METHOD OF COMBINING OPTICAL BRIGHTENERS WITH POLYMERS FOR STABILITY IN BLEACH AND ENCAPSULATED PRODUCT

United States Patent
Briggs

[54] METHOD OF COMBINING OPTICAL BRIGHTENERS WITH POLYMERS FOR STABILITY IN BLEACH AND ENCAPSULATED PRODUCT

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References Cited
UNITED STATES PATENTS
3,544,500 12/1970 Osmond et al. 252/316 X

ABSTRACT
Optical brighteners are protected against oxidative degradation by aggressive environments such as aqueous hypochlorite bleach to be effectively depositable onto fabrics from bleach by combining the brightener with emulsion polymer prepared from a major portion of the polymer precursors and encapsulating the brightener-polymer combination with the balance of the polymer precursors. Suitable precursors are styrene and acrylic or methacrylic acid, in weight ratios of 65 to 98 parts of the former to two to 35 parts of the latter.

20 Claims, No Drawings
3,666,680

METHOD OF COMBINING OPTICAL BRIGHTENERS WITH POLYMERS FOR STABILITY IN BLEACH AND ENCAPSULATED PRODUCT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention has to do with protecting optical brighteners from oxidative degradation by aggressive chemicals. More particularly the invention is concerned with means enabling incorporation of oxidation sensitive compounds into oxidizing environments such as hypochlorite bleach solution for subsequent deposition onto fabric without loss of brightening effectiveness through oxidative destruction.

The invention further concerns provision of opacifiers for bleach and other aggressive chemical solutions to improve the aesthetic appearance of such solutions.

2. Prior Art

The use of opacifiers in bleach is taught in e.g. Zimmerer, U.S. Pat. No. 3,393,153, issued July 16, 1968. The combination of a polymer latex with optical brighteners has also been suggested in order to carry onto the fabric chemicals which brighten what bleach has whitened.

Brightening of fabrics has been realized in the past through the use of particular dyes termed optical brighteners in detergents. While bleach functions to remove colored impurities from fabrics by chemical conversion e.g. into colorless products by oxidation and “bluing” of fabrics renders undesired yellow color invisible by color compensation, brighteners operate to compensate for a yellow cast in fabric occasioned by absorption of short wavelength blue light by yellow bodies in the fabric by a partial replacement of the absorbed or “lost” light. This way the eye “sees” a complete white, without loss of light. Optical brighteners absorb the invisible ultraviolet portion of the daylight spectrum and convert the energy there into blue visible light through fluorescence. Optical brightening thus effectively adds light to fabrics.

The conjunct use of detergent and bleach however as in a typical household wash operation may destroy portions of the optical brightener through oxidation by the bleach. Thus the net whitening and brightening is not strictly additive.

The combination of optical brightener with bleach would result in higher levels of brightener in the wash water if the brightener could be preserved while in the bleach. Zimmerer, above noted, suggests heating a polymer latex and brightener together to so associate the brightener and polymer that the stability of the latter will somehow accrue to the benefit of the former. This result is not achieved, however, if there is access of bleach to the brightener.

It is necessary to exclude bleach-brightener contact in bleach solutions and in wash water if the full benefits of brighteners is to be realized.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the invention to provide method means for combining optical brighteners, and other dyes, with synthetic organic polymer in a manner protective of the brightener when in contact with aqueous bleach solution.

