrochloric acid with water, and dried. There was thus obtained 67.0 g. of product which melted at 242° C. It was a mixture which consisted chiefly of the mono acid phthalates of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4' - {1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene (derivatives where in Formula II only one of the hydroxylic hydrogens is replaced by the acyl radical ortho—HOOC—C_6H_4—CO—; and R^1, R^2, R^3, and R^4=H).

EXAMPLE 4

Acid phthalates of dihydroxypropylated 4,4'-bis(benzimidazol-2-yl)stilbene

The starting material for this example was dihydroxypropylated 4,4'-bis(benzimidazol-2-yl)stilbene prepared as described in Example 28 of U.S. Patent 2,838,504, issued June 10, 1958, and interacted with sufficient ethylene oxide to ensure that no unreacted 4,4'-bis(benzimidazol-2-yl)stilbene remained in the product. The product consisted chiefly of 4-benzimidazol-2-yl-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]benzimidazol-2-yl}stilbene and lesser amounts of O- and N-hydroxyethylated derivatives thereof together with small amounts of 4-(benzimidazol - 2 - yl)-4'-[1-(2-hydroxyethyl)benzimidazol-2-yl)-stilbene and 4-(benzimidazol-2-yl)-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene.

27.3 g. of the above-indicated starting material, 100 ml. of dimethyl sulfoxide, and 10 ml. of pyridine were heated together at 115–120° C. for five minutes to ensure that all of the solid had dissolved. There was then gradually added to the hot solution 15.5 g. of phthalic anhydride over a period of about fifteen minutes. The reaction mixture was heated at 115–120° C. for one hour, and then was cooled and stirred with a mixture of 900 ml. of water, 17 ml. of concentrated hydrochloric acid, and 100 g. of ice. The mixture was filtered to collect the solid precipitate, which was washed free of hydrochloric acid with water and dried. There was thus obtained 34.8 g. of product which melted at 153° C. with evolution of gas. The chief components of this mixture were acid phthalates of 4-(benzimidazol-2-yl)-4'-{1-[2-hydroxy-3-(2,3 - dihydroxypropoxy)propyl]benzimidazol-2-yl}stilbene. It was soluble in ammoniacal 95% ethanol and in triethanolamine.

EXAMPLE 5

Acid phthalates of dihydroxypropylated 4,4'-bis[5(or 6)-methoxybenzimidazol-2-yl]stilbene

When 30.0 g. of 4-[5(or 6)-methoxybenzimidazol-2-yl]-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]-5-(or 6)-methoxybenzimidazol-2-yl}stilbene, prepared as described in Example 19 of U.S. Patent 2,838,504, issued June 10, 1958, is acylated with 15.5 g. of phthalic anhydride using a procedure similar to that described in Example 4 above, there are produced the acid phthalates of this hydroxy-benzimidazolstilbene.

EXAMPLE 6

Bis(acid 3- and 4-chlorophthalates) of 4-[1-(2-hydroxyethyl)-benzimidazol-2-yl]-4'-{1-[2-(2-hydroxyethoxy)]ethyl-benzimidazol-2-yl}stilbene

27.2 g. of crude 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1 - [2 - hydroxyethoxy)ethyl]benzimidazol-2-yl} stilbene, 20.0 g. of a mixture of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride, 100 ml. of dimethyl sulfoxide, and 10 ml. of pyridine were heated together at 100–120° C. for thirty minutes. The reaction mixture was stirred with a solution of 17 ml. of concentrated hydrochloric acid in 1000 ml. of water. The solid precipitate was collected on a filter, washed free of hydrochloric acid with water, and dried. There was thus obtained 43.3 g. of product which melted at 162–164° C. It consisted chiefly of a mixture of the bis(3-chlorophthalate) and the bis(4-chlorophthalate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl] - 4' - {1 - [2-(2-hydroxyethoxy)ethyl]benzimidazol - 2 - yl}stilbene (Formula III:

Z^1=3- and 4-Cl—C_6H_4—COO—CH_2CH_2—; Z^2=3- and 4-Cl—C_6H_4—COO—CH_2CH_2—O—CH_2CH_2—

R^1, R^2, R^3, and R^4=H). The product was soluble in dilute aqueous ammonia solution.

