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[54] **DETERGENT COMPOSITION HAVING POLYMER BONDED INDICATOR**

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[58] **Field of Search** 252/89, 408, 135, 546, 252/DIG. 2

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[57] **ABSTRACT**

A detergent composition has been formed by the combination of a detergent and a pH indicative polymer, which is prepared by bonding a polymer to a pH indicator, such as phthalein indicator, sulfophthalein indicator, azo indicator, or the like. The indicator is condensed or addition polymerized onto the polymer or with the monomer to obtain a pH indicative polymer which can be used for indicating any decrease in the activity of the detergent.

7 Claims, No Drawings

DETERGENT COMPOSITION HAVING POLYMER BONDED INDICATOR

RELATIONSHIP WITH CO-PENDING APPLICATIONS

This is a continuation-in-part of application Ser. No. 194,036 filed Oct. 29, 1971.

BACKGROUND OF THE INVENTION

1. Field Of The Invention

This invention relates to a novel detergent composition. More particularly, this invention relates to a detergent composition comprising a detergent and pH indicative polymer.

2. Description Of The Prior Art

Fatty acid soaps, synthetic detergents, alkaline agents and acidic agents have been used as detergents for fibers, fabrics, various types of cloth, metals, machine parts, ceramics, and general household utility. The detergent solution is usually formed with variable amounts of detergent, depending upon the particular operator's experience, and use of additional detergent or changing of the detergent solution will occur depending upon the visible extent of dirtiness of the detergent solution, regardless of whether additional detergent or changing of the detergent solution is actually required. Consequently, there is often a severe waste of detergent or detergent solution, or there is the possibility of using inadequate or partially inactive quantities of the detergent or detergent solution.

Moreover, since visual examination is the usual means of determining detergent efficiency, occasionally undetected changes in the pH quality of the detergent will occur which will adversely affect the articles being treated, particularly when the detergent is being used for laundry operations or the like. Control of detergent solutions has, therefore, been quite difficult.

It is known that the main component or main additive of the detergent is an electrolyte or is affected by the hydrogen ion concentration. The extent of detergency can thus be indicated by the pH of the detergent solution so that in those instances, such as laundry or other washing in which injury or corrosion can occur if the detergent solution has an improper pH, control can be effectively provided by use of a pH indicator in the detergent solution.

The selection of pH indicator, however, is a very difficult matter, since it must not stain the articles being treated. Particularly in laundry cleaning operations, in which coloring is a critical factor, the indicator must not stain or affect the coloring of the articles being treated.

SUMMARY OF THE INVENTION

Accordingly, it is one object of this invention to provide a detergent composition which is self-pH-indicating, but which will not adversely affect the coloring of the articles treated with said composition.

It is another object of this invention to provide a detergent composition which is self-pH-indicating so that injury or corrosion of the articles treated with said composition is prevented.

It is another object of this invention to provide a pH indicator which will not be absorbed into laundry or other articles being washed and which will be removed with the detergent.

These and other objects have now been attained by providing a detergent composition containing a detergent and pH indicative polymer, wherein said polymer is prepared by bonding a polymer to a pH indicator or by polymerizing a monomer in contact with a suitable indicator. The pH indicative polymer will thus indicate a change in the pH of the detergent solution by a color change. When the detergent is being used for laundry operations, the pH indicative polymer will not be absorbed into the laundry and will be completely removed with the detergent solution. It will therefore not stain or, in any other way, adversely affect the laundry.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In this invention, the term "detergent" refers to all agents which are used in water or aqueous medium for the removal of soils or stains from articles. Suitable detergents include household detergents for cloth, tableware and furniture; industrial fiber detergents for washing of wool, washing of natural and synthetic fibers, and for refining; industrial metal and machine detergents for washing of metals and machine parts; cleaning detergent for laundry; and detergents for pulp and paper industry, car and ship washing, glass and ceramic washing, can and bottle washing, etc.