This and other objectives of the invention, to be made apparent as the description proceeds, are realized by the method of combining optical brightener compound with synthetic organic polymer consisting essentially per 100 parts by weight of 65 to 98 parts of a styrene monomer having eight to 12 carbon atoms and two to 35 parts of a water soluble monocarboxyl acid having three or four carbon atoms in a manner to retain optical brightening properties in aqueous bleach solutions which includes the steps of:

a. dissolving optical brightener compound in a major weight proportion but less than 90 percent by weight of said styrene monomer;

b. dissolving at least a major weight proportion of said vinyl acid in water;

c. combining the optical brightener containing styrene monomer from step (a) with the aqueous vinyl acid solution of step (b);

d. emulsion polymerizing the mixture of step (c) to form a copolymer latex incorporating the optical brightener compound in the particulate copolymer so formed;

e. adding the balance of the styrene monomer and the balance of the vinyl acid monomer, if any, to the latex from step (d), and;

f. emulsion polymerizing the added monomers in step (e) onto the copolymer particles from step (d).

Means thus are provided for protectively carrying oxidizer sensitive compounds in aqueous bleach comprising particles having an inner portion consisting essentially of an oxidizer sensitive compound and a styrene-acrylic polymer and an outer portion forming an encapsulating layer over the inner portion and consisting essentially of styrene polymer free of the brightener compound. The particle comprises per 100 parts of polymer from 65 to 98 parts of a styrene monomer having eight to 12 carbon atoms and conversely from two to 35 parts of methacrylic or acrylic acid copolymerized therewith. The particle inner portion contains a major proportion but less than 90 percent by weight of the styrene content of the particle and at least a major proportion of the acid monomer, with the balance of the monomers being contained in the particle outer portion forming the encapsulating layer.

The oxidation sensitive compound is generally an optical brightener which may be selected from 4,4′-diaminostilbene-2,2′ disulfonic acids, dibenzothiophene-5,5′-dioxides and azoles and be present in an amount between 0.5 and 5 percent by weight based on the weight of the styrene. The polymer particles typically range from 0.1 to 2 microns in average particle size. A portion of the styrene component e.g. five to 10 parts by weight per 100 parts of the polymer, may be replaced by five to 10 parts of a hydrophilic monomer selected from the hydroxyether, ether, amide and cyano derivatives of acrylic or methacrylic acid or a vinyl sulfonate monomer having the formula R—CH = CH—SO_{3}Me in which R is hydrogen or an aromatic or alkyl radical having up to 10 carbon atoms and Me is alkali metal.

The safe incorporation of optical brighteners and other dyes and oxidation susceptible compounds in aggressive environments such as aqueous bleach is realized by combining the brightener in a polymer in a manner to insulate the brighteners from the harsh environment while permitting its useful brightening function. To so combine the brightener compound with polymer, the brightener is first dissolved in the oil soluble monomer of the polymer and the monomer-brightener solution is copolymerized with vinyl acid, i.e. acrylic or methacrylic acid which has been previously dissolved in water, by conventional emulsion polymerization techniques. Subsequently a second emulsion polymerization is effected to coat the particles resulting from the first polymerization with a bleach impervious polymer free of brightener thus to protect the brightener compound in the first or inner center portion of the polymer particle. While the emulsion recipes are conventional, the sequence of operations is not conventional and enables the realization of the invention.

It is known to emulsion polymerize styrene and acrylic acid by dissolving an emulsifying agent in all the water and adding the acrylic acid and possibly a hydrophilic comonomer.

Styrene or other oil soluble, principal monomer is added to the mixture and stirred to achieve emulsification. The temperature of the emulsion is raised to 120°-140° F and a peroxycacid peroxide catalyst is added with or without a reducing agent to form a redox couple to produce free radicals to initiate the polymerization reaction. The temperature of the emulsion rises exothermically as the monomer species are converted into polymer. Usually no external heat is required and almost all of the monomer is polymerized to provide a milky aqueous suspension of particles (a latex) in which the particles typically range from 0.1 to 2 microns in average par-
article size and contain about 30 to 60 percent of the total polymer. In the present invention, the above common procedure is modified to achieve the purposes of the invention. Thus only a portion of the monomer components are first reacted together and the brighter is first dissolved in the oil soluble monomer (stylene) to assure intimate incorporation of the brighter compound in the polymer. In a second stage of the preparation the balance of the monomers is added and after sufficient intermixing and addition of catalyst, a second emulsion polymerization is effected overcoated the first formed particles with additional, separately formed polymer which it has been found will protect the brighter in the first stage polymer.

While not wishing to be bound to any particular theory of operation it is believed the remarkable stability of the brightening compound in the products of the invention against oxidative attack may derive from the formation of micelles upon the addition of the emulsifier-surfactant to water. The micelles are lamellar colloidal particles having structures dependent on the hydrophobic/hydrophilic orientation of the surfactant molecule. Upon the addition of the hydrophobic (stylene) monomer containing dissolved dye in the first stage of preparation, these monomer droplets and hydrophilic monomer become encapsulated in the micelles. Addition of catalyst causes polymerization to proceed within the confines of the micelle until the discrete particles of polymer if formed, still enclosed by the micelle structure. Upon the addition of the second portion of the hydrophobic (stylene) monomer, in the absence of additional surfactant for formation of new micelles the added monomer enters the previously formed polymer particle micelles and forms a layer of reactive monomer over the outside of the polymer particles. With the addition of more catalyst, this newly added monomer polymerizes and forms a shell of basically hydrophobic polymer over the inner particle portion containing the brightening compound. This shell prevents chemically active molecules such as oxidizing molecules of bleach from entering the particle to the brightener compound. The second added portion of hydrophobic monomer may contain brightener compound, but such compound in the outer layer of the particles is readily destroyed in contact with bleach.

The particulate polymer in which the brightener compound protectively inhere consists essentially of a styrene monomer, acrylic or methacrylic acid and optionally a hydrophilic comonomer. As the hydrophobic monomer component there may be employed styrene per se, i.e. vinyl benzene, or a substituted styrene such as vinyl toluene or butyl styrene i.e. alkyl substituted styrenes in which the alkyl groups contain from 1 to 4 carbon atoms such that the styrene monomer contains from 8 to 12 carbon atoms, inclusive. Or the styrene monomer may be monoalcohol ring substituted such as chlorostyrene or bromostyrene. The acid component may be described generally as a water soluble \( \alpha, \beta \) ethylenically unsaturated monocarboxylic acid, i.e. vinyl acid having three to four carbon atoms namely acrylic or methacrylic acids. The proportion by weight of combined styrene monomer and acid monomer is the particular polymer ranges between 63 to 98 parts styrene and two to 35 parts of the vinyl acid per 100 parts by weight of the terpolymer.

Polymerization is carried out as hereinafter described to provide particle polymers ranging in size between 0.01 and 5 microns and preferably between 0.1 and 2 microns where an opacifying effect is desired. It is often desirable to incorporate a further hydrophobic monomer in the polymer such as a derivative of methacrylic or acrylic acid containing up to 10 carbon atoms and free of carboxyl groups, such as ester, hydroxyster, ether, amide or cyano derivatives of acrylic or methacrylic acids. These may be used in amounts of between 0.5 and 25 parts by weight preferably from five to 10 parts, in substitution for an equal weight amount of the styrene monomer, per 100 parts of the final opacifying polymer. A water soluble vinyl sulfonate monomer may be the additional hydrophilic component e.g. having the formula \( R-CH=CH-SO_3Me \) in which \( R \) is a hydrocarbon radical free of aliphatic unsaturation having up to 10 carbon atoms or an aromatic radical such as tolyl, benzyl or phenyl radical; an alkyl radical such as methyl, ethyl, propyl, butyl, isobutyl, pentyl, neopentyl, hexyl, heptyl, octyl, 2-ethyl hexyl, nonyl and decyl, or hydrogen and Me is an alkali metal e.g. sodium, potassium, lithium and cesium. Specific termomers of choice include the hydroxethyl esters of methacrylic acid in which the alkyl group contains from one to four carbon atoms and particularly hydroxyethyl and hydroxypropyl methacrylate, and acrylamide, methacrylamide, acrylonitrile, methacryl vinyl ether, sodium or potassium vinyl sulfonate and styrene sulfonate.

The monomers just described are emulsion polymerized using conventional catalysts, oxidizers or reducers, temperatures and pressures but with the critical steps of first dissolving the brightener compound in the styrene monomer and dissolving the water soluble vinyl acid and hydrophilic comonomer, if used, in water, suitably with the emulsifying surfactant, prior to addition of the styrene. Apart from the herein discussed sequential reactant, the preparation of the polymers is carried out as for any other exothermic emulsion polymerization in each stage. Thus an aqueous solution of a suitable surfactant is mixed with the water soluble vinyl acid. Thereafter the water insoluble styrene reactant into which the brightener compound is incorporated previously dissolved, suitably emulsified with water by stirring at concentrations between 0.5 and 5 percent based on the total of styrene in the polymer and preferably at least 1 percent by weight same basis, is mixed in and agitated until emulsified as the oil phase. The emulsion is then maintained at an elevated temperature through exothermic and/or added heat if necessary in admixture with a suitable catalyst e.g. and preferably water soluble peroxides such as ammonium and sodium and potassium persulfate and peroxides e.g. hydrogen peroxide; and other catalysts such as t-butyl perbenzoate and t-butyl hydroperoxide, as well as other oil soluble materials such as bisazobutyronitrile and cumene hydroperoxide. Following reaction for the required period and at temperatures between 130°-200°F and boiling the reaction mixture is cooled and neutralized with alkali. The latex may be spray or otherwise dried without loss of dispersibility or stability in liquid household bleach.

In the preparation of brightener protective polymer particles according to the present invention the hydrophobic monomer e.g. styrene is divided into two or more separate emulsion polymerizations. The first portion of the first emulsion polymerization comprises a major weight proportion, but less than all of the styrene to be used in forming the polymer, i.e. at least 50 percent by weight of the 65 to 98 parts by weight of styrene ultimately to be used per 100 parts of polymer is employed in the first polymerization. All of the optical brightener to be incorporated in the polymer is dissolved in this first portion of styrene. As indicated elsewhere this will be from 0.5 to 5 percent by weight of brightener compound based on the total weight of styrene monomer in the polymer. Preferably at least 1 percent by weight of brightener is dissolved in the first styrene portion. The first styrene portion will generally be less than 90 percent by weight of the total polymer styrene content and will typically be between 60 and 80 percent by weight of the polymer total styrene content. The acrylic or methacrylic acid comonomer may also be divided into two portions for sequential polymerization. The first portion employed in the first polymerization, will be a major weight proportion of the acid in the total polymer i.e. at least 50 percent by weight of total polymer acid. This first portion may range up to 100 percent by weight of the total polymer portion of acrylic or methacrylic acid, but typically from 60 to 80 percent of the total polymer acid will be included in the first acid portion.

As mentioned above from five to 10 parts by weight of the styrene monomer may be replaced on a weight for weight
basis by certain hydrophilic comonomers. This substitution may be made in either the first or second styrene monomer portion, and preferably from 60 to 80 percent by weight of the five to 10 parts of hydrophilic comonomer, is used, is incorporated in the first styrene portion. The balance of each monomer comprises a second portion for use in the second emulsion polymerization.

With the monomers having been thus divided for two polymerizations, the optical brightener is dissolved in the styrene monomer first portion. The acid first portion is dissolved in water and the two solutions are mixed together in a suitable vessel. The mixture is emulsion polymerized by the conventional techniques above described by adding a surfactant, a polymerization catalyst and heating. Heating is initially to about 130°F, but the temperature rises with the reaction exotherm to about 190°F, or somewhat higher or lower. The first reaction product is a latex of styrene-acid polymer (or terpolymer with the hydrophilic comonomer) having from 30 to 60 percent by weight of polymer present as particles suspended in an aqueous medium.

The reaction product is cooled before the next stage of polymerization. Cooling typically will be to less than 130°F or to a lower temperature of the second polymerization mixture. The reaction mixture is prepared by adding the balance of each of the monomers to the cooled first polymerization reaction product. The mixture is mixed together and permitted to stand from 15 to 30 minutes or longer. Thereupon additional polymerization catalyst is added and the temperature of the reaction mixture permitted to rise above 130°F to 190°F or for higher or lower, with the reaction exotherm. Reaction is continued to produce a latex containing polymer particles having an average particle size between 0.1 and 2 microns. The optical brightener is within these particles and protectively carried there in. Suitable surfactants for effecting emulsion polymerization as described and/or for suspending the finely particulate polymer in bleach or other aqueous liquid are the nonionic types i.e. anionic, nonionic or amphoteric. Various of these surfactants will show greater or less tolerance for the harsh environment of liquid household bleach, depending on the concentration and pH thereof.

Among suitable surfactants are anionic aromatic compounds, e.g. water-soluble higher alkyl aryl sulfonates particularly those having from eight to about 15 carbon atoms in the alkyl group. It is preferred to use the higher alkyl benzene sulfonates, although other mononuclear alkyl nuclei, such as toluene, xylene, or phenol, may be used also. The higher alkyl substituent on the aromatic nucleus may be branched or straight-chained in structure, examples of such group being nonyl, decyl, and tridecyl groups derived from polymers of lower mono-olefins, decyl, keryl, and the like. Illustrative of suitable aliphatic anionic compounds are the normal and secondary higher alkyl sulfates, particularly those having about eight to 15 carbons in the fatty alcohol residue, such as lauryl (or coconut fatty alcohol) sulfate. Other suitable members of this class are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids; the oleic acid ester of isethionic acid; the higher fatty acid (e.g. coconut) ethanolidylates; the higher fatty acid amides of amino alkyl sulfonic acids, e.g. lauric acidamide of taurine; and the like.

Illustrative of suitable alkyl aromatic anionic compounds are those having about eight to 15 carbons in the fatty alcohol residue, such as lauryl (or coconut fatty alcohol) sulfate. Other suitable members of this class are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids; the oleic acid ester of isethionic acid; the higher fatty acid (e.g. coconut) ethanolidylates; the higher fatty acid amides of amino alkyl sulfonic acids, e.g. lauric acidamide of taurine; and the like.

Typical specific examples are the sodium salt of a sulfate ester as an alkylalkyl ether (ethylenoxy) ethanol, the mononuclear salt of this sulfate ester, sodium methyl oleyl taurate, sodium alkyl naphthalene sulfonate, sodium acyl sodium sulfonate, sodium tetraphenylphosphate sulfonate, sodium alkyl aryl sulfonate, sodium alcoholsulfonate, cocomegolglyceride sulfate, dodocylbenzene sodium sulfonate, dodoclybenzene sulionic acid, tridecylbenzene sodium sulfonate, fatty alcohol sodium sulfonate, sodium dodecyl diphenyl oxide disulfonate, sulfonated castor oil, polyethanolalkyl benzene sulfonate, triethanolamine salts, sodium triethanolamine alkyl aryl sulfonate, magnesium lauryl sulfate, potassium lauryl sulfate, sodium lauryl ether sulfate, ammonium lauryl ether sulfate, sodium tallow sulfonate, dodocyclbenzene sodium sulfonate, oleyl methyl tauride, ammonium lauryl sulfate, amide sulfonate, and the like.

In general, suitable nonionic surfactants include those such as produced by the introduction of alkylenz oxide group into an organic hydrophobic compound or group having an aliphatic or aromatic structure. The hydrophobic organic group generally contains at least eight carbon atoms and up to about 30 carbon atoms. Condensed with the hydrophobic group are at least five and preferably up to about 50 alkylene oxide groups. It is preferred to use the polyoxyethylene condensates derived from ethylene oxide. It is preferred to use the polyalkylene oxide condensates of alkyl phenol, such as the polyoxyethylene ethers of alkyl phenols having an alkyl group of at least about six, and usually about eight to 12 carbons, and preferably 8 to 9 carbon atoms, and an ethylene oxide ratio (No. of moles per phenol) of about 7.5, 8.5, 11.5 or 20, though the number of ethylene oxide groups will usually be from about eight to 40. The alkyl substituent on the aromatic nucleus may be di-isobutylen, diamin, polymerized propylene, dimerized C12 - C18 olefin. and the like.

Further suitable nonionics are the polyoxymethylene esters of organic acids, such as the higher fatty acids, rosan acids, tall oil acids, or acids from the oxidation of petroleum, et cetera. These polypoly esters will contain usually from about 12 to about 30 moles of ethylene oxide or its equivalent and about eight to 22 carbons in the acyl group. Suitable products are refined tall oil condensed with 16 or 20 ethylene oxide groups, or similar polypoly esters of lauric, stearic, oleic acids, et cetera.

Additional nonionic agents are the polyalkylene oxide condensates with higher fatty acid amides, such as the higher fatty acid primary amides, mono- and di-ethanolamides. Suitable agents are coconut fatty acid amide condensed with about 10 to 50 moles of ethylene oxide. The fatty acyl group will have similarly about 8 to 22 carbons, and usually about 10 to 18 carbon atoms, in such products. The corresponding sulfonamides may be used also if desired.

Other suitable polyether nonionics are the polyalkylene oxide ethers of high aliphatic alcohols. Suitable fatty alcohols having a hydrophobic character, preferably alcohols, are lauryl, myristyl, cetyl, stearyl and oleyl alcohols which may be condensed with an appropriate amount of ethylene oxide, such as at least about 6, and preferably about 10 to 30 moles. A typical product is oleyl alcohol condensed with about 12, 15 or 20 moles of ethylene oxide. The corresponding higher alkyl mercaptans or thio-alcohols condensed with ethylene oxide are suitable in the present invention also. The water-soluble polyoxyethylene condensates with hydrophobic polyoxypropylene glycols may be employed also, e.g. the ethylene oxide condensates with condensates of propylene oxide and propylene glycol.

Further suitable nonionic materials are the higher fatty acid alkanolamides, such as the monoethanolamides, diethanolamides and isopropanolamides wherein the acyl radical has about 10 to 14 carbon atoms and amine oxides. Examples are coconut (or equivalent lauric), capric and myristic diethanolamide, monoethanolamide and isopropanolamide, dodecyl dimethyl amine oxide and dimethyl acetyloxylamine oxide where acyl is C12 - C14.

Generally, these surfactants comprise from 0.05 to 10 percent by weight, and preferably from 0.5 to 3 percent of the reaction mixture and the latex added to the liquid household bleach.

The optical brighteners useful herein include that species of dyes which are fluorescing compounds, generally optically colorless and nonabsorptive in the visible portion of the spectrum. Generally, suitable brighteners are aromatic or heterocyclic compounds having a series of conjugated double bonds.
Primary among typical compounds useful herein are:

I. The derivatives of 4,4'- dianisodimethylene -2,2'- disulfonic acid, particularly the bistriazinyl, bisacryl and mixed acryl triazinyl derivatives. Naphthazarinostilbene sulfonic acid may be mentioned. Azinyl radicals may be substituted on the carbons of the heterocyclic ring with many radicals including hydroxy, aminos, alkoxys, hydroxalkoxy, chloro, thio, alkoxybenzyl, amines, morpholinos and others. Acyl radicals include acetyl, phenoxacyetyl, alkoxybenzoyl tolyl, benzoyl and aminobenzoyl. Benzoyl acyl radicals are generally substituted in the ortho and/or para position e.g. p-acetaminobenzoyl, methyl, methoxy, acetoxy, 2-hydroxyethoxy, halogenoalky or akenyloxy groups. The sulfonic acid group substituent in the stilbene may be replaced with an electron donor radical such as alkyl, alkoxy or sulfamoyl.

II. The derivatives of dibenzothenophene-5,5-dioxide, specifically 3,7-dianisodibenzothenephene 2,8-disulfonic acid-5,5-dioxide in which the preferred acyl groups are alkoxybenzoyl groups. See e.g. U.S. Pat. Nos. 2,563,795; 2,573,652; 2,702,759; 2,719,155; and 2,733,165 which are incorporated herein by reference; and

III. The amino acids described generally by diatizonation of 4-aminoazostilbene-2-sulfonic acid, coupling with an orthocoupling naphthylamine derivative (or benzene or a heterocyclic) and oxidation to the triazole. See U.S. Pat. Nos. 2,784,197; 2,713,057; 2,817,665; 2,784,184; 2,972,611; 2,640,056; 2,639,990; British Pat. No. 808,113; Belgian Pat. No. 572,498; U.S. Pat. No. 2,765,304; 2,765,239; and German Pat. No. 735,478, which are incorporated herein by reference; e.g. naphthiazole, bis-benzimidazolyl compounds and benzimidazolones;

IV. Coumarin and derivatives;

V. Pyrazine and derivatives; and

VI. 4-Aminonaphthalamide.

In addition, dyes and pigments may be used in place of or with the foregoing e.g. chromates, polysulfides, thianaphthanes and phthalocyanines such as potassium dichromate, Ultramarine blue, Sulfantherine Pink FFD Paste and Monastral Fast Green GWD, for the purpose of contributing "blue" light or various tints. As used herein the term "brightening compound" is intended to be inclusive of these colorants as well as the fluorescing, colorless dyes. The presently described means for protectively carrying brighteners finds particular application in liquid household bleach. Such product may be opacified and fabrics cleansed therewith by brightened by incorporation of brightener containing polymer in accordance with this invention. "Bleaching herein refers to any hypochlorite ion containing solution containing sufficient free alkali to have a pH of 10 and preferably 11.5 and higher, typically from 0.1 to 1.0 percent by weight free alkali. Per cent concentrations of hypochlorite ion will range between 1 and 10 per cent by weight with a practical minimum being 2.5 percent. Most bleaches fall between 3 and 7 percent hypochlorite ion, and this concentration is most suited to the use of the invention. Various bleaching agents including the heterocyclic N-chlorimides, such as the following are useful herein: trichlorocarboxylic acid, dichlorocarboxylic acid and salts thereof as the alkali metal salts e.g. sodium and potassium tri- and dichlorocyanurates. Other imides are hypochlorite ion generating also in aqueous solution and may be used e.g. N-chlorosuccinimide, N-chloromalonimide, N-chlorophthalimide and N-chloronaphthalimide. Other materials are the hydantoins e.g. the 1,3-dichloro-5,5-dimethyl hydantoin, N-monochloro-C, C-dimethylhydantoin, methylene bis (N-chloro-C, C-dimethylhydantoin), 1,3-dichloro-5-methyl-5-isobutylidihydantoin, 1,3-dichloro-5 methyl-5-ethylhydantoin, 1,3-dichloro-5-methyl-5-ethylhydantoin and the like as well as trichloromelamine. Preferred sources of hypochlorite ion are the water soluble inorganic salts such as lithium, calcium, potassium and particularly sodium hypochlorite.

The invention is illustrated by the following Examples, in which all parts and percentages are by weight.
b. dissolving at least a major weight proportion of said vinyl acid in water;

c. combining the optical brightener containing styrene monomer from step (a) with the aqueous vinyl acid solution of step (b);

d. emulsion polymerizing the mixture of step (c) to form a copolymer latex incorporating the optical brightener compound in the particulate copolymer so formed;

e. adding the balance of the styrene monomer and the balance of the vinyl acid monomer, if any, to the latex from step (d), and

f. emulsion polymerizing the added monomers in step (e) onto the copolymer particles from step (d).

2. Method according to claim 1 in which from 0.5 to 5 percent by weight of the optical brightener compound is dissolved in the styrene monomer in step (a) based on the total weight of the monomer incorporated in the polymer.

3. Method according to claim 1 including maintaining a reaction temperature above about 130°F in the polymerization mixture during steps (d) and (f).

4. Method according to claim 3 including also cooling the reaction mixture to less than 130°F between step (d) and step (f).

5. Method according to claim 1 including forming particles in step (f) having an average particle size between 0.1 and 2 microns.

Method according to claim 1 including also adding from 0.5 to 25 parts of a hydrophilic monomer selected from acrylic monomers selected from the hydroxyster, ether, amide and cyano derivatives of methacrylic and acrylic and vinyl sulphonate monomers having the formula R—CH—CH—SO₃Me in which R is hydrogen or a hydrocarbon radical free of aliphatic unsaturation having up to 10 carbon atoms and Me is an alkali metal, in place of an equal weight amount of the styrene monomer.

7. Method according to claim 1 in which said optical brightener compound is selected from 4,4'-diaminostilbene-2,2'-disulfonic acids, dibenzothiophene-5,5-dioxides, azoles, coumarin, pyrazine, and 4-aminoanaphthalimides.

8. Method of combining an optical brightener compound with synthetic organic polymer consisting essentially per 100 parts by weight of 88 to 92 parts of styrene and eight to 12 parts of an acrylic or methacrylic acid to retain optical brightening properties in aqueous bleach solutions, which includes the steps of:

a. dissolving at least 10% by weight based on the total amount of styrene in the polymer of an optical brightener compound selected from 4,4'-diaminostilbene-2,2'-disulfonic acid derived, dibenzothiophene-5,5-dioxide derived, and azole derived optical brightener compounds in from 60 to 80 percent by weight of the total styrene monomer;

b. dissolving from 50 to 100% by weight of the total acrylic or methacrylic monomer in water;

c. combining the optical brightener containing styrene from step (a) and the aqueous vinyl acid solution of steps (b) with surfactant to form an emulsion polymerization mixture;

d. 1. heating the mixture of step (c) to an elevated temperature less than 130°F in the presence of a polymerization reaction catalyst and reacting the monomers at the temperatures of the exotherm;

d. 2. cooling the polymerization reaction mixture to less than 130°F;

e. adding the balance of the styrene and acrylic acid or methacrylic acid monomer and maintaining at less than 130°F for at least 15 minutes following addition;

f. adding additional polymerization catalyst to the reaction mixture heating the mixture with the ensuing exotherm to a temperature above 130°F to polymerize the added styrene monomer onto the polymer of step (d-1) to form a particulate polymer having an average particle size between 0.1 and 2 microns which protectively incorporates said brightener compound.
parts of methacrylic or acrylic acid copolymerized therewith said center portion containing from 60 to 80 weight percent of the styrene present in said particles and from 50 to 100 percent of the acid present in said particles, said outer portion containing the balance of the styrene and acid present in the particles.

20. Particles according to claim 19 including also in replacement of a like weight amount of styrene in said particles from 5 to 10 parts by weight of a hydrophilic comonomer selected from the hydroxyester, ether, amide and cyano derivatives of acrylic or methacrylic acid or a vinyl sulfonate monomer having the formula \( R-\text{CH} = \text{CH-SO}_2\text{Me} \) in which \( R \) is hydrogen or an aromatic or alkyl radical having up to 10 carbon atoms and Me is sodium or potassium, said center portion containing from 60 to 80 percent of said hydrophilic comonomer and said outer portion the balance thereof.

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