EXAMPLE 7

Bis(acid tetrachlorophthalate) of 4-[1-(2-hydroxyethyl)-benzimidazol-2-yl]-4'-{1-[2-(2 - hydroxyethoxy)ethyl]-benzimidazol-2-yl}stilbene

A mixture of 27.1 g. of crude 4-[1-(2-hydroxyethyl)-benzimidazol - 2-yl] - 4'-{1-[2-(2-hydroxyethoxy)ethyl]-benzimidazol-2-yl}stilbene, 28.6 g. of tetrachlorophthalic anhydride, 100 ml. of dimethyl sulfoxide, and 10 ml. of pyridine was heated at 100–120° C. for thirty minutes. The reaction mixture was mixed with a solution of 17 ml. of concentrated hydrochloric acid in 1000 ml. of water. The insoluble product was collected on a filter, washed free of hydrochloric acid with water, and dried. There was thus obtained 49.0 g. of product which melted at 186–188° C. It consisted chiefly of the bis(tetrachlorophthalate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4' - {1 - [2 - (2-hydroxyethoxy)ethyl]benzimidazol-2-yl} stilbene (Formula III:

Z^1=3,4,5,6-Cl_4—2—HOOC—C_6—COO—CH_2CH_2—

Z^2=3,4,5,6-Cl_4—2—HOOC—C_6—COO—CH_2CH_2—O—CH_2CH_2—

R^1, R^2, R^3, and R^4=H). The product was slightly soluble in dilute aqueous ammonia solution.

EXAMPLE 8

Acid tetrachlorophthalates of 4-[5(or 6)-chlorobenzimidazol-2-yl]-4'-{1-[2-hydroxy-3-(2,3-dihydroxpropoxy)-propyl]-5(or 6)-chlorobenzimidazol-2-yl}stilbene

When 33.4 g. of 4-[5(or 6)-chlorobenzimidazol-2-yl]-4'-{1-[2-hydroxy-3-(2,3 - dihydroxypropoxy)propyl]-5(or 6)-chlorobenzimidazol - 2 - yl}stilbene (prepared as described in Example 20 of U.S. Patent 2,838,504, issued June 10, 1958) and 14.3 g. of tetrachlorophthalic anhydride are interacted following a procedure similar to that described above in Example 7, there is obtained a product consisting of a mixture of the acid tetrachlorophthalates of the hydroxy-benzimidazolylstilbene.

EXAMPLE 9

Mixed acid phthalate and acid maleate esters of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2 - hydroxyethoxy)ethyl]-benzimidazol-2-yl}stilbene

A mixture of 27.1 g. of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2 - (2 - hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene, 100 ml. of dimethyl sulfoxide, and 10 ml. of pyridine was heated to 110–120° C. and to the hot mixture there was added 7.5 g. of phthalic anhydride. The reaction mixture was stirred at 110–120° C. for five minutes, then 5.0 g. of maleic anhydride was added, and stirring and heating at 110–120° C. were continued for one hour. The reaction mixture was cooled and poured into a solution of 17 ml. of concentrated hydrochloric acid in 1000 ml. of water. The insoluble precipitate was collected on a filter, washed free of hydrochloric acid with water, and dried. There was thus obtained 37.7 g. of product which melted at 160–162° C. It consisted of a mixture of the bis(acid phthalate), the bis(acid maleate), and the mixed acid phthalate-acid maleate esters. The product was soluble in ammoniacal 95% ethanol.

EXAMPLE 10

Mixed acid phthalate and acid maleate esters of dihydroxypropylated 4,4'-bis[5(or 6)-methylbenzimidazol-2-yl]stilbene

By acylating 30 g. of the dihydroxypropylated 4,4'-bis-[5(or 6)-methylbenzimidazol-2-yl]stilbene described in the latter portion of Example 18 of U.S. Patent 2,838,504, issued June 10, 1958, with 7.5 g. of phthalic anhydride and then with 5.0 g. of maleic anhydride, using a procedure similar to that described above in Example 9, there is obtained a mixture consisting chiefly of bis(acid phthalate), bis(acid maleate), and mixed acid phthalate-acid maleate esters.