The detergents which can be utilized as the components of the detergent compositions of this invention are the following:

1. Anionic surface active agents
   a. Water-soluble soap: Examples of the suitable soaps for use of this invention are the sodium, potassium, ammonium, alkanolammonium (e.g. mono-, di-, thiethanolammonium and N,N-dimethylethanolammonium) salts of higher fatty acids (C_{10}–C_{22}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from cocomut oil and tallow, i.e., sodium and potassium coconut and tallow soaps.
   b. Anionic synthetic non-soap detergents; Examples are the water-soluble salts, particularly the alkali metal salts, of organic sulfuric acids, organic phosphoric acids and organic sulfonic acids having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and/or an aryl radical selected from the group consisting of phenyl and naphthyl radical. Important examples are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8–C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates in which the alkyl group can be a straight or branched chain and contains from about 9 to about 15 carbon atoms; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to about 12 carbon atoms; the reaction product of fatty acids esterified with

isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a N-methyl taurine in which the fatty acids, for example, are derived from coconut oil; sodium or potassium salts of sulfonated C_{10}–C_{24} α-olefins; sodium or potassium salts of naphthalene sulfonate-formaldehyde condensate.

2. Nonionic surface active agents

a. Polyoxyethylene alkyl ether type detergents; These compounds are the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

b. Polyoxyethylene alkyl phenol ether type detergents; These compounds are the 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 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene or nonene, for example.

c. Polyoxyethylene alkyl ester type detergents; These compounds are the condensation products of fatty acids having an acyl moiety of from about 8 to about 18 carbon atoms. These acyl moieties are normally derived from naturally occurring glycerides, e.g. coconut oil, palm oil, soybean oil and tallow, but can be derived synthetically, e.g. by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process.

d. Polyoxyethylene-polyoxypropylene block copolymer type detergents; These 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 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.

e. Fatty acid ethanolamide type detergents; These compounds are monoethanol and diethanol amides of fatty acids having an acyl moiety of from about 8 to about 18 carbon atoms, and the ethylene oxide condensation products with these fatty acid ethanol amide. These acyl moiety are derived from natural glycerides, e.g., coconut oil, palm oil, soybean oil and tallow, and can be derived synthetically, e.g., by the oxidation of petroleum or by hydrogenation of carbon monoxide by the Fisher-Tropsch process.

f. Those nonionic synthetic detergents derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. For example, 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 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having molecular weight of the order of 2,500 to 3,000 are satisfactory.

g. Long chain tertiary amine oxide type detergent; These compounds are oxidized products of long chain tertiary amines having as substituents of the nitrogen atom in their molecular structure, one long chain radicals selected from the group consisting of alkyl radical and alkyl(mono- to about deca-)oxyethylene radical, these alkyl radicals having from about 8 to about 24 carbon atoms, and two short chain radicals selected from the group consisting of methyl, ethyl or hydroxyethyl radicals. Specific examples of amine oxide detergents include dimethyldodecylamine oxide and bis(2-hydroxyethyl)dodecylamine oxide.

h. Long chain tertiary phosphine oxide type detergents; These compounds are oxidized product of long chain phosphines having as substituents of the phosphorus atom in their molecular structure, one long chain radicals selected from the group consisting of alkyl, alkenyl or monohydroxyalkylradical ranging from 10 to 24 carbon atoms in chain length and two short chain radicals selected from the group consisting of alkyl or monohydroxyalkyl radicals containing from 1 to 3 carbon atoms. Specific examples of phosphine oxide detergents include dimethyldodecyl phosphine oxide and dimethyl (2-hydroxydodecyl) phosphine oxide.

i. Long chain sulfoxide type detergents; These compounds have as substituents of the sulfur atom of the sulfoxide radical in their molecular structure, one long chain radicals selected from the group consisting of alkyl, alkyl(mono- to about penta)oxyethylene, and mono- or dihydroxy alkyl radicals, ranging from 10 to about 28 carbon atoms in chain length and at least 10 to about 18 carbon atoms in these alkyl moiety, and one short chain radical selected from the group consisting of alkyl and mono- or dihydroxy alkyl radicals ranging from 1 to 3 carbon atoms. Specific examples of these sulfoxides are dodecyl methyl sulfoxide and 3-hydroxy tridecyl methyl sulfoxide.

3. Ampholytic synthetic detergents;

a. One type of these compounds are derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be a straight or branched chain, 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 group. Examples of compounds are sodium 3-dodecylaminopropionate and sodium 3-dodecylaminopropane sulfonate.

b. Other types of these compounds are derivatives of aliphatic quarternary ammonium, phosphonium and sulfonium compounds in which the aliphatic radical may be straight or branched chain, 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 phosphano group. Examples of compounds are 3-N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hex-

adecylammonio)-2-hydroxypropane-1-sulfonate.

4. Alkali detergents;

Examples of the alkali detergents are sodium hydroxide, sodium sesquisilicate, sodium metasilicate, sodium orthophosphate, water glass (Na_2O, 1.6 SiO_2; Na_2O, 2 SiO_2; Na_2O, 3.2 SiO_2), sodium carbonate, sodium pyrophosphate and sodium borate.

5. Acid detergents;

Examples of the acid detergents are sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, sulfamic acid, oxalic acid and citric acid.

These anionic, nonionic and ampholytic detergent compounds, and alkali and acid detergents can be used singly or in combination. The above examples are merely illustrations of the numberous suitable detergents. Other organic and inorganic detergent compounds can also be used.

The detergent may be admixed with other additives or "builders", such as sodium sulfate, sodium metasilicate, sodium sequisilicate, sodium orthosilicate, sodium carbonate, sodium bicarbonate, sodium orthophosphate, sodium tripolyphosphate, sodium hexametaphosphate, sodium choride, carboxymethyl cellulose, methyl cellulose, hydroxyethel cellulose, ethylenediamine tetraacetic acid, or fluorescent brightening agents. Suitable pH indicative polymers used in the composition of this invention are those compounds having a polymeric structure bonded to a pH indicator. It should be capable of sharply changing color within specific pH ranges. This type of polymer can be prepared by any of the following processes:

A. A pH indicator having a condensable or addition condensable radical is condensed or reacted with a polymer or polymerizable monomer which also has a condensable or addition condensable radical.

B. A pH indicator having a diazonium radical is admixed with an α,β-ethylenic unsaturated monomer and the monomer is addition polymerized using the pH indicator as a polymerization initiator.

C. A pH indicator having an α,β-ethylenic unsaturated radical is admixed with an α,β-ethylenic unsaturated monomer and is addition polymerized.

D. Combinations of the above.

In those processes, instead of a pH indicator, an intermediate can be used which will form the indicator upon further condensation reaction or addition reaction. Conventional dyes, pigments or polymer bonding coloring matter can be used to improve the sharpness of the color change or to adjust the pH color changing range. It is also possible to reach the pH indicative polymer with a dye, pigment, or polymer bonding coloring matter or derivative thereof, either per se or as an intermediate, at any time before, after or during the primary bonding reaction. When an intermediate is used, a developing treatment will usually be required.

Suitable pH indicators used in this invention are the weakly acidic or weakly basic indicators, whose visible absorption spectrum is different when in the form of a dissociation type molecule and when in the form of a normal type molecule. For instance, good results are obtainable with such pH indicators as:

a. phthalein indicators, such as phenolphthalein, O-cresol phthalein, thymol phthalein, p-xylenol phthalein, α-naphthol phthalein, dibromophenol phthalein, phenol-4-carboxy phthalein, thymol-4-carboxyphthalein, p-xylenol-4-carboxyphthalein, phenol-3,4,5,6-tetrachlorophthalein, etc.;

b. sulfophthalein indicators, such as phenol Red, cresol Red, m-cresol Purple, p-xylenol Blue, thymol Blue, xylenol Orange, bromophenol Red, bromocresol Purple, bromocresol Green, bromothymol Blue and bromophenol Blue, etc.;

c. azo indicators, such as Congo Red, methyl Orange, p-ethoxycrysoizine, α-naphthyl Red, Tropeorin 000, Alizarin Yellow R, methyl Red, and azo Blue;

d. Other indicators, such as methyl Violet 6B, crystal Violet, pentamethoxy Red, litmus quinoline Blue, Nile Blue and indigo carmine.

The polymer used for preparing the pH indicative polymer according to the above process (A), should have at least one radical which is condensable or addition condensable, such as an amino radical, hydroxy radical, carboxy radical, carbamide radical, sulfamide radical, lower alcohol ester radical, lower fatty ester radical, a radical of an aromatic nucleus having a substitutable hydrogen, N-methylol radical, N-halogenomethyl radical, C-methylol radical, C-halogenomethyl radical, epoxy radical, halohydrine radical, aldehyde radical, isocyanate radical, acid chloride radical, halogenotriazine radical or diazonium radical.

The pH indicator having the reactive radical can be either the pH indicator itself which contains at least one reactive radical, or it can be a compound which contains a reactive radical and which upon further reaction will form the pH indicator. Any conventional polymer or polymerizable monomer which is reactable with the pH indicator by condensation or by addition condensation can be used. For instance, suitable polymers and monomers include:

1. Polymers and monomers used having a methylol radical alkoxymethyl radical, halogenomethyl radical, etc. as a condensation bonding radical.
   a. condensates of formaldehyde with melamine, urea, phenol, dimethylaniline, p-toluenesulfamide or naphthalene sulfonic acid; co-condensates thereof, alkoxymethyl derivatives thereof, halogenomethyl derivatives thereof, and components for providing said condensates.
   b. compounds resulting from the reaction of formaldehyde with polyamide, glue, polyacrylamide or acrylamide copolymer, and components for providing said compounds.
   c. homopolymers of unsaturated methylol amides, such as N-methylolacrylamide; and copolymers thereof with other monomers.
2. Polymers and monomers used for the preparation of the pH indicative polymers having an epoxy radical or halohydrine radical as the condensation bonding radical.
   a. condensates of polyvalent amine, polyvalent phenol, or polyvalent amide with epihalohydrine, dihalohydrine or polyepoxy compound, and co-condensates, and components for providing said condensates.
   b. homopolymers of unsaturated epoxy compound or chlorohydrine compound such as glycidyl methacrylate, α-chloro-β-hydroxy-N-propylmethacrylate, and copolymer thereof, with other monomer or monomers.
   c. ethyleneoxide, ethylenechlorohydrine, propyleneoxide.
3. Polymers and monomers used for the preparation of the pH indicative polymer having a carboxyl radical acid chloride radical, acid anhydride radi-

cal, lower alcohol ester radical, or lower fatty ester radical, as the condensation bonding radical.

a. Reaction products of polyvalent alcohols, such as ethylene glycol, propylene glycol, neopentyl glycol, glycerine, sorbitane, polyethylene glycol, polypropylene glycol, diethanolamine, triethanolamine, methyl cellulose, hydroxyethyl cellulose with polyvalent carboxylic acids, such as maleic anhydride, fumaric acid, phthalic anhydride, 4-sulfophthalic acid, adipic acid, citric acid, tartaric acid, and components for providing said reaction products.

b. Reaction products of ethylene diamine, hexamethylene diamine, ethanolamine, mono(polyethyleneglycol)amine with said polyvalent carboxylic acid, and components for providing said reaction products.

Where one component of the starting material is a polymer and the pH indicator has a radical which is reactive with the polymer, or the reactive radical is substituted onto the pH indicator, the pH indicative polymer can be prepared by reacting the pH indicator with the polymer. The condensation reaction of the reactive pH indicator and the reactive polymer or component thereof is carried out by condensation, depending upon the type of reactive radicals and the chemical properties of said compounds.

When the polymer used for bonding is a curable resin, it is possible to obtain a water-soluble or organic solvent-soluble pH indicative polymer by stopping said condensation reaction at some initial stage. It is also possible to obtain an insoluble pH indicative polymer by completing the condensation reaction. This material can be used as particles.

Process (B) is conducted by admixing an α,β-ethylenic unsaturated monomer with a pH indicator having a diazonium radical, and then polymerizing the monomer, using the pH indicator as the polymerization initiator. The diazonium radical may be a diazonium chloride radical and a heavy metal complex salt, alkylsulfonate salt, alkyl sulfate salt, aryl sulfonate, alkylarylsulfonate and fluoroborate of diazonium chloride, or a diazoamino radical.

The diazonium compound is prepared by diazotization of an amino compound of the pH indicator. If necessary, a stabilizer for the diazonium radical may be added.

The α,β-ethylenic unsaturated monomer used can be any conventional free radical polymerizable unsaturated monomer, such as unsaturated carboxylic acid, e.g., acrylic acid, methacrylic acid; an alkylester, hydroxyalkyl ester, polyalkyleneglycol ester or dialkylaminoethyl ester thereof; an acid amide, N-alkoxymethyl acid amide or glycidyl ester thereof, acrylonitrile, vinylacetate, or styrene.

It is believed that the polymerization of the α,β-ethylenic unsaturated monomer is initiated by the decomposition of the diazonium radical of the pH indicator, caused by heat, light, change in pH or effect of a diazo decomposition agent, such as titanium trichloride, cuprous chloride, or copper powder. Free radicals are thus formed and polymerization of the α,β-ethylenic unsaturated monomer is effected. Simultaneously conjugate-bonding of the resulting polymer to the pH indicator will occur. The preparation of the pH indicative polymer (c) will be shown.

Process (C) is conducted by copolymerizing an α,β-ethylenic unsaturated pH indicator with an α,β-ethylenic monomer. α,β-ethylenic unsaturated radicals include acrylamide, methacrylamide, methacrylol oxy-β-hydroxy-N-propyl amino, methacrylol oxy-β-hydroxy-N-propyl ether, acrylamide methylene and vinyl, etc. The α,β-ethylenic unsaturated radicals can be introduced into the pH indicator at some intermediate stage or after the preparation of the pH indicator. Similarly, α,β-ethylenic unsaturated monomers to be used in process (C) include those mentioned above as to process (B).

The pH indicator is conjugate-bonded to the polymer by copolymerization in the presence of such conventional polymerization initiaitors as potassium persulfate, ammonium persulfate, azobisisobutyronitrile, or benzoyl peroxide.

In preparations (B) and (C), the pH indicative polymer can be prepared by a solution polymerization in an aqueous medium or in an organic solvent, emulsion polymerization, suspension polymerization in water or bulk polymerization. The pH indicative polymers obtained by said process can be water-soluble, alcohol soluble, organic solvent soluble or capable of being completely cured to insolubility, depending upon the particular properties of the polymer being bonded.

Where the resulting pH indicative polymer has a reactive radical, it can be substituted with an anionic, nonionic or cationic hydrophilic radical by reaction with chloroacetic acid, sodium bi-acid sulfite, sulfamic acid, sulfuric acid, ethylene oxide, lower amine, pyridinium salt of hydrochloride or ethylene imine. The reactive radical can also be substituted with a hydrophobic radical by reaction with a higher aliphatic or aromatic amine, alcohol, carbamide, methylol carbamide, acid chloride or isocyanate, etc. The resulting pH indicative polymers will change color depending upon pH degree of solubility, and the manner in which the polymer is bonded to the pH indicator.

For example, pH indicative polymers, containing phenolphtalein as the indicator portion and condensates of melamine-formaldehyde as the polymer, are colorless in an acidic medium but are reddish-violet in an alkaline medium. The pH range of the color change of the water soluble pH indicative polymer, is 7.9 – 9.5 and the pH range of the color change of the water insoluble pH indicative polymer is 6.5 – 12.0, although phenolphthalein itself is colorless in the acidic pH ranges, it is red in the alkaline pH ranges of 8.0 – 9.6 of pH.

Since the degree of sensitivity of the water insoluble pH indicative polymer particles to pH change will depend upon the size and physical characteristics of the polymer, such as water wettability, it is preferable to use fine particles.

The ratio of the pH indicative polymer to the detergent in the final composition should be sufficient to cause a change in color tone in the detergent solution. The actual ratio of pH indicative polymer to the detergent is not specifically limited; however, it is preferred that it be within the range of 50% to 0.1%, and preferably 10% to 1% for water insoluble pH indicative polymer powders, and preferably 5% to 0.1% for water soluble pH indicative polymers.

The ratio of pH indicator to polymer will depend upon the particular type of reaction, the particular combination of the starting materials, the molecular weight of the polymer, and the conditions of preparation. Good results are obtainable within the range of 50% to 0.1% and preferably 30% to 1%.

The pH indicative polymer can be admixed with a neutral "builder", surface active agent, wetting agent, or moisture proofing agent. It can also be admixed with the detergent in any convenient form, such as an aqueous solution, aqueous dispersion, paste, fine powder, beads and capsules, depending upon the form of detergent.

in order to form beads, the pH indicative polymer may be admixed with a small amount of water, or volatile organic solvent, and if necessary, a surface active agent or "builder". The mixture is then granulated with a stirrer. Where the detergent is a dired powder, an aqueous solution or organic solvent solution can be spray dried. A wetting paste can also be used for granulation.

Household detergents are mainly used for washing cloth, tableware and furniture. Typical examples of weak alkaline detergent compositions comprise 15 – 30% of a surface active agent, such as sodium alkylbenzene sulfonate, sodium α-olefin sulfonate, or sodium higher aliphatic alcohol sulfate, 1 – 2% of sodium benzene sulfonate, 10 – 30% of tripolyphosphate, as a "builder", 2 – 6% of sodium silicate, 20 – 50% of sodium sulfate, a small amount of carboxymethyl cellulose, and a fluorescent brightening agent. These components are spray dried from a slurry to form hollow granules or "prills".

During washing, about 50 g. of the detergent composition is dissolved into about 30 liters of water in a washing machine. The effective pH range for imparting optimum detergency is usually in the weak alkaline range, and is preferably within the range of about 9.5 – 10.0 pH. During the washing operation, the pH of the washing bath will gradually decrease because of contamination and decomposition, and simultaneously the detergency will be decreased.

By admixing a pH indicative polymer having a 10.0 – 9.5 pH alkaline coloring range, and a 9.0 – 8.5 pH of acidic coloring range with the detergent composition, the concentration of the detergent in the washing bath can be easily and economically controlled. Moreover, the presence of dirty materials and possible inactivation of the washing bath by decomposition of detergent, can be easily determined so that the need for addition of detergent and the need for changing of the wash bath can more effectively, and more economically, be determined.

Moreover, since the pH indicative polymer of this invention is a polymer, it can be dispersed in the form of fine particles or microfine particles so that staining of the article being washed is avoided.

In the metal industry, the metal may sometimes become corroded or injured if the pH of the wash bath is not controlled. Such corrosion may occur at pH's of higher than 10.0 for zinc, higher than 10.0 for aluminum, higher than 11.0 for tin and higher than 11.5 for bronze. The present invention makes possible a means for avoiding accidental corrosion during the washing of the metal.

In the fiber industry, it is necessary to prevent the injury of the fibers during refining, washing and bleaching, or depasting. For example, wool will be partially decomposed at a pH of higher than 9 and silk should be treated at a pH of lower than 10.5, preferably lower than 10.0. Rayon should be treated at a pH of lower than 10.0. The process and quality control can be easily and accurately accomplished by the use of a detergent composition containing the present pH indicative polymer, having a suitable color change pH range.

Depasting involves the use of an enzyme and a nonionic surface active agent. The suitable pH for depasting will depend upon temperature, time and type of enzyme, and is usually in a range of 6.3 – 6.5 pH, when the bath is prepared with 7 – 12 g/l of commercial amylase, 0.04% of nonionic surface active agent, and is used at 60°–70°C. It is possible to operate depasting most successfully by using a pH indicative polymer having an appropriate color changing pH range.

As stated above, the detergent composition can provide a simple and clear indication of color change for various applications, so that pH can be controlled so that washing can be accomplished under the most effective conditions of detergent uses and to prevent operation within a range which could injure laundry or other articles being washed.

Moreover, laundry or other articles being washed can be washed without danger of stains being caused by the pH indicator. The detergent can be effectively and economically used, the operation of washing can be simply and accurately controlled, and the quality of laundry or other washing can be effectively controlled.

Having now generally described the invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified. All parts and percents are shown by weight.

EXAMPLE 1

0.32 parts of powdered thymolphthalein-4-carbamide polyethylene glycol, a pH indicative polymer of about 4,000 molecular weight, was prepared by the above-mentioned process (A) and was found to be colorless in an acidic medium and bright blue in an alkaline medium. It was found to exhibit a color change at a pH of 8.9–9.5. This material was admixed with 100 parts of the following detergent compositions:

Sodium dodecylbenzene sulfonate	25 parts
Sodium tripolyphosphate	30 "
Sodium metasilicate	10 "
Anhydrous sodium sulfate	34 "
Carboxymethyl cellulose	1 "

About 50 g. of the resulting detergent composition was added to 30 liters of water in an electric washing machine and was stirred for about 10 seconds. A bright blue color was obtained in the washing bath at a pH of 9.8.

A stained and soiled cloth was placed into the bath and was washed. After several minutes, the blue color of the bath suddenly changed to a gray reddish-brown color, similar to a dirty bath. At this time, the pH of the bath water was 9.0. When 50 g. of the detergent composition was added to the bath, the color of the bath returned to its bluish color, and the pH of the bath was found to be 9.7. The cloth was then washed with water and dried. No staining of the cloth due to the pH indicative polymer was observed.

EXAMPLE 2

40 parts of a co-condensate of p-xylenol-4-carboxyphthaleinnaphthalene sulfonic acid-formaldehyde-Rhodamine B(15 : 74 : 11 : 0.1) (pH indicative polymer) was prepared by the above-mentioned process (A). The product was found to exhibit a reddish color

in an acid medium and a bluish color at a pH range of 8.8–9.5.

Polyethylene glycol (average M.W.about 8,000)	5 parts
Anhydrous sodium sulfate	55 parts

The pH indicative polymer, polyethylene glycol and anhydrous sodium sulfate were admixed in a high speed blender and the mixture was granulated in a granulator to form beads of a size smaller than 80% through a 20 mesh screen.

The following granule type detergent composition was separately prepared:

Sodium dodecylbenzene sulfonate	25 parts
Sodium tripolyphosphate	30 "
Sodium metasilicate	10 "
Anhydrous sodium sulfate	33.9 "
Carboxymethyl cellulose	1 "
Fluorescent brightener	0.1 "

100 Parts of this detergent was uniformly admixed with 0.6 part of said pH indicative polymer composition to yield a detergent composition having many spots of red particles.

In accordance with Example 1, about 50 g. of this detergent composition was placed into 30 liters of water in an electric washing machine, and was stirred for about 10 seconds to yield a bright blue colored washing cloth having a pH of 9.8. A stained and soiled cloth was placed into the bath and was washed.

After several minutes, the blue color of the bath suddenly changed to a reddish-gray-brown color. At this time, the pH of the bath was 9.0. When about 50 g. of this composition was added to the bath, the color of the bath again turned bluish, and the pH of the bath became 9.7. No stains were observed on the cloth being washed.

EXAMPLE 3

30 parts of a dibromothymolphthalein bonding copolymer of acrylic acidhydroxyethylmethacrylate (1 : 2 : 2) was prepared by process (B). It was found to be colorless in an acidic medium but turned bright blue in an alkaline medium when the pH was between 8.5–9.5.

Poly(sodium methylene naphthalene sulfonate) (degree of polymerization; about 4 to 5)	30 parts
Polyethylene glycol (average M.W. about 8,000)	5 parts
Anhydrous sodium sulfate	435 parts

The pH indicative polymer, poly(sodium methylene naphthalene sulfonate), polyethylene glycol and anhydrous sodium sulfate in the above amounts were uniformly mixed. 3 parts of the mixture were further uniformly admixed with 100 parts of the detergent composition shown in Example 1, to prepare the detergent composition of this invention. Similar results were observed in washing tests as in Example 1.

EXAMPLE 4

30 Parts of dibromothymol 4-copolymer of methacryl amidephthaleinacrylamidehydroxyethylmethacrylate (1 : 2 : 2)(pH indicative polymer) prepared by the above-mentioned process (C) was found to be colorless in an acidic medium and bright blue in an alkaline medium and showed a color range within the 8.5–9.5 pH range.

Poly(sodium methylene naphthalene sulfonate) (degree of polymerization; about 4 to 5)	30 parts
Polyethylene glycol (average M.W. about 8,000)	5 parts
Anhydrous sodium sulfate	35 parts

The pH indicator, poly(sodium methylene naphthalene sulfonate), polyethylene glycol and anhydrous sodium sulfate were uniformly mixed. 0.8 part of the mixture was further uniformly admixed with 100 parts of the detergent composition shown in Example 1, to prepare the detergent composition of this invention. As a result of washing tests, in accordance with Example 1, similar results were observed.

EXAMPLE 5

50 parts of a completely cured powder co-condensate of dibromopheno-3,4,5,6-tetrachlorophthalein-melamine-formaldehyde-Rhodamine B (8 : 47 : 45 : 0.12)(pH indicative polymer) prepared by the above-mentioned process (A) was found to be red in acidic medium and blue in an alkaline medium and exhibited a color change within the 10.5–9.5 pH range.

Poly(sodidum methylene naphthalene sulfonate) (degree of polymerization; about 4 to 5)	50 parts

The pH indicator and poly(sodium methylene naphtalene sulfonate) in said formula were uniformly mixed, and the mixture was granulated by a granulator, to yield beads having a size of more than 80% on a 20 mesh. 4 parts of the bead type pH indicative polymer composition were uniformly admixed with 100 parts of the detergent shown in Example 2, to yield a detergent composition having many spots of red particles. As a result of washing tests, in accordance with Example 2, similar results were observed.

EXAMPLE 6

40 Parts of a co-condensate of p-xylenol-4-carboxyphthaleinnaphthalene sulfonic acid-formaldehyde (15 : 74 : 11)(pH indicative polymer) prepared by the above-mentioned process (A) was found to be colorless in an acidic medium and blue in an alkaline medium and exhibited a color change in the 8.8–9.5 range.

	Parts
2-methoxy-4-anilinocarbonyl benzene-azo-3-hydroxy-2' naphtoenic anilide (-4''-)bonding to copolymer of acrylic acid-hydroxymethyl methacrylate (1 : 4 : 5)(polymer bonding red color material	0.5
Poly(sodium methylene naphthalene sulfonate) (degree of polymerization; about 4 to 5)	10
Polyethylene glycol (average M.W. about 8,000)	5
Anhydrous sodium sulfate	44.5

The above compounds were mixed in a high speed blender and the mixture was granulated by a granulator to yield beads having a size of more than 80% on a mesh. 0.8 part of the bead type pH indicative polymer composition was uniformly admixed with 100 parts of

the detergent shown in Example 2, to yield a detergent composition having many spots of red particles. As a result of washing tests, in accordance with Example 2, similar results were observed.

EXAMPLE 7

The following granule type detergent composition was prepared:

Polyoxyethylene nonylphenyl ether (moles of ethylene oxide; about 10)	20 parts
Sodium tripolyphosphate	30 parts
Sodium metasilicate	10 parts
Anhydrous sodium sulfate	38.9 parts
Carboxymethyl cellulose	1 part
Fluorescent brightner	0.1 part

100 Parts of this detergent was uniformly admixed with 0.32 part of the pH indicative polymer of Example 1, to prepare the detergent composition of this invention. Similar results were observed in washing tests as in Example 1.

EXAMPLE 8

When the following detergents are included or substituted, either wholly or in part for the detergent substances in the previous examples, substantially similar results are obtained: sodium tallow alkyl sulfate; the condensation product of one mole of coconut alcohol with 14 moles of ethylene oxide; dimethyldecylamine oxide; cetyldimethyl phosphine oxide; sodium 3-dodecylaminopropionate; and 3-(N,N-dimethyl-N-hexadecylammonio)propane-propan-1-sulfonate.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention.

What is claimed as new and intended to be covered by letters patent is:

1. A detergent composition consisting essentially of a synthetic organic detergent selected from the group consisting of anionic, nonionic, cationic and amphoteric surface active agents and mixtures thereof and 0.1–50% by weight of a pH indicative polymer, based on the weight of said detergent, wherein said pH indicative polymer consists of a pH indicator bonded to a polymer and which is soluble or dispersable in an aqueous solution of the detergent.

2. The detergent composition according to claim **1**, wherein the pH indicative polymer is dispersible in a colloidal form in an aqueous solution of the detergent.

3. The detergent composition according to claim **1**, wherein said detergent composition contains a detergent builder selected from the group consisting of sodium sulfate, sodium metasilicate, sodium sesquisilicate, sodium orthosilicate, sodium carbonate, sodium bicarbonate, sodium orthophosphate, sodium tripolyphosphate, sodium hexametaphosphate, sodium chloride, carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose, ethylenediamine tetraacetic acid.

4. The detergent composition according to claim **1**, wherein said pH indicative polymer is in the form of granules.

5. The detergent composition according to claim **1**, wherein said pH indicator is a phthalein indicator, a sulfonphthalein indicator, or an azo indicator.

6. A detergent composition according to claim **1**, wherein the pH indicative polymer has the polymer component bonded to the pH indicator component, and the polymer component is formed by a polymer or polymerizable monomer having a condensable or addition polymerizable radical.

7. The detergent composition according to claim **1**, wherein the pH indicator component is in a range of about 50 to 0.1 percent by weight to said pH indicative polymer.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,926,830

DATED : December 16, 1975

INVENTOR(S) : Shojiro Horiguchi, Michiei Nakamura, Keiji Nakajima, and Yoshio Seino

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

Change Assignee from "Dainichiswika Color & Chemical Mfg. Co." to --Dainichiseika Color & Chemicals Mfg. Co., Ltd.--

Signed and Sealed this

twentieth Day of April 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks