OPTICAL BRIGHTENER COMPOUNDS AND DETERGENT AND BLEACH COMPOSITIONS CONTAINING SAME

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ABSTRACT OF THE DISCLOSURE

Optical brightener compounds defined as isoindolinyl compounds. The optical activity of these compounds can be employed to advantage in the optical brightening of a wide variety of natural and synthetic materials. They are useful in the brightening of fabrics and find application in the preparation of laundry detergent compositions and hypochlorite bleach-containing compositions.

BACKGROUND OF THE INVENTION

This invention relates to optical brightening agents. More particularly, it relates to optical brightening agents useful in the optical brightening of a wide variety of materials and to detergent and hypochlorite bleach-containing compositions containing them.

In recent years, the use of optical brightening agents, oftentimes termed optical bleaches or fluorescers, has grown enormously. These compositions which are colorless dyestuff functions by absorbing light in the ultraviolet invisible range (300—400 nm.) such as is contained in natural daylight and remitting this as visible, blue-white light (400—500 nm.). This fluorescence masks natural yellowing of textile fibers and results in a highly desirable blue-white “glow” on white goods and a fresher, cleaner appearance of colored goods. The fluorescence of optical brightening agents, while in the blue range, varies somewhat in dominant wavelength. Where the dominant wavelength is longer, the blue fluorescence is considered to have a slightly greenish tinge. A shorter dominant wavelength near the violet end of the spectrum results in blue fluorescence which is slightly reddish. For practical purposes, particularly for use in laundry detergent formulations, a neutral blue fluorescence is generally preferable.

Optical brighteners suitable for textile applications must exhibit a high degree of fluorescence. Frequently, the fluorescence of conventional optical brighteners is destroyed or quenched by contact with hypochlorite and similar oxidizing bleaches. Since many of the deeply embedded soils and stains encountered in the laundering of textile fabrics are conventionally removed by the action of chemical bleaching, great effort has been expended in the search for optical brighteners which resist the destructive effects of hypochlorite bleaches.

Accordingly, it is an object of this invention to provide optical brighteners having a high degree of fluorescence and resistance to the destructive effects of hypochlorite bleaches.

Another object of this invention is to provide detergent compositions containing an organic detergent, an alkaline builder salt and an optical brightener.

A further object of this invention is to provide laundry detergent compositions containing an organic detergent, an alkaline builder salt, a hypochlorite bleach and an optical brightener.

Still another object of this invention is to provide aqueous and granular hypochlorite bleach compositions containing an optical brightener.

SUMMARY OF THE INVENTION

The above and other objects of this invention are achieved by the present invention which comprises the provision of optical brightener compounds of the formula:

wherein each a is an integer from 1 to 4; x is 0 or 1; each A is selected from hydrogen; alkyl of 1 to 10 carbon atoms (e.g., methyl, ethyl, propyl, butyl, octyl, decyl), preferably of 1 to 4 carbon atoms; halogen (e.g., chlorine, bromine); alkoxy of 1 to 10 carbon atoms (e.g., methoxy, ethoxy, hexoxy, deoxy); aryl of from 6 to 12 carbon atoms (e.g., phenyl, biphenyl, naphthyl); alkylsulfonyl of from about 1 to 10 carbon atoms (e.g., methylsulfonyl, ethylsulfonyl, decylsulfonyl); alkoxyalkyl of from 2 to 10 carbon atoms (e.g., methoxymethyl, butoxymethyl, ethylhexyloxymethyl); polyethyleneoxy of the formula

wherein n is an integer from 1 to 10 (e.g., CH2CH2O)n—

haloalkyl of from 1 to 10 carbon atoms (e.g., trifluoromethyl, perfluoroethyl, dichloroethyl); alkylammonium of from 2 to 10 carbon atoms (e.g., acetyl, propionyl, hexanoyl, octanoyl, decanoyl); cyanogen; polyhydroxyalkyl of from 1 to 10 carbon atoms (e.g., 1,2,3-trihydroxypropyl, sorbitol); when x is 0, Z is a monovalent radical selected from

wherein each b is an integer from 1 to 4 and each B is defined as A above; —SO3M where M is hydrogen or alkali metal; or

where R and R' are each hydrogen, alkyl of 1 to 4 carbon atoms, hydroxyalkyl of from 1 to 4 carbon atoms, aryl, glucosyl; or together comprise a ring structure; and

wherein each A is as hereinbefore defined and each p is 1 or 2; and when x is one, Z is a bivalent radical of the formula

wherein each B and each b are as defined hereinbefore.

The compounds prepared according to the present invention are excellent optical brighteners for use in a variety of natural and synthetic materials and are especially characterized by their resistance to the destructive action of chlorine-containing bleaching compounds. Accordingly, they can be employed in detergent compositions
containing alkaline builder compounds and active chlorine-containing bleaching compounds and in aqueous and granular bleach compositions.

DETAILED DESCRIPTION OF THE INVENTION

The optical brightener derivatives of the present invention having the hereinbefore defined formula are termed herein as isoidolinyl compounds and are characterized by the presence of the group

\[
\begin{align*}
A & \quad a \\
\end{align*}
\]

wherein A and a are as defined hereinbefore. As will be apparent from the hereinbefore described formulae and definitions, the compounds of the invention are characterized by the presence of at least one of such groups.

The optical brighteners of the present invention are derived from fluorescent aromatic primary mono- or diamines characterized by ultraviolet absorption in the 310 to 400 nanometer range and fluorescence in the 400 to 475 range. These fluorescent amines may be represented by the formula \((H_2N)_{b}Z\), wherein \(Z\) represents the residue of the fluorescent amine, i.e., the entire molecule exclusive of the amino group and \(b\) is one in the case of a monoamine and two in the case of a diamine. The equimolar condensation reaction of a monoamine with a reactive aromatic halide to form a mono-isoidolinyl compound is illustrated by the following reaction scheme:

\[
\begin{align*}
Aa & \quad H_2N-Z + HX \quad \rightarrow \quad As + N-Z + HX \\
\end{align*}
\]

wherein \(X\) is halogen (e.g., chlorine, bromine) and \(Z\) is the residue of a fluorescent aromatic amine as hereinbefore defined.

Similarly, fluorescent aromatic diamines having the same spectral characteristics and represented as \(H_2N-Z-NH_2\) undergo reaction with a reactive aromatic halide according to the following scheme:

\[
\begin{align*}
Aa & \quad H_2N-Z-NH_3 + HX \quad \rightarrow \quad As + N-Z + HX \\
\end{align*}
\]

wherein \(X\) is halogen (e.g., chlorine, bromine).

The radical, \(Z\), where employed herein is used to represent the radical derived by abstraction of one or two primary amino groups from a fluorescent aromatic amine described hereinbefore. It will be understood that this radical is considered as being derived by abstraction for convenience only and that the characterization of the amine residue in such terms is not intended to imply that abstraction in a chemical sense is actually involved in the formation of the brightener compounds of the present invention.

The amines which can be employed to prepare the optical brighteners of the present invention are fluorescent aromatic primary mono- and diamines characterized by ultraviolet absorption in the range of 310 to 400 nm and fluorescence in the 400-475 nm range. These compounds are conventional brightener chromophores known to those skilled in the art. Examples of fluorescent amines having the prescribed spectral characteristics and their monovalent or bivalent radicals \((Z)\) include the following:

- 4-aminostilbenes of the formula:

\[
\begin{align*}
H_2N- & \quad CH=CH- \\
Bb & \quad Bb \\
\end{align*}
\]

where each \(b\) is as defined above and each \(B\) is defined as \(A\) above or \(-SO_3\) or

\[
\begin{align*}
\begin{array}{c}
R \\
-R' \\
\end{array}
\end{align*}
\]

where \(M\) is hydrogen or an alkali metal (e.g., sodium, potassium, lithium); and \(R\) and \(R'\) are each hydrogen or alkyl of 1 to 4 carbon atoms, (e.g., methyl, ethyl, n-propyl, isopropyl, sec-butyl); aryl (e.g., phenyl); glucosyl; hydroxyalkyl of 1 to 4 carbon atoms (e.g., 2-hydroxyethyl) or \(R\) and \(R'\) together comprise a ring structure (e.g., pyridyl, morpholino);

- 4,4'-diaminostilbenes of the formula:

\[
\begin{align*}
H_2N- & \quad CH=CH- \\
Bb & \quad Bb \\
\end{align*}
\]

where each \(b\) is as defined above and each \(B\) is defined the same as \(A\) above or \(-SO_3\) or

\[
\begin{align*}
\begin{array}{c}
R \\
-R' \\
\end{array}
\end{align*}
\]

where \(M\) is hydrogen or an alkali metal; and \(R\) and \(R'\) are each hydrogen; alkyl of 1 to 4 carbon atoms; aryl; glucosyl; hydroxyalkyl of 1 to 4 carbon atoms or together comprise part of a ring structure; and

- 7-aminocoumarins of the formula:

\[
\begin{align*}
\begin{array}{c}
Ap \\
Ap \\
A'p \\
\end{array}
\end{align*}
\]

wherein each \(p\) is 1 or 2 and each \(A\) is as hereinbefore defined.

Preferred amines for reasons of facility in undergoing the desired reaction with a reactive halide and excellent bleach stability of the brightener compounds obtained, are the 4-aminostilbenes (e.g., 4-amino-4'-methoxy-2,2'-stilbenedisulfonic acid, the disodium salt thereof; 4-amino-4'-methoxy-2,2'-stilbenedisulfonamide, 4-amino-2-stilbenesulfonic acid,
and the sodium salt thereof) and the 4,4'-diaminostilbenes (e.g., 4,4'-diamino-2,2'-stilbenedisulfonic acid, the disodium salt thereof; and 4,4'-diamino-2,2'-stilbenedisulfonamide).

Optical brighteners derived from amines of the present invention have the following structures:

(1)

(2)

(3)

wherein \( a, b, p, A \) and \( B \) have the meanings defined above.

Optical brighteners prepared from preferred amines have the structures:

(4)

(5)

(6)

wherein \( M, R \) and \( R' \) are as hereinbefore defined.

The mono- and di-isoinodolyl compounds of the present invention can be prepared by reaction of a 1,2-di-(halomethyl)benzene and a suitable amine hereinbefore described. Preferred reactants include 1,2-di(chloromethyl)benzene and 1,2-di(bromomethyl)benzene. The reaction can be carried out at a temperature in the range of from 0°C to 150°C.

The proportions of 1,2-di(halomethyl)benzene to fluorescent primary amine which can be employed are generally in the range of from 0.3:1 to 3:1 on a molar basis. In the case of the preparation of compounds of the formula

\[
\begin{align*}
\text{(4)} & & \text{and} \\
\text{(5)} & & \text{and} \\
\text{(6)} & & \text{and}
\end{align*}
\]

wherein \( x \) is zero, a range of about 0.3:1 to 1:5:1 is employed. Since the reaction is nearly quantitative, a molar proportion of 1:1 of 1,2-di(halomethyl)benzene to fluorescent primary amine is preferred. In the case of the preparation of compounds having a bis-structure, i.e., those wherein \( x \) in the above described formula is one, the molar proportion of 1,2-di(halomethyl)benzene to fluorescent primary amine employed is from 1.8:1 to 3:1, the ratio of 2:1 being preferred. When asymmetrical isoinodolyl derivatives are desired, two or more dissimilar 1,2-di(halomethyl)benzenes can be employed.

Preferably, the 1,2-di(halomethyl)benzenes are sequentially reacted with the fluorescent amine.

While the reaction can be effected by reacting at a temperature of from 0°C to 150°C, a preferred temperature range is about 50°C to about 100°C. Reactions conducted at the lower temperature of the suitable range, i.e., at about 0°C normally are effected in a period of time of about 24 hours. Conversely, reactions at about 100°C require less time and may be effected in good yield in about 30 minutes.

The isoinodolyl compounds of the invention can be prepared in a polar organic solvent which is essentially non-reactive to either the 1,2-di(halomethyl)benzene or fluorescent amine employed in the reaction. The amount of solvent employed is an amount at least sufficient to dissolve the fluorescent amine, an amount of about three times the weight of amine employed being sufficient. Examples of suitable essentially non-reactive solvents which can be employed are water, alcohols, N,N-dialkyl low molecular weight amides such as dimethylformamide, cyclic ethers such as tetrahydrofuran and dioxane, aromatic hydrocarbons such as benzene and certain organic solvent-water mixtures such as dimethylformamide-water, e.g., dimethylformamide containing from about 1 to about 60% water on a volume/volume basis. A preferred solvent is water.

The preparation of the optical brighteners of the invention is accompanied by formation of hydrochlooric acid by-product. This acid can be neutralized in a conventional manner by addition of a suitable base, e.g., sodium carbonate, sodium bicarbonate, sodium hydroxide, triethylamine, or pyridine to the reaction product. Preferred herein is sodium bicarbonate.

The optical brighteners of the present invention exhibit remarkable stability in the presence of hypochlorite bleach. While applicants do not wish to be bound by any theory as to the nature of such stability, it is believed that the stability is due in part to the presence of essential moieties of the formula

where and to the absence of a free hydrogen attached to a nitrogen atom. These moieties, named herein as substituents on a fluorescent stilbene or coumarin nucleus, i.e., isoinodolyl, provide resistance to the harmful effects of hypochlorite bleaches and resulting loss of fluorescent. Other fluorescent aromatic amines can likewise be rendered resistant to degenerative attack by hypochlorite bleeding compounds. Examples of such chromophoric amines are 5-aminio-1,8-naphthalenecarboxylides, 2-aminonaphthalenes, 3-aminio-2,5-diaryl-pyrazoles and -furans and the like.

Specific examples of optical brightener compounds of the invention include the following:

(1) 3-phenyl-7-(isoinodolyl) coumarin
(2) 3-methyl-7-(isoinodolyl) coumarin
(3) 3-chloro-7-(isoinodolyl) coumarin
(4) 4-(isoinodolyl)-4'-methylstilbene
(5) 4-(isoinodolyl)-4'-methoxy-stilbene
(6) sodium 4-(isoinodolyl)-4'-stilbenesulfonate
(7) 4-(isoinodolyl)-4'-phenylstilbene
(8) 4-(isoinodolyl)-3-methoxy-4'-methylstilbene
(9) 4-(2-chloroisoinodolyl)-4'(2-methyiosinodolyl)-2,2'-stilbenedisulfonic acid
(10) disodium 4,4'-diisoinodolyl-2,2'-stilbene disulfonamide
The optical brightener compounds of the present invention can be employed for the optical brightening of a wide variety of natural and synthetic materials. Natural materials include organic fibrous materials such as silk and wool. Synthetic fibers include such materials as polyester, polyamide, acetylated polyvinyl alcohol and polyolefin and cellulose acetate fibers. The brightener compounds of the invention provide excellent brightening and light fastness and can be employed in aqueous or solvent-containing brightening compositions. These compositions can contain bleaching compositions, such as hypochlorites without substantial loss of fluorescent.

The optical brighteners of the present invention can be incorporated into polymeric melts and processed to a variety of products including synthetic fibers. Alternatively, they can be applied to a substrate by application of a solution to the surface of a polymeric substrate.

The treatment of fibrous materials can be carried out by immersion of the fibrous materials in an aqueous dispersion of the optical brightening compound of the invention and a surface-active agent. Suitable surface-active agents include anionic or nonionic compounds such as alkylenesulfonic acid, the condensation product of naphthalenesulfonic acid and formaldehyde or polyoxyethylenealkyl ether and the like. The fibrous material is immersed in the aqueous dispersion of brightener at a temperature of from 50° C. to 130° C. depending on the kind of fibrous material. The fibrous material is normally dried by heating at a temperature of from 160° C. to 220° C. for a time of from 0.5 to 2 minutes.

The brightener compounds of the invention can also be employed in laundry detergent compositions to provide an improved appearance to laundered goods. When so employed, they range from 0.01% to 3% of the detergent composition. A preferred amount of brightener is from 0.5% to 1.5%. In addition to these brightener compounds, the laundry detergent compositions of the invention comprise at least 10% of a mixture of an organic detergent and an alkaline builder salt in a ratio in the range of from 5:1 to 1:20, preferably from 2:1 to 1:10. This mixture can be as much as the balance of the composition. The organic detergent compounds and alkaline builder salts are more fully described below.

ORGANIC DETERGENTS

The organic detergent compounds which can be utilized in the detergent compositions of this invention are the following:

(a) Water-soluble soaps.—Examples of suitable soaps for use in this invention are the sodium, potassium, ammonium and alkanolammonium (e.g., mono-, di-, and triethanolammonium salts of higher fatty acids (C_{10}-C_{20}). Particularly useful are the sodium and potassium salts of the mixture of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

(b) Anionic synthetic non-soap detergents.—A preferred class can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric acid reaction products having in their molecular structure the sodium or potassium alkly sulfates, especially those obtained by saturating the higher alcohols (C_{7}-C_{14} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alklybenzenesulfonates, in which the alkyl group can be a straight or branched chain and contains from about 9 to about 15 carbon atoms, especially those derived synthetically, e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process.

(c) Nonionic synthetic detergents.—The alkane of nonionic detergents can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. These products are formed with particular hydrophilic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. A second class of nonionic detergents comprises higher fatty amines. A third class of nonionic detergents has semi-polar characteristics. These three classes can be defined in further detail as follows:

(1) One class of nonionic synthetic detergents is marketed under the trademark of "Pluronic." These detergent compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility, has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product.

(2) Alkylphenol-polyethylene oxide condensates are condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the said ethylene oxide being present in amounts equal to about 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituents in such compounds may be derived from polyoxyethylene, propylene, dibutylene, octene, or none, for example.

(3) Nonionic synthetic detergents can be derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine and include compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000. Such compounds result from the reaction of ethylene oxide with a hydrophobic base, and the product of the resulting ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000.

(4) Other nonionic detergents include condensation products of aliphatic alcohols having from 8 to 22 carbon atoms, in straight chain or branched chain configuration, with ethylene oxide, and with a coconut alcohol or ethylene oxide condensate having from about 30 to 50 moles of ethylene oxide per mole of coconut alcohol.

(5) The ammonium, monooethanol and diethanol amines of fatty acids having an acyl moiety of from 8 to about 18 carbon atoms are useful nonionic detergents. These acyl moieties are normally derived from naturally occurring glycerides, e.g., coconut oil, palm oil, soybean oil and tallow, but also derived synthetically, e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process.
(6) Semi-polar nonionic detergents include long chain tertiary amine oxides corresponding to the following general formula

$$\text{R}^1 \text{N}=\text{O} \text{N}$$

wherein \( \text{R}^1 \) is an alkyl radical of from about 8 to about 18 carbon atoms, \( \text{R}^2 \) and \( \text{R}^3 \) are each methyl, ethyl or hydroxyethyl radicals, \( \text{R}^4 \) is ethylene, and \( n \) ranges from 0 to about 10. The arrow in the formula is a conventional representation of a semi-polar bond. Specific examples of amine oxide detergents include dimethyldodecylamine oxide and bis-(2-hydroxyethyl) dodecylamine oxide.

(7) Other semi-polar nonionic detergents include long chain tertiary phosphate oxides corresponding to the following general formula \( \text{R'} \text{R'}^1 \text{R'}^2 \text{R'}^3 \text{P}=\text{O} \) wherein \( \text{R'} \) is an alkyl, alkenyl or monohydroxyalkyl radical containing from 10 to 20 carbon atoms and \( \text{R'}^1 \) and \( \text{R'}^2 \) are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphate oxides are found in U.S. Pat. 3,304,263 which issued Feb. 14, 1967, and include: dimethyldodecylphosphine oxide and dimethyl-(2-hydroxydodecyl) phosphine oxide.

(d) Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical can be straight chain or branched alkyl and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are sodium-3-dodecylaminopropionate and sodium-3-dodecylamino propane sulfonate.

(e) Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds, in which the aliphatic radical can be straight chain or branched alkyl, and wherein one of the aliphatic substituents contains from about 8 to 24 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato or phosphono. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy propane-1-sulfonate which are preferred for their cool water detergency characteristics. See, for example, Snooby et al., Canadian Pat. 708,148.

These soap and non-soap anionic, nonionic, ampholytic and zwitterionic detergent compounds can be used singly or in combination. The above examples are merely illustrations of the numerous suitable detergents. Other organic detergent compounds can also be used.

**BUILDER SALTS**

The detergent compositions of this invention also contain water-soluble, builder salt either of the organic or inorganic types.

Examples of suitable water-soluble, inorganic alkaline detergent builder salts are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates, carbonates and sulfates. Specific examples of such salts are sodium and potassium tetraborates, perborates, bicarbonates, carbonates, tripolyphosphates, pyrophosphates, orthophosphates and hexametaphosphates.

Examples of suitable organic alkaline detergent builder salts are: (1) water-soluble aminopolyacetates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates and N(2-hydroxyethyl)-nitriloacetates; (2) water-soluble salts of phytic acid, e.g., sodium and potassium phytates—see U.S. Pat. 2,739,942; (3) water-soluble polyphosphonates, including specifically, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid, sodium, potassium and lithium salts of methylene diphosphonic acid, sodium, potassium and lithium salts of ethylene diphosphonic acid, and sodium, potassium and lithium salts of ethane-1,1,2-triphosphonic acid. Other examples include the alkali metal salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxyethane-diphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-1,1,2-triphosphonic acid, propane-1,1,3-triphosphonic acid, propane-1,1,2,2-tetraphosphonic acid, and propane-1,1,2,3,3-tetraphosphonic acid; (4) water-soluble salts of polycarboxylate polymers and copolymers as described in the patent of Francis L. Diehl, U.S. Pat. 3,308,067 issued Mar. 7, 1967. Specifically, a detergent builder material comprising a water-soluble salt of a polymeric phosphonic acid having the following structural relations as to the position of the carboxylate groups and possessing the following prescribed physical characteristics: (a) a minimum molecular weight of about 30 calculated as to the acid form; (b) an equivalent weight of about 30 to about 50 calculated as to acid form; (c) at least 45 mole percent of the monomeric species having at least two carboxyl radicals separated from each other by not more than two carbon atoms; (d) the site of attachment to the polymer chain of any carboxy-containing radical being separated by not more than three carbon atoms along the polymer chain from the site of attachment of the next carboxy-containing radical. Specific examples are polymers of itaconic acid, aconic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid, and citraconic acid and copolymers with themselves and other compatible monomers such as ethylene.

Mixtures of organic and/or inorganic builders can be used and are generally desirable. One such mixture of builders is disclosed in Canadian Pat. 755,038 of Burton H. Gedge, e.g., ternary mixtures of sodium tripolyphosphate, trisodium nitroliacteate and trisodium ethane-1-hydroxy-1,1-diphosphonate. The above described builders can also be utilized singly in this invention.

The preferred builders are sodium tripolyphosphate and sodium nitroliacteate, alone or in admixture. The preferred organic detergents are the anionic sulfates and sulfonates. The detergent compositions preferably provide pHs in the range of about 8.5 to about 11.5.

The laundry detergent compositions of this invention can contain, if desired, in addition to the brightener, organic detergent and builder, any of the usual additives for such compositions which make them more attractive or effective. For example, perfumes, dyes, proteolytic enzymes, corrosion inhibitors, oxygen and chlorine bleaches, soil redeposition agents and other brighteners can be used. Diluents such as water, moisture and sodium sulfate can also be used to make up any balance of a composition comprising brighter, organic detergent and alkaline builder salt.

The optical brighteners of the invention are stable to attack by hypochlorite compounds. Accordingly, they are advantageously employed in laundry compositions which contain from 0.5% to 25%, usually 3-17%, of an active-chlorine containing bleach compound. Examples of such compounds are: dichlorocyanuric acid; 1,3-dichloro-5,5'-dihydroxy-1,3-dichlorobenzonemide; N,N'-dichloroformazin; paratoluene sulfondichloramide; trichloromelamine; N-chloroaniline; N-chlorosuscinimide; N,N'-dichloroazodi carbonamide; N-chloroacetamide; N,N'-dichloroacetamido; N,N'-dichlorobutadiene; chlorinated dicyandiamide; sodium hypochlorite; calcium hypochlorite; lithium hypochlorite; chlorinated trisodium phosphate. Preferred compounds are dichlorocyanurates, i.e., dichlorocyanuric acid and the sodium and potassium salts thereof.

In other embodiments of the present invention the optical brighteners are employed in aqueous and granular bleach compositions. In general, aqueous bleach compo-
3,646,015

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tions are prepared by dissolving or dispersing an optical brightener in an aqueous solution of alkali metal hypo-
chlorite bleach. The optical brighteners of the present invention are readily soluble in aqueous hypochlorite solu-
tions and remain stable over an extended period of time so that they can be successfully packaged, shipped and stored
without rendering ineffective the whitening action of the optical brightener or the oxidizing action of the bleach.

Liquid bleach compositions prepared in accordance with the present invention are characterized by a pH ranging
from 10.5 to 13.0 and consist essentially of from 1.0% to 10% alkali metal hypochlorite bleach, from 0.002% to
2% of the optical brightener and the balance water.

Preferred hypochlorite bleach-containing compositions contain the alkali metal hypochlorite bleach component in
an amount of from 1% to 10%, preferably from 5% to 7%, with about 5.2% being especially preferred.

The bleach component can be any one of the alkali metal hypochlorites. Examples of such useful bleaches are sodium hypochlorite, potassium hypochlorite, lithium hypo-
chlorite, and the like. However, sodium hypochlorite is highly preferred because of its superior properties and its ready availability.

The optical brightener is present in the liquid bleach compositions of this invention in an amount ranging from
0.002% to 2.0%, preferably from 0.01% to 0.1% with about 0.05% being especially preferred.

The brighteners of the present invention are capable of retaining their whitening and brightening effects even
after exposure to aqueous 1–10% hypo-
chlorite-containing bleach solutions for extended periods of time, e.g., several weeks of storage. The bleach stability
which is normally ascribed to conventional optical brighteners is commonly understood to mean that these optical
brighteners are not ineffective when exposed to dilute solutions of bleach for limited periods of time, e.g., at
washing machine conditions where the hypochlorite bleach is present in aqueous solutions at about 0.02% hypo-
chlorite level for up to 20 to 30 minutes. In contradistinction to the bleach compatibility commonly understood in
the art, the presently claimed optical brighteners retain their desirable effects after exposure to hypochlorite
bleach concentrations much higher than normally found in the course of the laundering process.

The desirable bleach compatibility of the optical brighteners of the present invention is employed to ad-
vantage in the use of these fresh hypochlorite or granular bleach-containing compositions. The latter compositions
normally comprise from 1% to 99% of an active chlorine-containing bleaching compound which is capable of evolving hypochlorite upon contact with water and from 0.05% to 10% of the optical
brightener of the present invention. Dispersible polymeric stabilizing or suspending agents can also be employed.

Suitable examples are described in U.S. Pat. 3,393,153 to
Zimmer et al., issued July 16, 1968. Preferably the granular bleaching compositions of the invention contain from
1% to 80% of the active chlorine-containing bleaching
compound, from 2% to 25% of an organic detergent
and from 5% to 60% of an alkaline builder salt, said bleaching compounds and builder salts being of the type
hereinbefore described.

The granular bleach compositions of this invention can contain, if desired in addition to the bleaching compound,
any of the usual additives for such compositions which make them more attractive or effective, for example, per-
fumes, dyes, proteolytic enzymes, corrosion inhibitors, other chlorine bleaches, soil redeposition agents and other
brighteners may be used.

These granular bleach compositions having a pH ranging
from about 8 to 12 and upon dissolution in water evolve active hypochlorite chlorine for the effective
bleaching of cellulosic fabrics.

Preparations of exemplary optical brighteners of this invention are described as follows:

Example I
Preparation of disodium 4,4′-(isoindolinyl)-
2,2′-stilbenedisulfonate

A solution of 5.28 parts (0.02 mole) of 1,2-di-
(bromomethyl)benzene, 4.6 parts (0.01 mole) of di-
sodium 4,4′-diamino-2,2′-stilbenedisulfonate, 4.2 parts
sodium bicarbonate and 150 ml. of water was heated on a
steam bath for 22 hours. The reaction was conducted in a
250-ml. one-necked, round-bottomed flask equipped with a
reflux condenser. The reaction mixture, light-brown in
color, was removed from the steam bath, cooled, to 0° C.,
filtered through a sintered glass funnel and washed with
acetone to yield 1.95 parts of a light-tan product. An
additional 6.54 parts of light-brown product was iso-
lated from the filtrate upon concentration. The combined
portions were washed with acetone, dried and identified as disodium 4,4′-(isoindolinyl)-2,2′-stilbenedisulfonate.

Calc. (percent): C, 56.7; H, 4.08; N, 4.40. Found (per-
cent): C, 56.3; H, 4.6; N, 3.2.

NMR analysis showed a singlet at 4.5 and a complex
aromatic multiplet centered at 1.8. The ultraviolet ab-
sorption λmax was 342; the fluorescence λmax was 457
nm.

Similar results are obtained when equimolar propor-
tions of

4,5-dichloro-1,2-di-(chloromethyl) benzene;
4-chloro-1,2-di-(chloromethyl) benzene;
3-isoproxy-1,2-di-(chloromethyl) benzene;
4-di-disopropyl-1,2-di-(chloromethyl) benzene;
4-butoxy-1,2-di-(chloromethyl) benzene;
3-trifluoromethyl-1,2-di-(chloromethyl) benzene;
3,1-(4,7-trioxanoyl)-1,2-di-(chloromethyl) benzene;
4-methoxymethyl-1,2-di-(chloromethyl) benzene;
3-phenyl-1,2-di-(chloromethyl) benzene;
3-naphthyl-1,2-di-(chloromethyl) benzene;
3-methylsulfonyl-1,2-di-(chloromethyl) benzene;
4-cyano-1,2-di-(chloromethyl) benzene; and
4-(1,2,3-trihydroxypropyl)-1,2-di-(chloromethyl)
benzene
are employed in place of 1,2-dibromomethylbenzene in
that the following fluorescent optical brighteners are obtained:

disodium 4,4′-(7,8-dichloro-1-isooindolinyl)-2,2′-
stilbenedisulfonate;
disodium 4,4′-(7-chloro-1-isooindolinyl)-2,2′-stilbenedisulf-
onate;
disodium 4,4′-(6-isoproxy-1-isooindolinyl)-2,2′-
stilbenedisulfonate;
disodium 4,4′-(7,8-dii-epoxy-1-isooindolyl)-2,2′-
stilbenedisulfonate;
disodium 4,4′-(7-butoxy-1-isooindolyl)-2,2′-stilbenedi-
sulfonate;
disodium 4,4′-(6-trifluoromethyl-1-isooindolinyl)-2,2′-
stilbenedisulfonate;
disodium 4,4′-(1,4,7-trioxanoyl)-1-isooindolinyl)-2,2′-
stilbenedisulfonate;
disodium 4,4′-(7-methoxymethyl-1-isooindolinyl)-2,2′-
stilbenedisulfonate;
disodium 4,4′-(6-phenyl-1-isooindolinyl)-2,2′-
stilbenedisulfonate;
disodium 4,4′-(6-naphthyl-1-isooindolinyl)-2,2′-
stilbenedisulfonate;
disodium 4,4′-(6-methylsulfonyl-1-isooindolinyl)-2,2′-
stilbenedisulfonate;
disodium (7-cyano-1-isoindolinyl)-2,2'-stilbenedisulfonate; and disodium 4,4’-(7-(1,2,3-trihydroxypropyl)-1-isoindolinyl)-2,2'-stilbenedisulfonate.

Similar results are obtained when equimolar proportions of disodium 4-amino-4'-ethoxy-2,2'-stilbenedisulfonate; disodium 4-amino-4'-methoxy-2,2'-stilbenedisulfonate; disodium 4-amino-4'-ethoxy-2,2'-stilbenedisulfonamide; and disodium 4-amino-4'-methyl-2,2'-stilbenedisulfonamide are employed in place of disodium 4,4’-diamino-2,2'-stilbenedisulfonate in that the following optical brightener compounds are obtained: disodium 4-isoindolinyl-4’-ethoxy-2,2'-stilbenedisulfonate; disodium 4-isoindolinyl-4’-methoxy-2,2'-stilbenedisulfonate; disodium 4-isoindolinyl-4’-ethoxy-2,2'-stilbenedisulfonamide; and disodium 4-isoindolinyl-4’-methyl-2,2'-stilbenedisulfonamide.

Example II

(a) Preparation of 4,4’-(isoindolinyl)-2,2'-stilbenedisulfonyl chloride

A suspension of 6.18 parts (0.01 mole) of disodium 4,4’-(isoindolinyl)-2,2'-stilbenedisulfonate, 20 parts thionyl chloride and 300 parts of dimethyl formamide is stirred at 25° C. temperature for 15 minutes. The resulting solid product is filtered, washed with water, acetone and dried to give the desired product, 4,4’-(isoindolinyl)-2,2'-stilbenedisulfonyl chloride.

(b) Preparation of 4,4’-(isoindolinyl)-2,2'-stilbenesulfonamide

A suspension of 6.15 parts (0.01 mole) parts of 4,4’-(isoindolinyl)-2,2'-stilbenedisulfonyle chloride prepared as described in part (a) above, 5 parts of 28% ammonium hydroxide, 10 parts pyridine and 100 parts of dimethyl formamide is stirred at 25° C. for three hours. The solid is filtered, washed with water, acetone and dried to yield the desired amide product, 4,4’-isoindolinyl-2,2'-stilbenesulfonamide.

Similar results are obtained when equimolar proportions of morpholine, diethanolamine, glucosamine, aniline, diethylyamine and 2-ethylaminoethanol are employed in place of ammonium hydroxide in that amides are obtained conforming to the formula and wherein R and R’ are described, respectively, in Table 1 as follows:

Table 1

<table>
<thead>
<tr>
<th>R</th>
<th>R’</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>CH3</td>
</tr>
<tr>
<td>CH3</td>
<td>H</td>
</tr>
</tbody>
</table>

Example III

Preparation of sodium 4-(isoindolinyl)-2-stilbenesulfonate

The suspension obtained by dissolving 1.75 parts (0.01 mole) of 1,2-di(chloromethyl)benzene, 3.10 parts (0.01 mole) of sodium 4-amino-2-stilbenesulfonate and 50 parts of water is placed onto a steam bath in a 100-ml. one-necked round-bottomed flask equipped with a reflux condenser. The reaction vessel is heated at a temperature of 80°-90° C. for 16 hours. The reaction mixture is concentrated under the pressure of an aspirator and at a bath temperature of 50° C. and filtered to provide a solid residue which is washed with acetone and dried to provide the desired product, sodium 4-(isoindolinyl)-2-stilbenesulfonate. The compound is a bleach-stable optical brightener.

Similar results are obtained when 4-chloro-1,2-di(chloromethyl) benzene; 4-propionyl-1,2-di(chloromethyl) benzene; 3-methoxy-1,2-di(chloromethyl) benzene; 4-methyl-1,2-di(chloromethyl) benzene; 4-phenyl-1,2-di(chloromethyl) benzene; 3-trifluoromethyl-1,2-di(chloromethyl) benzene; 4-cyano-1,2-di(chloromethyl) benzene; and 3-methylsulfonyl-1,2-di(chloromethyl) benzene are employed in place of 1,2-di(chloromethyl) benzene in that the correspondingly substituted optical brightener compounds are obtained, respectively, as follows: sodium 4-(7-chloro-1-isoindolinyl)-2-stilbenesulfonate; sodium 4-(7-propionyl-1-isoindolinyl)-2-stilbenesulfonate; sodium 4-(6-methoxy-1-isoindolinyl)-2-stilbenesulfonate; sodium 4-(7-methyl-1-isoindolinyl)-2-stilbenesulfonate; sodium 4-(6-trifluoromethyl-1-isoindolinyl)-2-stilbenesulfonate; sodium 4-(7-cyano-1-isoindolinyl)-2-stilbenesulfonate; and sodium 4-(6-methylsulfonyl-1-isoindolinyl)-2-stilbenesulfonate.

Similar results are obtained when the sodium 4-amino-2-stilbenesulfonate is replaced by 4-amino-4’-ethoxy-2,2'-stilbenedisulfonic acid; disodium 4-amino-4’-methoxy-2,2'-stilbenedisulfonate; 4-amino-4’-methoxy-2,2'-stilbenedisulfonamide; and 4-amino-2-stilbenesulfonic acid; in that the following bleach-stable optical brighteners are obtained: sodium 4-’(isoindolinyl)-2-stilbenesulfonate; 4-(isoindolinyl)-4’-ethoxy-2,2'-stilbenedisulfonic acid; disodium 4-’(isoindolinyl)-4’-methoxy-2,2'-stilbenedisulfonamide; and 4-(isoindolinyl)-2-stilbenesulfonic acid.
15
Example IV
Preparation of 3-phenyl-7-(isoindolinyl)coumarin

![Chemical Structure]

The suspension obtained by adding 2.37 parts (0.01 mole) of 7-amino-3-phenylcoumarin to 2.64 parts (0.01 mole) of o-di(bromomethyl)benzene and 50 parts of water is heated on a steam bath (80–90°C) for a period of 16 hours. The heating is conducted in a 100-ml., one-necked, round-bottom flask equipped with a reflux condenser. The resulting solution is cooled to 0°C and filtered through a sintered glass funnel to provide the desired product, 3-phenyl-7-(isoindolinyl)coumarin. An additional portion of the desired product is isolated from the aqueous filtrate by concentrating the filtrate to dryness, extracting with methanol, recrystallizing with methanol and diethyl ether and filtering the product. The resulting compound is an optical brightener having bleaching compatibility properties.

Similar results are obtained when
- 7-amino-4-phenylcoumarin;
- 7-amino-5-chlorocoumarin;
- 7-amino-3-phenyl-8-methoxycoumarin;
- 7-amino-3-methylocoumarin;
- 7-amino-3,5,8-trimethoxycoumarin;
- 7-amino-3,5-diphenylocoumarin;
- 7-amino-3-phenyl-5-chloromethylcoumarin;
- 7-amino-5-(3',5',7'-trioxanoyl)-3-phenylocoumarin

are employed in place of 7-amino-3-phenylcoumarin in that the following bleach-stable optical brightener compounds are formed:
- 7-(isoindolinyl)-4-phenyl coumarin;
- 7-(isoindolinyl)-5-chlorocoumarin;
- 7-(isoindolinyl)-3-phenyl-8-methoxycoumarin;
- 7-(isoindolinyl)-3-methylocoumarin;
- 7-(isoindolinyl)-3,5,8-trimethoxycoumarin;
- 7-(isoindolinyl)-3,5-diphenylocoumarin;
- 7-(isoindolinyl)-3-phenyl-5-chloromethylcoumarin;
- 7-(isoindolinyl)-5-(3',5',7'-trioxanoyl)-3-phenylocoumarin.

A bleach stability test was performed to evaluate the bleach compatibility of the brighteners of the present invention in concentrated aqueous hypochlorite-containing solution. Aqueous sodium hypochlorite solution containing approximately 5.25% sodium hypochlorite and 0.5% of the compound of Example I was formulated by dissolving the optical brightener in the aqueous hypochlorite-containing solution. The resulting solution was visually examined periodically under ultraviolet light for fluorescence. The solutions continued to exhibit strong fluorescence after a storage period of two hours indicating a high degree of stability under extremely adverse hypochlorite degradative conditions.

The detergent (laundring and brightening) compositions of this invention are exemplified by the following examples which describe built formulations in which the optical brighteners of the invention can be employed. These compositions provide pHs in the range of 8.5–11.5. The invention is not limited by these examples, however, which are merely illustrative.

Example V

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium soap of 20:80 coconut:tailor fatty acids</td>
<td>35%</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>10%</td>
</tr>
<tr>
<td>Tetrasodium pyrophosphate</td>
<td>40%</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>5%</td>
</tr>
</tbody>
</table>
| Disodium 4,4'-diisooindolyl-2,2'-stibenedisulfonate | 0.05%
| Moisture | Balance |

Example VI

A granular built synthetic detergent composition having the following formulation can be prepared with the brightening agents of this invention incorporated therein. The composition, in addition to performing well in its cleaning capacity, imparts effective fluorescence to fabrics cleaned in the solution.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium linear dodecyl benzene sulfonate</td>
<td>17.5%</td>
</tr>
<tr>
<td>Sodium trioleylphosphate</td>
<td>5%</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>14%</td>
</tr>
<tr>
<td>Sodium carboxymethylcellulose</td>
<td>0.5%</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>7%</td>
</tr>
</tbody>
</table>
| 4,4'-diisooindolyl-2,2'-stibenedisulfonamide | 0.10%
| Moisture | Balance |

Substantially similar results are obtained when the following optical brighteners are employed in lieu of 4,4'-diisooindolyl-2,2'-stibenedisulfonamide in that effective cleaning compositions which impart fluorescence to cleaned fabrics are obtained: 4,4'-diisooindolyl-2,2'-stibenedisulfonic acid; the disodium salt thereof; 4-methoxy-4'-isoindolyl-2,2'-stibenedisulfonic acid; the disodium salt thereof; 4-methoxy-4'-isoindolyl-2,2'-stibenedisulfonamide.

Example VII

The following granular composition containing an effective chlorine bleaching agent performs very well in cleaning, whitening and brightening:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium tallow alkyl sulfate</td>
<td>75%</td>
</tr>
<tr>
<td>Sodium linear dodecylbenzenesulfonate</td>
<td>7%</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>50%</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>10%</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>10%</td>
</tr>
<tr>
<td>Potassium dichlorocynurate</td>
<td>15%</td>
</tr>
<tr>
<td>Sodium 4-(isoindolinyl)-2-stibenesulfonate</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
| Sodium 4-(7-chloro-1-isoindolinyl)-2-stibenesulfonate | 0.05%
| Moisture | Balance |

Example VIII

A built liquid laundering composition which brightens as it cleans and which is suitable for laundering household fabrics can have the following composition:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium-3-dodecylaminopropionate</td>
<td>6%</td>
</tr>
<tr>
<td>Sodium linear dodecylbenzenesulfonate</td>
<td>6%</td>
</tr>
<tr>
<td>Potassium pyrophosphate</td>
<td>20%</td>
</tr>
<tr>
<td>Potassium thiole sulfonate</td>
<td>8%</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>3.8%</td>
</tr>
</tbody>
</table>
| Carboxymethyl hydroxyethyl cellulose | 0.3%
| 3-phenyl-7-(isoindolinyl)coumarin | 0.05%
| Water | Balance |

Example IX

A household laundering composition can contain the following ingredients:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium salt of SO4-sulfonate tetradecene</td>
<td>10%</td>
</tr>
<tr>
<td>Dimethyl coconut alkyl ammonio acetate</td>
<td>10%</td>
</tr>
<tr>
<td>Trisodium ethane-hydroxy triphosphonate</td>
<td>60%</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>10%</td>
</tr>
</tbody>
</table>
| 3-methyl-7-(isoindolinyl)coumarin | 0.10%
| Moisture | Balance |
An effective granular detergent composition has the following formulation:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium linear dodecylbenzenesulfonate</td>
<td>7.5</td>
</tr>
<tr>
<td>Sodium tallow alkyl sulfate</td>
<td>2</td>
</tr>
<tr>
<td>Hydrogenated marine oil fatty acid suds depressant</td>
<td>2.2</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>4</td>
</tr>
<tr>
<td>Trisodium nitritoacetate</td>
<td>4</td>
</tr>
<tr>
<td>Sodium silicate (ratio of SiO₂:Na₂O of 2:1)</td>
<td>10</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>2</td>
</tr>
<tr>
<td>Dihydroxydiphenylmethane-2,2'-stilbenedisulfonate</td>
<td>0.5</td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Example XI

An effective cool water built granular composition according to this invention, particularly useful with resin treated cotton fabrics, has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium tallow alkyl sulfate</td>
<td>8</td>
</tr>
<tr>
<td>3-(N,N'-dimethyl-N-hexadeclammonio)-propane-1-sulfonate</td>
<td>5</td>
</tr>
<tr>
<td>Dimethylbisdecylphosphate oxide</td>
<td>10</td>
</tr>
<tr>
<td>Trisodium ethane-1-hydroxy-1,1-diphosphate</td>
<td>5</td>
</tr>
<tr>
<td>Trisodium nitritoacetate</td>
<td>10</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>10</td>
</tr>
<tr>
<td>Sodium silicate (Na₂O:SiO₂=1:2.5)</td>
<td>10</td>
</tr>
<tr>
<td>Sodium carboxymethyl cellulose</td>
<td>3</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>10</td>
</tr>
<tr>
<td>4,4'-(isodindolyl)-2,2'-stilbenedisulfonamide</td>
<td>0.3</td>
</tr>
<tr>
<td>Moisture</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The aqueous and granular bleach composition of this invention are exemplified by the following examples which are formulations in which the optical brighteners of the invention can be employed. The invention is not, however, limited by these examples which are merely illustrative.

Example XII

An excellent aqueous bleach composition which improves the whitening of bleached textiles has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hypochlorite</td>
<td>5.2</td>
</tr>
<tr>
<td>4,4'-(isodindolyl)-2,2'-stilbenedisulfonate</td>
<td>0.2</td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Example XIII

The following granular bleach composition which dissolves readily in a household automatic washing machine has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium dichloroiodate</td>
<td>65</td>
</tr>
<tr>
<td>Sodium linear dodecylbenzenesulfonate</td>
<td>6</td>
</tr>
<tr>
<td>Potassium pyrophosphate</td>
<td>25</td>
</tr>
<tr>
<td>4,4'-(isodindolyl)-2,2'-stilbenedisulfonate</td>
<td>3</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Example XIV

A granular bleach formulation which improves the appearance of bleached textiles has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dichloroiodate</td>
<td>40</td>
</tr>
<tr>
<td>Sodium tallow alkyl sulfate</td>
<td>10</td>
</tr>
<tr>
<td>Potassium tripolyphosphate</td>
<td>25</td>
</tr>
<tr>
<td>3-methyl-7-(isodindolyl)cumarin</td>
<td>1</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The foregoing description of the invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of this invention.

What is claimed is:

1. A compound of the formula

$$\text{Aa} \quad \text{Bb} \quad \text{Z} \quad \text{R}$$

wherein each a is an integer of from 1 to 4; x is 0 or 1; each A is selected from hydrogen; alkyl of 1 to 10 carbon atoms; halogen; alkoxy of from 1 to 10 carbon atoms; aryloxy of from 6 to 12 carbon atoms, alkylsulfonyl of from 1 to 10 carbon atoms; alkoxyalkyl of from 2 to 10 carbon atoms; ethylxenoy of the formula H(CH₂CH₂O)ₙ where n is an integer from 1 to 10; haloalkyl of from 1 to 10 carbon atoms; alkanoyl of from 2 to 10 carbon atoms; cyano; and polyhydroxylalkyl of from 1 to 10 carbon atoms; when x is 0, Z is a monovalent radical selected from

(1)

wherein each b is an integer from 1 to 4 and each B is selected from groups A above; —SO₂OM where M is hydrogen or alkali metal; and

(2)

where R and R' are each hydrogen; alkyl of 1 to 4 carbon atoms, hydroxyalkyl of from 1 to 4 carbon atoms, phenyl, glycosyl or together comprise a pyridyl or morpholino group; and

wherein each A is as defined above and each p is 1 or 2; and when x is 1, Z is a bivalent radical of the formula

wherein each b is an integer of from 1 to 4 and each B is selected from groups A above; —SO₂OM where M is hydrogen or alkali metal; and

where R and R' are each hydrogen, alkyl of 1 to 4 carbon atoms, phenyl, glycosyl or together comprise a pyridyl or morpholino group.

2. A compound of claim 1 wherein x is i; and Z is a bivalent radical of the formula

where each A is hydrogen; each a is 1; each B is —SO₂OM, where each M is hydrogen or alkali metal or

where R and R' are each hydrogen, alkyl of 1 to 4 carbon atoms, hydroxyalkyl of 1 to 4 carbon atoms, phenyl, glycosyl or together comprise a pyridyl or morpholino group.
3,646,015

3. A compound of claim 2 wherein each B is —SO₂OM, where M is alkali metal; and each b is 1.

4. A compound of claim 2 wherein each B is

\[
\text{SOC}_2M
\]

where R and R' are hydrogen.

5. A compound of claim 1 wherein x is 0, and Z is a monovalent radical of the formula

\[
\text{SOC}_2M
\]

wherein each b is an integer from 1 to 4 and each B is selected from groups A above; —SO₂OM where M is hydrogen or alkali metal; and

\[
\text{SOC}_2M
\]

where R and R' are each hydrogen, alkyl of 1 to 4 carbon atoms, hydroxyalkyl of from 1 to 4 carbon atoms, phenyl, glucosyl or together comprise a pyridyl or morpholino group.

6. A compound of claim 5 wherein each B is hydrogen or —SO₂OM, where M is alkali metal; and each b is 1.

7. A compound of claim 5 wherein each B is

\[
\text{SOC}_2M
\]

where R and R' are hydrogen.

8. A compound of claim 1 wherein x is 0; and Z is a monovalent radical of the formula

\[
\text{SOC}_2M
\]

wherein each A is as defined above and each p is 1 or 2.

References Cited


JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

117—33.5; 252—95, 98, 99, 152, 301.2 W; 260—211.5, 240.1, 326.1
UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION


Inventor(s) Lewis R. Hamilton

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 26, "phoshine" should be -- phosphine --.

Column 14, line 53, after "sodium 4-(7-methyl-l-isoiindoliny1)-
2-stilbenesulfonate;" insert -- sodium 4-(7-phenyl-l-
isoiindoliny1)-2-stilbenesulfonate --.

Signed and sealed this 11th day of July 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR. ROBERT GOTTSCHALK
Attesting Officer Commissioner of Patents
CERTIFICATE OF CORRECTION


Inventor(s)    Lewis R. Hamilton

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 26, "phoshine" should be -- phosphine --.

Column 14, line 53, after "sodium 4-(7-methyl-1-isooindolyl)-2-stilbenesulfonate;" insert -- sodium 4-(7-phenyl-1-isooindolyl)-2-stilbenesulfonate --.

Signed and sealed this 11th day of July 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.                          ROBERT GOTTSCHALK
Attesting Officer                           Commissioner of Patents