EXAMPLE 11

Bis(acid succinate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene

A mixture of 8.0 g. of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl stilbene, 4.0 g. of succinic anhydride, 25 ml. of dimethyl sulfoxide, and 3 ml. of pyridine was heated at 100–120° C. for thirty minutes. The reaction mixture was mixed with a solution of 5.6 ml. of concentrated hydrochloric acid in 400 ml. of water and the insoluble precipitate was collected on a filter, washed free of hydrochloric acid with water, and dried. There was thus obtained 10.0 g. of product which melted at 124–126° C. It consisted chiefly of the bis(acid succinate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene (Formula III:

$$Z^1=HOOC—CH_2CH_2—COO—CH_2CH_2—;$$

$$Z^2=HOOC—CH_2CH_2—COO—CH_2CH_2—O—CH_2CH_2—;$$

R^1, R^2, R^3, and R^4=H).

EXAMPLE 12

Acid dodecylsuccinate of 4-(benzimidazol-2-yl)-4'-[1-(2,3-dihydroxypropyl)benzimidazol-2-yl]stilbene

Interaction of 25 g. of 4-(benzimidazol-2-yl)-4'-[1-(2,3-dihydroxypropyl)benzimidazol - 2 - yl]stilbene (obtained as described in Example 28A of U.S. Patent 2,838,504, issued June 10, 1958) with 14 g. of dodecylsuccinic anhydride, following a procedure similar to that described above in Example 11, yields the acid dodecylsuccinate of the hydroxy-benzimidazolylstilbene starting material.

EXAMPLE 13

Acid dodecenylsuccinate of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2 - hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene

27.1 g. of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1 - [2 - (2 - hydroxyethoxy)ethyl]benzimidazol-2-yl}-stilbene, 13.3 g. of dodecenylsuccinic anhydride, 100 ml. of dimethyl sulfoxide, and 10 ml. of pyridine were heated together at 100–120° C. for thirty minutes. The reaction mixture was mixed with a solution of 17 ml. of concentrated hydrochloric acid in 1000 ml. of water. The insoluble precipitate was collected on a filter, washed free of hydrochloric acid with water, and dried. There was thus obtained 40.0 g. of product which melted at 150° C. with evolution of gas. It was a mixture which consisted chiefly of mono acid dodecenylsuccinates of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol - 2 - yl}stilbene (derivatives where in Formula II only one of the hydroxylic hydrogens is replaced by the radical

$$HOOC—C_2H_3(C_{12}H_{23})—CO—$$

and R^1, R^2, R^3, and R^4=H), with minor amounts of unreacted hydroxy-benzimidazolylstilbene and of the bis-(acid dodecenylsuccinate). The product was soluble in alkaline 95% ethanol.

EXAMPLE 14

Bis(acid 1,2-cyclohexanedicarboxylate) of 4-[1-(2-hydroxyethyl)benzimidazol - 2 - yl]-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene

27.2 g. of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2 - (2 - hydroxyethoxy)ethyl]benzimidazol - 2 - yl}-stilbene, 16.7 g. of 1,2-cyclohexanecarboxylic anhydride, 100 ml. of dimethyl sulfoxide, and 10 ml. of pyridine were heated together at 100–120° C. for thirty minutes. The reaction mixture was mixed with a solution of 17 ml. of concentrated hydrochloric acid in 1000 cc. of water. The insoluble precipitate was collected on a filter, washed free of hydrochloric acid with water, and dried. There was thus obtained 23.0 g. of product which melted with decomposition at 165–167° C. It consisted chiefly of the bis(acid 1,2-cyclohexanedicarboxylate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl] - 4' - {1 - [2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene (Formula III:

$$Z^1=2—HOOC—C_6H_{10}—COO—CH_2CH_2—;$$

$$Z^2=2—HOOC—C_6H_{10}—COO—CH_2CH_2—O—CH_2CH_2—;$$

R^1, R^2, R^3, and R^4=H). The product was soluble in dilute aqueous ammonia solution and was also moderately soluble in water.

EXAMPLE 15

Acid phthalate of 4-(benzimidazol-2-yl)-4'-[1-(2-hydroxy-2-sulfopropyl)benzimidazol-2-yl]stilbene

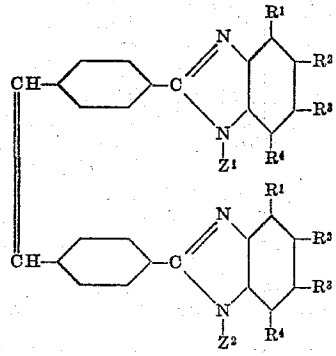
When 27.5 g. of 4-(benzimidazol-2-yl)-4'-[1-(2-hydroxy-2-sulfopropyl)benzimidazol-2-yl]stilbene (obtained by acidification of the sodium salt disclosed in Example 25 of U.S. Patent 2,838,504, issued June 10, 1958) is treated with 7.5 g. of phthalic anhydride by a procedure similar to that described in Example 3 above, there is obtained the acid phthalate of the hydroxy-benzimidazolylstilbene.

When the carboxy-esters described in the foregoing examples are dissolved in aqueous media, the solutions thus obtained fluoresce blue-white under ultraviolet light and show a wide range of absorption in the ultraviolet region. By incorporating the products into soaps and anionic and non-ionic detergents, there were obtained compositions highly useful, for example, for whitening white fabrics of cotton, nylon, and cellulose acetate. The preparation of compositions containing these carboxy-esters can be carried out in a manner similar to that described for the benzimidazolylstilbenes in U.S. Patent 2,838,504, issued June 10, 1958. Thus, for instance, in the preparation of compositions comprising 0.02–0.5% by weight of the above-described carboxy-esters, the following procedure was used. A solution of the carboxy-ester in dilute aqueous ammonia solution was added in appropriate amount to aqueous solutions of soap (for example a soap consisting of four parts by weight of the sodium salts of the C_{12}–C_{18} fatty acids derived from tallow), of synthetic anionic detergents (for example, (1) 21.8% of a mixture of sodium lauryl sulfate and sodium dodecylbenzenesulfonates, 18.2% of sodium sulfate, and 60% of sodium triphosphate and (2) 19.1% of sodium dodecylbenzenesulfonates, 15.6% of sodium sulfate, 55.0% of sodium triphosphate, and 10.3% of sodium carbonate), and of non-ionic detergents (for example, tert-dodecylmercaptopolyethoxyethanol, Nonic 218). The compositions thus obtained were found to impart a blue-white hue to white fabrics of cotton, nylon, and cellulose acetate, for instance.

This application is a division of my co-pending application Serial No. 575,353, filed April 2, 1956, now U.S. Patent 2,878,248, issued March 17, 1959.

I claim:

1. A detergent composition comprising a detergent selected from the group consisting of water-soluble soaps, water-soluble non-soap synthetic organic anionic detergents, and water-soluble synthetic organic non-ionic detergents and dissolved therein 0.02–0.5% by weight of a carboxy-ester having the structural formula

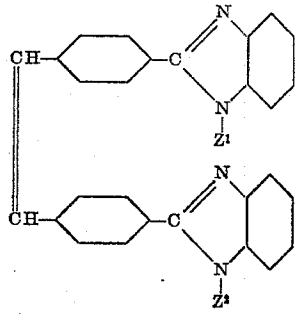


where R^1, R^2, R^3, and R^4 are radicals of the class consisting of hydrogen, lower alkyl containing 1–4 carbon atoms, lower alkoxy containing 1–4 carbon atoms, and halo, Z^1 is a radical of the class consisting of hydrogen, lower alkyl containing 1–6 carbon atoms, carboxy-lower alkyl containing 2–6 carbons atoms, cyano-lower alkyl containing 3–6 carbon atoms, allyl, methallyl, monocyclic aralkyl containing 7–11 carbon atoms, acyloxy-lower alkyl wherein lower alkyl contains 2–6 carbon atoms, 2-acyloxy-3-sulfopropyl, and acyloxy-oxaalkyl wherein oxaalkyl contains 3–15 carbon atoms, and Z^2 is a radical of the class consisting of acyloxy-lower alkyl wherein lower alkyl contains 2–6 carbon atoms, 2-acyloxy-3-sulfopropyl, and acyloxy-oxaalkyl wherein oxaalkyl contains 3–15 carbon atoms, said acyloxy being defined in each instance in the definitions of Z^1 and Z^2 by the formula

HOOC—A—COO—

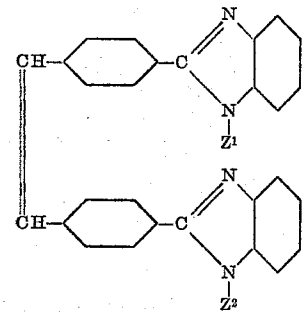
where A is the residue of an acid of the group consisting of aromatic hydrocarbon-1,2-dicarboxylic acids and aromatic halohydrocarbon-1,2-dicarboxylic acids containing 8–20 carbon atoms, aliphatic hydrocarbon-1,2-dicarboxylic acids containing 4–22 carbon atoms, and cycloaliphatic hydrocarbon-1,2-dicarboxylic acids containing 7–8 carbon atoms.

2. A detergent composition comprising a water-soluble synthetic organic anionic detergent and dissolved therein 0.02–0.5% by weight of a carboxy-ester having the structural formula



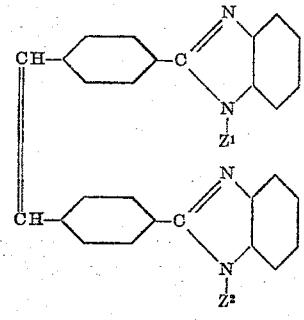
where Z^1 is acyloxy-lower alkyl wherein lower alkyl contains 2–6 carbon atoms and Z^2 is acyloxy-oxaalkyl wherein oxaalkyl contains 3–15 carbon atoms, said acyloxy being defined in each instance in the definitions of Z^1 and Z^2 by the formula HOOC—A—COO— where A contains 6–18 carbon atoms and is the residue of an aromatic hydrocarbon-1,2-dicarboxylic acid containing 8–20 carbon atoms.

3. A detergent composition comprising a water-soluble synthetic organic anionic sulfonated detergent and dissolved therein 0.02–0.5% by weight of a carboxy-ester having the structural formula



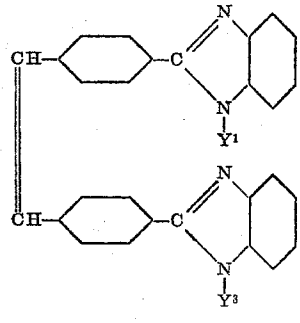
where Z^1 is acyloxy-lower alkyl wherein lower alkyl contains 2–6 carbon atoms and Z^2 is acyloxy-oxaalkyl wherein oxaalkyl contains 3–15 carbon atoms, said acyloxy being defined in each instance in the definitions of Z^1 and Z^2 by the formula HOOC—A—COO— where A contain 6–18 carbon atoms and is the residue of an aromatic hydrocarbon-1,2-dicarboxylic acid containing 8–20 carbon atoms.

4. A detergent composition comprising a water-soluble synthetic organic non-ionic detergent and dissolved therein 0.02–0.5% by weight of a carboxy-ester having the structural formula



where Z^1 is acyloxy-lower alkyl wherein lower alkyl contains 2–6 carbon atoms and Z^2 is acyloxy-oxaalkyl wherein oxaalkyl contains 3–15 carbon atoms, said acyloxy being defined in each instance in the definitions of Z^1 and Z^2 by the formula HOOC—A—COO— where A contains 6–18 carbon atoms and is the residue of an aromatic hydrocarbon-1,2-dicarboxylic acid containing 8–20 carbon atoms.

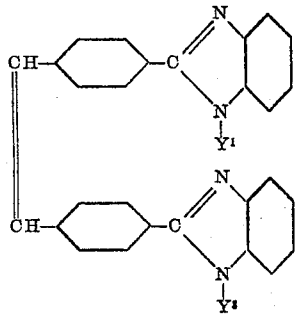
5. A detergent composition comprising a water-soluble synthetic organic anionic detergent and dissolved therein 0.02–0.05% by weight of an acid phthalate of a hydroxybenzimidazolylstilbene having the structural formula



where Y^1 is hydroxy-lower alkyl containing 2–6 carbon atoms and Y^3 is hydroxy-oxaalkyl containing 3–15 carbon atoms.

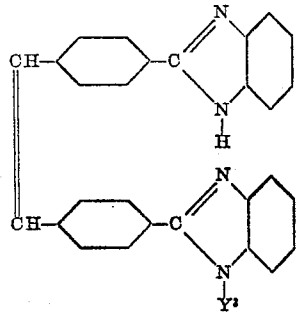
6. A detergent composition comprising a water-soluble synthetic organic anionic detergent and dissolved therein

0.02–0.05% by weight of an acid maleate of a hydroxy-benzimidazolylstilbene having the structural formula



where Y^1 is hydroxy-lower alkyl containing 2–6 carbon atoms and Y^3 is hydroxy-oxaalkyl containing 3–15 carbon atoms.

7. A detergent composition comprising a water-soluble synthetic organic anionic detergent and dissolved therein 0.02–0.05% by weight of an acid phthalate of a hydroxy-benzimidazolylstilbene having the formula

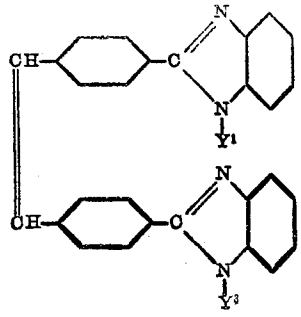


where Y^3 is hydroxy-oxaalkyl containing 3–15 carbon atoms.

8. A detergent composition comprising a water-soluble synthetic organic anionic detergent and dissolved therein 0.02–0.05% by weight of an acid phthalate of 4-(benzimidazol-2-yl)-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]benzimidazol-2-yl}stilbene.

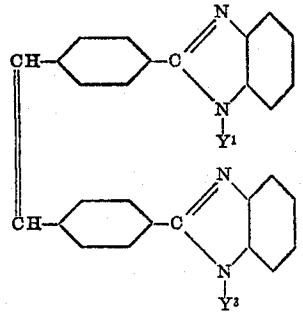
9. A detergent composition comprising a water-soluble synthetic organic anionic detergent and dissolved therein 0.02–0.05% by weight of a bis(acid halophthalate) of 4-[1-(2-hydroxyethyl)benzimidazol-2-yl]-4'-{1-[2-(2-hyroxyethoxy)ethyl]benzimidazol-2-yl}-stilbene.

10. A detergent composition comprising a water-soluble synthetic organic non-ionic detergent and dissolved therein 0.02–0.05% by weight of an acid phthalate of a hydroxy-benzimidazolylstilbene having the structural formula



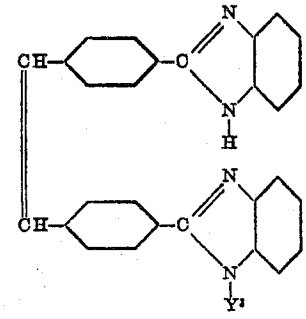
where Y^1 is hydroxy-lower alkyl containing 2–6 carbon atoms and Y^3 is hydroxy-oxaalkyl containing 3–15 carbon atoms.

11. A detergent composition comprising a water-soluble synthetic organic non-ionic detergent and dissolved therein 0.02–0.05% by weight of an acid maleate of a hydroxy-benzimidazolylstilbene having the structural formula



where Y^1 is hydroxy-lower alkyl containing 2–6 carbon atoms and Y^3 is hydroxy-oxaalkyl containing 3–15 carbon atoms.

12. A detergent composition comprising a water-soluble synthetic organic non-ionic detergent and dissolved therein 0.02–0.05% by weight of an acid phthalate of a hydroxy-benzimidazolylstilbene having the formula



where Y^3 is hydroxy-oxaalkyl containing 3–15 carbon atoms.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,937,997 May 24, 1960

Nathan N. Crounse

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 67, for "[2-hydroxyethoxy)ethyl]" read -- [2-(2-hydroxyethoxy)ethyl] --.

Signed and sealed this 6th day of December 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents