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DISPERSIONS OF BENZIMIDAZOLYLSTILBENE WHITENING AND BRIGHTENING AGENTS AND PRODUCTION THEREOF

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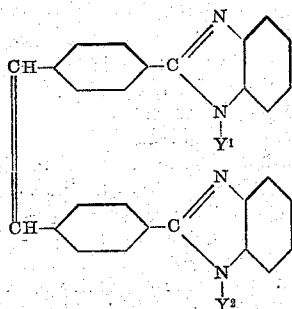
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This invention relates to the production of compositions comprising certain water-insoluble benzimidazolylstilbene whitening and brightening agents and higher fatty acid amides or alkanolamides, to the compositions thus obtained, and to the use of said compositions in the preparation of detergent compositions having whitening and brightening properties.

The incorporation of relatively small amounts of fluorescent whitening and brightening agents into water-soluble synthetic organic anionic detergents intended for use in laundering is now a common practice. This procedure is of course quite simple when whitening and brightening agents have suitable water-solubility are employed, since conventional mixing and dispersing procedures of the detergent art readily afford homogeneous aqueous compositions, which if desired can be dried in the usual fashion, as by spray-drying. However, when substantially water-insoluble fluorescent whitening and brightening agents are involved, there arises the problem of obtaining uniform and satisfactory dispersion of the relatively small quantity of the fluorescent agent in the detergent as reflected in the recovery of the full dyeing strength. While it is frequently possible to dissolve the water-insoluble fluorescent agent in one of the usual liquid organic solvents, such as an alcohol, ketone, or hydrocarbon, and thus facilitate its uniform incorporation into the detergent, toxicity and explosion hazards may be encountered with such solvents. Moreover, because of handling problems, some detergent manufacturers prefer not to receive the whitening and brightening agent in the form of a liquid preparation, preferring instead to receive and handle solid materials.

In Crouse U.S. Patent 2,838,504, issued June 10, 1958, there are described benzimidazolylstilbene whitening and brightening agents, certain of which have the structural formula



FORMULA I

wherein Y¹ and Y² are radicals of the class consisting of: hydrogen; lower alkyl containing 1–6 carbon atoms, for example methyl, ethyl, n-propyl, isobutyl, and n-hexyl; hydroxyl-lower alkyl containing 2–6 carbon atoms, for example 2-hydroxyethyl and 2,3-dihydroxypropyl; 2-hydroxy-3-sulfopropyl; hydroxy-oxaalkyl containing 3–15 carbon atoms, for example 2-hydroxy-3-(2,3-dihydroxypropoxy)propyl, 2-hydroxy-3-(2-hydroxyethoxy)-propyl, and 2-hydroxy-3-[2-(2-hydroxyethoxy)ethoxy]propyl; carboxy-lower alkyl containing 2–6 carbon atoms, for example carboxymethyl and 2-carboxyethyl; cyano-lower alkyl containing 3–6 carbon atoms, for example 2-cyano-

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ethyl and 3-cyanopropyl; allyl; methallyl; monocyclic aralkyl containing 7–11 carbon atoms, for example benzyl and benzyl containing 1–3 substituents, which can be the same or different, in the benzene ring, as halobenzyl, such as ortho-chlorobenzyl, para-fluorobenzyl, 2,4-dichlorobenzyl, and meta-bromobenzyl, lower alkylbenzyl such as ortho-methylbenzyl and para-isopropylbenzyl, and lower alkoxy-benzyl such as p-methoxybenzyl and 3,4-diethoxybenzyl, as well as 2-chloro-4-methoxybenzyl, 3-methoxy-4-methylbenzyl, 2-methoxy-4-chlorobenzyl, and the like; at least one of the radicals Y¹ and Y² being other than hydrogen. In general, the compounds of Formula I above are high-melting yellow or green-yellow solids which are substantially insoluble in water.

It is an object of the instant invention to provide novel and improved means for facilitating the uniform dispersal of relatively small proportions by weight of the water-insoluble benzimidazolylstilbene whitening and brightening agents of Formula I above in aqueous media containing water-soluble synthetic organic anionic detergents. A further object of this invention is the provision of these benzimidazolylstilbenes in a solid composition which can be uniformly dispersed, either as a comminuted solid or in melted, liquid form, in aqueous pastes of water-soluble synthetic organic anionic detergents to produce detergent compositions providing the full dye strength of the benzimidazolylstilbene when used in laundering.

In accordance with the present invention, a substantially water-insoluble benzimidazolylstilbene whitening and brightening agent of Formula I above is dissolved in an amide of the class consisting of higher fatty acid amides and higher fatty acid (lower alkanol)amides at a temperature in the approximate range 140–200° C., thereby forming a composition adapted to facilitate the preparation of detergent compositions containing a uniform dispersion of a relatively small quantity of the benzimidazolylstilbene in a relatively large quantity of an aqueous paste of a water-soluble synthetic organic anionic detergent, that is, detergent compositions having up to about 0.5% by weight of the benzimidazolylstilbene dispersed therein. Using any suitable means of stirring or blending, an appropriate amount of a solution of the benzimidazolylstilbene in the amide obtained in this manner can be added while in hot, liquid form to the detergent paste or, if desired, allowed to solidify by cooling and then added at any convenient time in re-melted, liquid form to the detergent paste. In the detergent compositions thus prepared, the benzimidazolylstilbene whitening and brightening agent is dispersed uniformly and satisfactorily, as evidenced by the fact that the dyeing strength of the detergent compositions is approximately 100% of the calculated amount based on the weight of the benzimidazolylstilbene employed, as determined by standard dye testing procedures.

The higher fatty acid amides useful in the practice of this invention are saturated aliphatic carboxylic primary amides of the general formula R—CO—NH₂ where R is an alkyl radical having about 8–18 carbon atoms. These amides are of course well-known and readily available compounds, being readily derived, for example, from the corresponding higher fatty acids obtained by the hydrolysis of various natural fats and oils such as coconut oil and tallow. The corresponding higher fatty acid (lower alkanol)amides, having 8–18 carbon atoms in the aliphatic chain, are likewise well-known and are readily prepared by amidation of the corresponding higher fatty acids or a suitable functional derivative thereof with a (mono- or di-lower alkanol)amine such as ethanolamine, diethanolamine, isopropanolamine, and the like. Among the preferred higher fatty acid amides and higher fatty

acid (lower alkanol) amides are: coconut fatty acid amides; coconut fatty acid (lower alkanol) amides such as coconut fatty acid ethanolamides and coconut fatty acid isopropanolamides; lauramide; lauric ethanolamide; lauric diethanolamide; stearamide; stearic ethanolamide; palmitic acid amide; palmitic acid ethanolamide; and the like. These amides and (lower alkanol) amides, in addition to functioning as a solvent for the brightening agent, can also function as a foam stabilizer, but of course other foam stabilizer substances can also be present in the detergent as known in the art.

The water-soluble synthetic organic anionic detergents involved in the practice of my invention are a well-known class of substances (for example, see McCutcheon's "Synthetic Detergents," McNair-Dorland Company, New York, 1950, pages 120-151) and include ordinary soaps (i.e., the alkaline metal salts of higher fatty acids), sulfonates, and sulfates. Examples of these detergents are alkyl aryl sulfonates, higher alkyl sulfates, sulfated and sulfonated amides and amines, sulfated and sulfonated esters and ethers, and higher alkyl sulfonates, for instance sodium p-dodecylbenzenesulfonate, sodium lauryl sulfate, the sodium salt of N-methyl-N-(2-sulfoethyl)oleic amide, the sodium salt of 2-sulfoethyl oleate, and sodium myristyl sulfonate. These detergents are of course frequently available in admixture with each other or with inorganic detergents or builders such as tetra sodium pyrophosphate, sodium tripolyphosphate, sodium metasilicate, sodium borate, and sodium perborate, or foam stabilizers such as lauric acid isopropanolamide and coconut fatty acid ethanolamides. These mixtures are also satisfactory for the present purposes.

In carrying out my invention, the amount of benzimidazolylstilbene which is dissolved in the amide can be varied as desired up to the saturation concentration involved in each instance. As indicated hereinabove the concentration of the benzimidazolylstilbene required in the anionic detergent paste for the desired whitening and brightening effect is relatively low, ordinarily being no more than 0.5% by weight and in most instances falling in the range 0.01-0.1% by weight. Accordingly, it is feasible to use dilute solutions of the benzimidazolylstilbene in the amide. However, I have found that solutions having about 5% or more by weight of the benzimidazolylstilbene have greater general usefulness than the more dilute solutions, since the latter are less convenient to handle, due to increased volume, and may in some instances involve introduction of a larger quantity of amide than desired into the anionic detergent. For most purposes, a concentration of 5-30% by weight of the benzimidazolylstilbene in the amide solution is convenient and satisfactory; using solutions of such concentration, the amount of the amide introduced into the detergent paste is minimized and in fact need be no greater than the amount in which amides of this type are conventionally used in anionic detergents to improve detergency.

As already indicated, the practical operative temperature range in dissolving the benzimidazolylstilbene in the amide is about 140-200° C. For preparation of relatively concentrated solutions, for instance 20% or more by weight of the benzimidazolylstilbene, it is generally preferable for best results to employ a temperature in the upper portion of the operative range, for instance 180-200° C. In the preparation of less concentrated solutions, any temperature in the range 140-200° C. is satisfactory for optimum results.

A particularly advantageous aspect of my invention is that it can be employed to provide compositions containing the benzimidazolylstilbene and the amide in a conveniently handled, comminuted solid form which can be readily and uniformly dispersed in aqueous pastes of water-soluble synthetic organic anionic detergents. For such purpose, a hot liquid solution containing up to about 20% by weight of the benzimidazolylstilbene, preferably

5-15%, in the amide is cooled as rapidly as possible to solidify it quickly, and if necessary the resulting solid is comminuted in suitable fashion, as by grinding.

In carrying out this procedure, I generally prefer to cool the hot liquid solution of the benzimidazolylstilbene in the amide rapidly and efficiently by spraying it into a reservoir, or alternatively by pouring it onto the chilled rolls of a flaker so that thin brittle flakes of the desired solid are produced. The solid product obtained by these methods can be dispersed directly by conventional techniques into an aqueous paste of a water-soluble synthetic organic anionic detergent to produce a detergent composition having a dyeing strength which is substantially 100% of the calculated strength based on the amount of benzimidazolylstilbene present.

If the hot liquid solution of the benzimidazolylstilbene in the amide is not cooled rapidly enough, use of the solid form will result in a detergent composition having less than 100% of the calculated dyeing strength, but the resulting solid can be used quite satisfactorily in re-melted, liquid form for addition to the detergent paste.

My invention is illustrated by the following examples without, however, being limited thereto. In these examples, the term "part" and "parts" are used to indicate part or parts by weight.

Example 1

A general procedure is as follows:

One part of a benzimidazolylstilbene having Formula I hereinabove is mixed with nine parts of a mixture of coconut fatty acid amides having the formula



where R represents the higher fatty aliphatic radicals corresponding to those in the coconut fatty acids, RCOOH, and the mixture is heated to 150° C. After all the solid has dissolved, the resulting solution is stirred well while being heated at 150-160° C. and then using preheated nitrogen is sprayed into a reservoir at room temperature (about 25° C.) to cool the liquid rapidly and solidify it. The resulting solid contains 10% by weight of the benzimidazolylstilbene.

Using the same general procedure, but melting the mixtures together in each instance at 180° C., there are employed appropriate amounts of the benzimidazolylstilbene and the mixture of coconut oil fatty acid amides to produce dry comminuted preparations containing 20% and 33%, respectively, of the benzimidazolylstilbene.

Appropriate amounts of the 10%, 20%, and 33% compositions obtained as described above are each readily and uniformly dispersed in aqueous pastes of various water-soluble synthetic organic anionic detergents to form detergent compositions having 0.01-0.5% concentrations of the benzimidazolylstilbene.

The following benzimidazolylstilbenes, which afford especially advantageous embodiments of my invention, were employed in accordance with the above described produces: 4-(benzimidazol-2-yl)-4'-[1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]benzimidazol-2-yl]stilbene, 4-(benzimidazol-2-yl)-4'-(1-allylbenzimidazol-2-yl)stilbene, and the mixture of hydroxyethylated derivatives of 4-(benzimidazol-2-yl)-4'-[1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]benzimidazol-2-yl]stilbene described in Example 28E of U.S. Patent 2,838,504. The water-soluble synthetic organic anionic detergents employed in preparing these compositions were: (1) Detergent I, consisting of 21.8% of a mixture of sodium lauryl sulfate and sodium dodecylbenzenesulfonates, 18.2% of sodium sulfate, and 60% of sodium triphosphate; (2) Detergent II, consisting of 19.1% of sodium dodecylbenzenesulfonates, 15.6% of sodium sulfate, 55% of sodium triphosphate, and 10.3% of sodium carbonate; and (3) white soap consisting of the sodium salts of the C₁₂-C₁₈ fatty acids derived from tallow. In each of the detergent compositions thus obtained, the whitening and

brightening effect of the composition as determined by standard dye testing procedures was 100% of that calculated on the basis of the weight of benzimidazolylstilbene present.

Substantially the same results as described above were obtained in each instance when the cooling and solidifying of the hot liquid solution of the benzimidazolylstilbene in the amide was carried out by pouring the liquid onto the chilled rolls of a flaker.

Example 2

Using the manipulative procedures described above in Example 1, two series of detergent compositions were prepared in which equal weights, respectively, of coconut fatty acid ethanolamides and coconut fatty acid isopropanolamides were substituted for the coconut fatty acid amides used in Example 1. In the two series of detergent compositions thus obtained, in each instance the whitening and brightening effect of the composition was 100% of the calculated amount, based on the weight of the benzimidazolylstilbene employed.

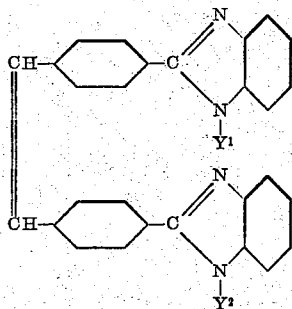
Example 3

The procedures described in Example 1 were repeated for the preparation of the 10% solutions of the benzimidazolylstilbenes in the amide with the exception that the hot liquid solution was cooled by pouring it into a steel tray which rested on a polyethylene bag filled with chipped ice. The dyeing strength of the detergent compositions prepared from the solidified product by dispersing the ground solid product in the aqueous detergent paste were in each instance approximately 85% of the strength calculated on the basis of the weight of the benzimidazolylstilbene employed. On the other hand, when the ground solid product, instead of being added as such to the detergent paste, was re-melted by heating it to 100–110° C. and the resulting hot liquid was mixed with a hot (76° C.) aqueous detergent paste, the detergent compositions thus obtained had a dyeing strength which was 100% of the calculated amount.

In the manipulative procedures of the foregoing examples, there can be used, as the whitening and brightening agent, the following: 4-(benzimidazol-2-yl)-4'-(1-methylbenzimidazol-2-yl)stilbene; 4,4'-bis[1-(2-hydroxyethyl)benzimidazol-2-yl]stilbene; 4-(benzimidazol-2-yl)-4'-[1-(2-hydroxy-2-sulfoethyl)benzimidazol-2-yl]stilbene; 4'-[1-(carboxymethyl)benzimidazol-2-yl]-4-(1-methylbenzimidazol-2-yl)stilbene; 4,4'-bis[1-(2-cyanoethyl)benzimidazol-2-yl]stilbene; 4-(benzimidazol-2-yl)-4'-(1-allylbenzimidazol-2-yl)stilbene; and 4,4'-bis[1-(orthochlorobenzyl)benzimidazol-2-yl]stilbene. In each instance, the resulting detergent compositions obtained have a dyeing strength which is approximately 100% of the calculated amount based on the weight of the benzimidazolylstilbene employed.

I claim:

1. The process for obtaining a uniform dispersion of a relatively small quantity of a benzimidazolylstilbene whitening and brightening agent having the formula



wherein Y¹ and Y² 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-

droxy-3-sulfoethyl, 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, at least one of the radicals Y¹ and Y² being other than hydrogen, in a relatively large quantity of an aqueous paste of a water-soluble synthetic organic anionic detergent which comprises: dissolving the benzimidazolylstilbene at a temperature in the range 140–200° C. in an amide of the class consisting of higher fatty acid amides and higher fatty acid lower alkanol amides; and mixing the resulting solution with the said aqueous paste in the proportion of 0.01–0.5 part by weight of the benzimidazolylstilbene per hundred parts by weight of the aqueous paste.

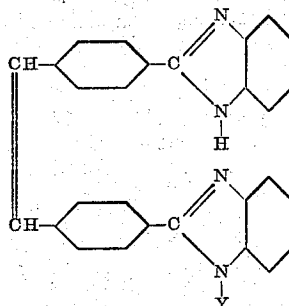
2. The process in accordance with claim 1 wherein Y¹ is hydrogen and Y² is a hydroxy-oxaalkyl radical containing 3–15 carbon atoms, and the amide is a higher fatty acid amide.

3. The process in accordance with claim 1 wherein Y¹ is hydrogen and Y² is a hydroxy-oxaalkyl radical containing 3–15 carbon atoms, and the amide is a higher fatty acid lower alkanolamide.

4. The process in accordance with claim 1 wherein Y¹ is a hydroxy-lower alkyl radical containing 2–6 carbon atoms and Y² is a hydroxy-oxaalkyl radical containing 3–15 carbon atoms, and the amide is a higher fatty acid amide.

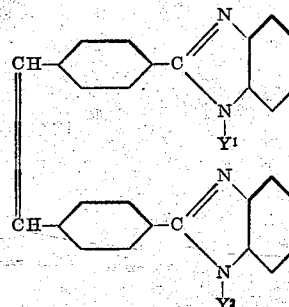
5. The process in accordance with claim 1 wherein Y¹ is a hydroxy-lower alkyl radical containing 2–6 carbon atoms and Y² is a hydroxy-oxaalkyl radical containing 3–15 carbon atoms, and the amide is a higher fatty acid lower alkanolamide.

6. The process for obtaining a dispersion of a relatively small quantity of a benzimidazolylstilbene whitening and brightening agent having the formula



where Y is a hydroxy-oxaalkyl radical containing 3–15 carbon atoms, in a relatively large quantity of an aqueous paste of a water-soluble synthetic organic anionic sulfonate detergent which comprises: dissolving the benzimidazolylstilbene at a temperature in the range 140–200° C. in a coconut fatty acid ethanolamide; and mixing the resulting solution with the said aqueous paste in the proportion of 0.01–0.5 part by weight of the benzimidazolylstilbene per hundred parts by weight of the aqueous paste.

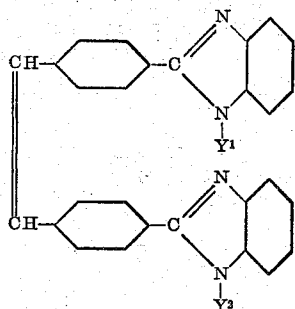
7. The process for obtaining a uniform dispersion of a relatively small quantity of a benzimidazolylstilbene whitening and brightening agent having the formula



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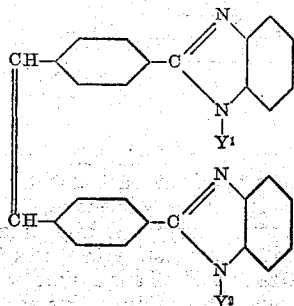
where Y^1 is a hydroxy-lower alkyl radical containing 2-6 carbon atoms and Y^2 is a hydroxy-oxaalkyl radical containing 3-15 carbon atoms, in a relatively large quantity of an aqueous paste of a water-soluble synthetic organic anionic sulfonate detergent which comprises: dissolving the benzimidazolylstilbene at a temperature in the range 140-200° C. in a coconut fatty acid ethanolamide; and mixing the resulting solution with the said aqueous paste in the proportion of 0.01-0.5 part by weight of the benzimidazolylstilbene per hundred parts by weight of the aqueous paste.

8. A composition obtained by dissolving at a temperature in the approximate range 140-200° C. a water-insoluble benzimidazolylstilbene whitening and brightening agent having the formula



wherein 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, at least one of the radicals Y^1 and Y^2 being other than hydrogen, in an amide of the class consisting of higher fatty acid amides and higher fatty acid lower alkanolamides.

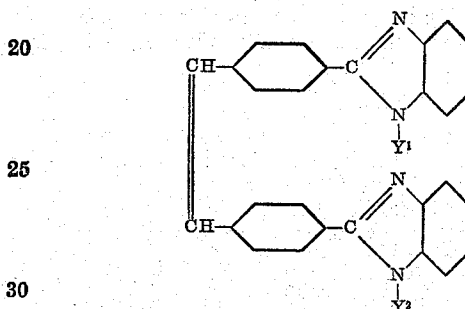
9. A solid composition obtained by dissolving at a temperature in the approximate range 140-200° C. about 5-15% by weight of a benzimidazolylstilbene whitening and brightening agent having the formula



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wherein 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, at least one of the radicals Y^1 and Y^2 being other than hydrogen, in an amide of the class consisting of higher fatty acid amides and higher fatty acid lower alkanolamides, and solidifying the resulting solution by cooling it rapidly.

10. A solid composition obtained by dissolving at a temperature in the approximate range 140-200° C. about 5-15% by weight of a benzimidazolylstilbene whitening and brightening agent having the formula



where Y^1 is a hydroxy-lower alkyl radical containing 2-6 carbon atoms and Y^2 is a hydroxy-oxaalkyl radical containing 3-15 carbon atoms, in a coconut fatty acid ethanolamide, and solidifying the resulting solution by cooling it rapidly.

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