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3,737,385

WASHING, BLEACHING AND CLEANSING AGENTS CONTAINING POLY-(N-ALKYLDICARBOXYLIC ACID)-ALKYLENEIMINES

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Claims priority, application Germany, Feb. 21, 1969, P 19 08 728.6; Mar. 27, 1969, P 19 15 652.6

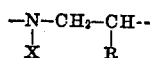
Int. Cl. C11d 7/54

U.S. Cl. 252-102

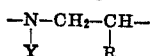
9 Claims

ABSTRACT OF THE DISCLOSURE

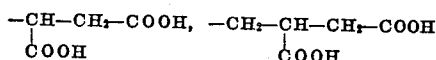
A washing, bleaching and cleansing agent having a content of from 50% to 99.9%, by weight, of customary components of washing, bleaching and cleansing agents and from 0.1% to 50%, by weight, of salts of poly-(N-alkyldicarboxylic acid)-alkyleneimines having an average molecular weight of from 500 to 500,000 in which at least one-third of the recurring substituted alkyleneimine groups have the following formula



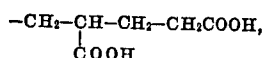
and the remainder of the recurring substituted alkyleneimine groups have the following formula



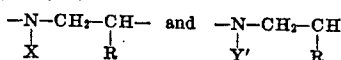
wherein, in both formulas, R represents a member selected from the group consisting of hydrogen and methyl, X represents



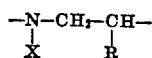
and/or



and Y represents a member selected from the group consisting of hydrogen,



and Y' represents a member selected from the group consisting of hydrogen and



REFERENCE TO A PRIOR APPLICATION

This application is a division of the copending commonly-assigned U.S. patent application S.N. 881,306, filed Dec. 1, 1969, now U.S. Pat. No. 3,686,128.

THE PRIOR ART

It has been common in the prior art to add to washing and cleansing agents, particularly those which contain bleaching compounds having active oxygen, complexing aminopolycarboxylic acids or their alkali salts, such as, nitrilotriacetic acid (NTA), ethylenediamine tetraacetic acid (EDTA), or diethylenetriamine pentaacetic acid (DTPA), in order to increase the stability of the bleaching agent, or to protect the optical brighteners contained in the detergents against an attack by the oxidizing agents. These compounds have, however, certain disadvantages. NTA can protect the optical brighteners only insufficiently from an oxidizing attack, while EDTA and

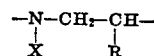
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DTPA are not completely stable against oxidizing agents and are oxidized to inactive compounds. The compounds named indeed increase the cleaning properties of washing agents. They are, however, in this respect inferior to the known inorganic builders, particularly to the polymeric phosphates.

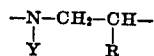
OBJECTS OF THE INVENTION

An object of the present invention is the obtaining of washing, bleaching and cleansing agents which have incorporated therein complexing aminodicarboxylic acids or their salts which increase the stability and cleaning properties of the washing agents and stabilize the optical brighteners present.

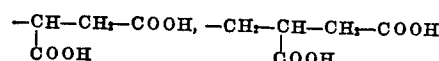
Another object of the invention is the obtaining of a washing, bleaching and cleansing agent having a content of from 50% to 99.9%, by weight, of customary components of washing, bleaching and cleansing agents and from 0.1% to 50%, by weight, of salts of poly-(N-alkyldicarboxylic acid)-alkyleneimines having an average molecular weight of from 500 to 500,000 in which at least one-third of the recurring substituted alkyleneimine groups have the following formula



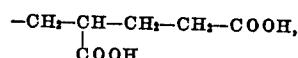
and the remainder of the recurring substituted alkyleneimine groups have the following formula



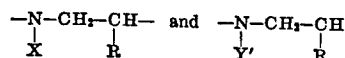
wherein, in both formulas, R represents a member selected from the group consisting of hydrogen and methyl, X represents



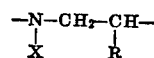
and/or



and Y represents a member selected from the group consisting of hydrogen,



and Y' represents a member selected from the group consisting of hydrogen and



These and other objects of the invention will become more apparent as the description thereof proceeds.

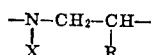
DESCRIPTION OF THE INVENTION

It has now been discovered that complexing aminopolycarboxylic acids or their salts of poly-(N-alkyldicarboxylic acid)-alkyleneimine having an average molecular weight of from 500 to 500,000, are complexing compounds for washing, bleaching and cleansing agents which, incorporated in said agents, are distinguished by a good stability against oxidizing substances, by an improved cleaning property, and by an effective stabilizing of the optical brighteners.

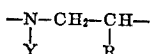
The invention therefore comprises a washing, bleaching and cleansing agent having a content of from 50% to 99.9%, by weight, of customary components of washing, bleaching and cleansing agents and from 0.1% to 50%, by weight, of salts of poly-(N-alkyldicarboxylic acid)-alkyleneimines having an average molecular weight of from 500 to 500,000 in which at least one third of the

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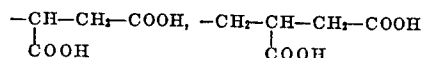
recurring substituted alkyleneimine groups have the following Formula I



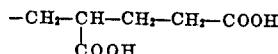
and the remainder of the recurring substituted alkyleneimine groups have the following Formula II



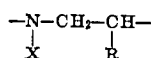
wherein, in both formulas, R represents a member selected from the group consisting of hydrogen and methyl, X represents



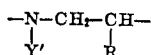
and/or



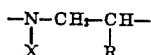
Y represents a member selected from the group consisting of hydrogen,



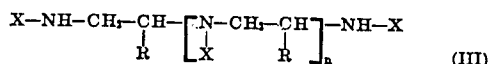
and



and Y' represents a member selected from the group consisting of hydrogen and

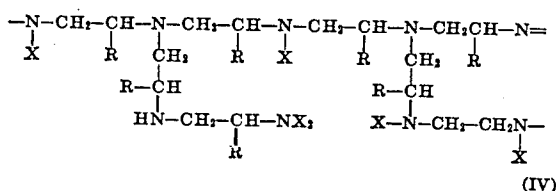


The amino groups present in the polyalkyleneimines can be completely or partially substituted by alkyldicarboxylic groups. Completely substituted polyalkyleneimines contain only the recurring groups according to Formula I and have a linear structure of the Formula III



wherein X and R are defined above and n is an integer from 2 to 130, preferably from 3 to 85, corresponding to a molecular weight of from 500 to 15,000, preferably from 500 to 10,000.

Such polymers in which only a part, for example, at least 33⅓% and less than 100% of the amino groups carry an alkyldicarboxylic group are mixed polymers which are built from the groups of the Formulas I and II. Usually they contain branched chains and are partially illustrated by the following Formula IV



where X and R are defined above. The branched and/or mixed polymers have average molecular weights of from 500 to 500,000.

Preferably such alkyldicarboxylic acid derivatives of polyethyleneimine or polypropyleneimine are used in which from 50% to 100% of the primary and secondary amino groups in the polyalkyleneimine molecule carry alkyldicarboxylic acid groups. Of particular practical interest are the N-alkyldicarboxylic acid derivatives of polyethyleneimines. The polymers derived from polyethyleneimine which are usable according to the invention in the Formula I are summarized in the following Table I.

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TABLE I

X	Name of the polymer
—CH—CH ₂ —COOH COOH	Poly-(N-succinic acid)-ethyleneimine.
—CH ₂ —CH—CH ₂ —COOH COOH	Poly-(N-methylenesuccinic acid)-ethyleneimine.
—CH ₂ —CH—CH ₂ —CH ₂ —COOH COOH COOH	Poly-(N-methylene-glutaric acid)-ethyleneimine.

The polymeric (N-alkyldicarboxylic acid)-ethyleneimines are amphoteric substances. They can, therefore, depending upon the alkalinity or acidity of the washing, bleaching, and cleansing agents, be present as salts of alkali metals and ammonium salts, especially salts of sodium and potassium, and as salts of organic ammonium bases, as inner salts, or as salts of strong acids, for example, mineral acids such as sulfuric acid and organic acids such as p-toluene sulfonic acid.

The preparation of the polymeric (N-alkyldicarboxylic acid)-alkyleneimines can be done according to various known methods. For the synthesis of linear polymers, first monomeric ethyleneimine or propyleneimine is alkylated on the nitrogen atom according to the principles of the Michael-Addition, with derivatives of olefinic-unsaturated dicarboxylic acids, such as, esters, amides and nitriles. Instead of olefinic-unsaturated dicarboxylic derivatives, also derivatives of halogenated dicarboxylic acids can be used for the alkylation on the nitrogen atom. Examples for suitable carboxylic acid derivatives and their reaction products with monomeric alkyleneimines are summarized in the following Table II.

TABLE II

Dicarboxylic acid derivatives suitable for reaction with alkyleneimine	Alkyleneimine derivatives
(a) Diester, diamide, or dinitrile of maleic, fumaric, or monobromosuccinic acid.	N-succinic acid derivative.
(b) Diester, diamide, or dinitrile of itaconic acid.	N-methylenesuccinic acid derivative.
(c) Diester, diamide, or dinitrile of α-methylene glutaric acid.	N-methyleneglutaric acid derivative.

Suitable starting materials are especially the lower alkyl esters, such as the methyl, ethyl, propyl, isopropyl and butyl esters of (N-alkyldicarboxylic acid)-aziridine. The polymerization takes place in the presence of Lewis type acids, for example, neutral sulfuric acid esters, preferably di-lower alkyl sulfates, such as dimethyl sulfate, diethyl sulfate, dipropyl sulfate, and dibutyl sulfate, or sulfonic acid esters, preferably lower alkylsulfonates and arylsulfonates, such as the methyl, ethyl, propyl and butyl esters of methanesulfonic acid, benzenesulfonic acid, and p-toluenesulfonic acid. The polymerization can also be conducted in the presence of solvents, especially of the lower halogenated hydrocarbons. The polymerization time is usually 2 to 60 hours. The reaction temperature is appropriately held between 30° and 90° C. by cooling. The ester, amide or nitrile derivatives of the polymeric (N-alkyl dicarboxylic acid)-alkyleneimines obtained are saponified in a known manner, for example, by heating with an alkali metal hydroxide solution such as aqueous sodium or potassium hydroxide. The alkali metal salts formed can be converted into the free acids by treating with ion-exchange resins. By subsequent neutralization with ammonia or organic ammonium bases, such as mono, di or triethanolamine, morpholine, or N-methylmorpholine, the free acids can be converted to the corresponding organic ammonium salts, or by neutralization with strong acids, the free acids can be converted to the corresponding acid salts.

The average molecular weights of the polymeric (N-alkyldicarboxylic acid)-alkyleneimines obtained in this way can vary within wide limits depending upon the type and amount of the polymerization catalyst used, the

polymerization temperature, and the reaction time. In general, the average molecular weight of such linear polymers is between 500 and 10,000. By separating out the low molecular components often present in the mixture, for example, by gel-chromatography on polymerized dextrans ("Sephadex"), polymers with varied average molecular weight can be obtained. Since the low molecular components do not disturb, they can remain in the product.

If the polymerization of the (N-alkyldicarboxylic acid)-alkyleneimine is conducted in the presence of unsubstituted monomeric ethyleneimine or propyleneimine, mixed polymers are formed which are built from groups of the Formulas I and II, and are more or less highly branched, as indicated in Formula IV. The ratio between substituted and unsubstituted monomeric ethyleneimine or propyleneimine is hereby selected in such a way that at least one third, preferably 50% to 100% of the alkyleneimine present in the polymerization mixture are substituted by alkyldicarboxylic acids, to obtain polymeric (N-alkyldicarboxylic acid)-alkyleneimines which are preferably from 50% to 100% substituted on the amino groups.

A further method of preparation of the salts of the polymeric (N-alkyldicarboxylic acid)-alkyleneimines starts from preformed polyalkyleneimines having an average molecular weight of from 300 to 150,000. The polyalkyleneimines are then reacted in alkaline aqueous medium with the derivatives or salts, preferably the alkali metal salts, of the unsaturated carboxylic acids, or halogenated carboxylic acids listed in the preceding Table II. Here the amount of dicarboxylic acid derivative should be selected in order that at least one third, preferably at least 50% of the primary and secondary amino groups in the preformed polyalkyleneimines are substituted. The compounds prepared from preformed polyalkyleneimines are usually more or less highly branched. Their average molecular weight depends upon the degree of polymerization of the preformed polyethyleneimines or polypropyleneimines, and can be from 500 to 500,000. In their performance, particularly in case of their use in washing, bleaching, and cleansing agents there is no essential difference between the linear and the branched polymeric (N-alkyldicarboxylic acid)-alkyleneimines.

The inner salts of the polymers can be obtained from the aqueous solutions by precipitation with mineral acids at the isoelectric point or by treating with ion-exchange resins. The inner salts are amorphous substances in solid form, which are insoluble in organic solvents and also predominately in water, but are readily soluble in acids and bases. From the free acids or inner salts, the corresponding ammonium salts can be prepared by neutralization with ammonia or organic ammonium bases, such as, mono-, di-, or triethanolamine, morpholine, or N-methylmorpholine. The washing, bleaching and cleansing agents according to the invention can also contain mixtures of different polymeric (N-alkyldicarboxylic acid)-alkyleneimines or their salts.

The preferably used poly-(N-alkyldicarboxylic acid)-ethyleneimines have the following average molecular weights:

Poly-(N-succinic acid)-ethyleneimine	500 to 300,000
Poly-(N-methylenesuccinic acid)-ethyleneimine	500 to 500,000
Poly-(N-methyleneglutaric acid)-ethyleneimine	500 to 500,000

The agents according to the invention contain at least one other cleaning or bleaching component, such as non-ionic, anionic and amphoteric surface-active materials, inorganic or organic builders, oxygen-containing bleaching agents, as well as other conventional washing and cleansing ingredients. The polymeric (N-alkyldicarboxylic acid)-alkyleneimines or their salts, particularly the

sodium salt, can be added to these ingredients in the form of their solutions or in solid form after previous drying.

Among the surface-active materials present as a component in the washing, bleaching and cleansing agents of the invention are, in the case where little foaming is essential, nonionic compounds, such as the polyalkyleneglycol-ether derivatives of alcohols, fatty acids and alkylphenols which contain 3 to 30 ethyleneglycolether groups and 8 to 20 carbon atoms in the hydrocarbon radical. Particularly suitable are polyethyleneglycolether derivatives in which the number of oxyethylene groups is from 5 to 15 and whose hydrocarbon radicals are derived from straight-chain primary alcohols with 12 to 18 carbon atoms, or from alkylphenols with a straight-chain alkyl chain of 6 to 14 carbon atoms. By the addition of 3 to 15 mols of propylene oxide to the last-named polyethyleneglycolethers, or by converting them into acetals, detergents are obtained which are distinguished by a specially low-foaming power.

Other suitable nonionic basic washing components with low-foaming properties are the water soluble polyethylene oxide adducts, adducted to polypropyleneglycol, ethylenediamine-polypropyleneglycol and alkylpolypropyleneglycol with 1 to 10 carbon atoms in the alkyl chain. Preferably, these adducts contain from 20 to 250 oxyethylene groups and 10 to 100 oxypropylene groups in the molecule. The named compounds contain usually 1 to 5 oxyethylene units per oxypropylene unit. Also nonionic compounds of the type of amino oxides and sulfoxides containing at least one hydrocarbon radical with 10 to 20 carbon atoms which, if necessary, can also be ethoxylated, are usable.

The washing and cleansing agents can also contain anionic basic washing components of the sulfonate or sulfate type. Primarily alkylbenzene sulfonates, such as dodecylbenzene sulfonate are suitable. However, olefin sulfonates, such as, are obtained by sulfonation of primary and secondary aliphatic monoolefins with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis, as well as alkylsulfonates obtainable from n-alkanes by sulfochlorination or sulfoxidation and subsequent hydrolysis, or neutralization, or by addition of bisulfite to olefins are also suitable. Also α -sulfo fatty acid esters, primary and secondary alkyl sulfates and the sulfates of ethoxylated or propoxylated higher alcohols are suitable. Other compounds of this class which can be occasionally present in the detergents are the higher molecular weight sulfated partial ethers and partial esters of polyhydric alcohols, such as, the alkali metal salts of the monoalkyl ethers, or mono-fatty acid esters of the glycerine monosulfuric acid esters, or, of 1,2 dihydroxypropane-sulfonic acid. Also sulfates of ethoxylated or propoxylated fatty acid amides and alkyl phenols as well as fatty acid taurides and fatty acid isethionates are suitable.

Other appropriate anionic basic washing components are alkali metal soaps of natural or synthetic fatty acids, such as, sodium soaps of coconut, palm kernel, or tallow fatty acids. As amphoteric basic washing components, alkylbetaines and, particularly, alkylsulfobetaines are suitable, for example, 3-(N,N-dimethyl-N-alkylammonium)-propane-1-sulfonate and 3-(N,N-dimethyl-N-alkylammonium)-2-hydroxypropane-1-sulfonate, preferably where alkyl is a lower alkyl such as methyl or ethyl.

The anionic basic washing components can be present in the form of the alkali metal salts such as the sodium and potassium salts as well as the ammonium salt, or as salts of organic bases, such as mono, di, and triethanolamine. Where the named surface-active nonionic, anionic and amphoteric compounds have a long-chain aliphatic hydrocarbon radical, the latter should preferably be straight-chained and should have from 8 to 22 carbon atoms. In the compounds with araliphatic hydrocarbon radicals the preferred straight alkyl chains contain an average of from 6 to 16 carbon atoms.

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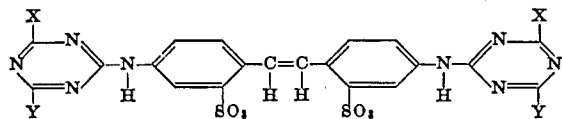
Appropriate mixture ingredients in addition to the above are also inorganic builders, particularly condensed phosphates, such as, pyrophosphates, triphosphates, tetraphosphates, trimetaphosphates, tetrametaphosphates as well as more highly condensed phosphates in the form of the neutral or acidic alkali metal salts such as the sodium and potassium salts as well as the ammonium salt. Preferably alkali metal triphosphates and their mixture with pyrophosphates are used. The condensed phosphates can also be partly or completely substituted by organic complexing agents containing phosphorus or nitrogen atoms. Such compounds are the alkali metal or ammonium salts of aminopolyphosphonic acids, particularly aminotri-(methylenephosphonic acid), ethylenediaminetetra-(methylenephosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, methylenediphosphonic acid, ethylenediphosphonic acid as well as the higher homologs of the named polyphosphonic acids, as well as the alkali metal or ammonium salts of low-molecular-weight aminopolycarboxylic acids, such as, NTA and EDTA. As other builders, alkali metal silicates are suitable, particularly sodium silicate in which the ratio $\text{Na}_2\text{O}:\text{SiO}_2$ is 1:3.5 to 1:1.

As further mixture ingredients are neutral salts, such as, sodium sulfate and sodium chloride, as well as compounds for adjustment of the pH, such as bicarbonates, carbonates, borates and hydroxides of sodium and potassium and acids, such as, lactic and citric acid. The amount of the alkaline reacting substances should be calculated so that the pH of a serviceable washing liquor for coarse laundry is 9 to 12 and for fine laundry 6 to 9.

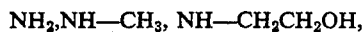
By appropriate combination of various surface-active basic washing components or builders with each other, in many cases increased effectiveness, such as a higher cleaning property or lower foaming power can be attained. Such improvements are possible, for example, by combination together of anionic with nonionic and/or amphoteric compounds, by combination of various nonionic compounds with each other or also by mixtures of basic washing components of the same type which differ in regard to the number of carbon atoms or the number and position of double bonds or branched chains in the hydrocarbon. Synergistically effective mixtures of inorganic and organic builders can also be used or combined with the precedingly named mixtures.

Depending upon the respective use, the washing agents of the invention can contain oxygen-releasing bleaching compounds, such as, hydrogen peroxide, alkali metal perborates, alkali metal percarbonates, alkali metal perphosphates, urea hydrogen peroxide and alkali metal persulfates or active-chlorine compounds, such as, alkali metal hydrochlorites, chlorinated trisodium phosphate and chlorinated cyanuric acid, or its alkali metal salts. The peroxide compounds can be present in a mixture with bleaching activators and stabilizers, such as, magnesium silicate.

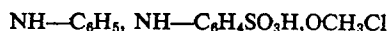
Optical brighteners suitable for cellulosic fibers used in the washing agents of the invention are those of the diaminostilbene disulfonic acid type of the formula:



in which X and Y have the following meanings:



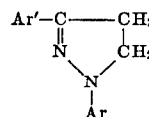
morpholino, dimethylmorpholino,



where X and Y can be the same or not. Particularly suitable are those compounds in which X is an anilino and Y a diethanolamino, or a morpholino group.

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As optical brighteners for polyamide fibers suitable for use in the washing agents of the invention are those of the diarylpyrazoline type of the following formula:



In this formula Ar and Ar' are aryl radicals, such as, phenyl, diphenyl, or naphthyl which can have further substituents, such as, hydroxy, alkoxy, hydroxyalkyl, amino, alkylamino, acylamino, carboxyl, sulfonic acid, and sulfonamide groups or halogen atoms. Preferred is a 1,3 diarylpyrazoline derivative in which the radical Ar is a p-sulfonamidophenyl group and the radical Ar' is a p-chlorophenyl group. In addition to the brighteners, whiteners suitable for the brightening of other fiber types can be present, for example, compounds of the type of naphthotriazolestilbene sulfonates, ethylene-bis-benzimidazoles, ethylene-bis-benzoxazoles, thiophene-bis-benzoxazoles, dialkylaminocoumarins, and the cyanoanthracenes. These brighteners or their mixtures can be present in the washing agents in amounts of from 0.01% to 1.5% by weight, preferably from 0.1% to 1% by weight.

Further suitable mixture ingredients for the washing agents of the invention are greying-inhibiting compounds, such as, sodium celluloseglycolate, as well as the water soluble sodium salts of synthetic polymers which contain free carboxylic groups. These latter include the polyesters or the polyamides of tri and tetracarboxylic acids and dihydric alcohols or diamines, and also polymeric acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, and aconitic acid as well as the mixed polymerizates of the named unsaturated carboxylic acids, or their mixed polymerizates with olefins.

Washing agents intended for the use in drum-washing machines contain appropriately known foam-suppressing substances such as saturated fatty acids with 20 to 24 carbon atoms, or their alkali metal soaps, or triazine derivatives which can be obtained by reacting one mol cyanuric chloride with 2 to 3 mols of aliphatic, straight-chained, branched-chained or cyclic primary monoamines or by propoxylating, or, butoxylating melamine.

For a further improvement of the dirt-loosening properties of the washing agents according to the invention they can also contain enzymes from the class of proteases, lipases, or amylases. These enzymes can be of animal or plant origin, for example, those obtained from digestive ferments or yeasts, such as pepsin, pancreatin, trypsin, papain, catalase and diastase. Preferably used are enzymatic active substances obtained from bacterial strains or molds, such as, *Bacillus subtilis* and *Streptomyces griseus* which are relatively stable against alkalis, peroxide compounds and anionic detergents and essentially not inactivated even at temperatures between 45° C. and 70° C.

The washing and cleansing agents can be present in liquid, pasty or solid form, as powder, granules or lumps. Liquid preparations may contain water-miscible solvents, particularly lower alkanols such as ethanol and isopropanol, as well as dissolving aids, such as, the alkali metal salts of benzene, toluene, xylene, or ethylbenzene sulfonic acids. For increasing of the foaming power and for the improvement of the skin compatibility alkylolamides, such as, fatty acid mono, or diethanolamides may, if necessary, be added. The mixture can also contain dyes or odorizing substances, bactericidally-active materials, activators as well as fillers, for example, urea.

The preparation of the agents according to the invention can be done in customary manner by mixing, granulating or spray-drying. Insofar as enzymes are used, it is recommended to mix them with the nonionic basic washing components and, if necessary, odorizing substances, or to disperse them in the melt of a salt con-

taining water of crystallization, such as Glaubers salt, and to combine these premixtures with the other powdery ingredients. By this procedure, the enzymes are cemented with the other power particles so that the mixtures do not tend to dust or separate.

The content of the washing, bleaching and cleansing agents or poly-(N-alkyldicarboxylic acid) - alkyleneimine or its alkali metal salts amounts from about 0.1% to 50% preferably 0.2% to 25% by weight, depending upon their use. The difference to 100% is taken up by the previously named detergent and bleaching active substances as well as, if necessary, the additional builders to improve the cleaning power. The qualitative and quantitative composition of these additional ingredients depend widely upon the special use of these agents. It corresponds in the case of the technically particular important washing and cleansing agents to the following recipe: (Data in percent by weight)

1% to 40% of at least one compound from the class of the anionic, nonionic, and amphoteric detergents.

0 to 80%, preferably

10% to 80% of at least one non-surface-active cleaning intensifying or complexing builder.

0 to 50%, preferably

10% to 50% of a per-compound, especially sodium perborate, with or without water of crystallization, as well as their mixtures with stabilizers and activators.

0 to 60%, preferably

0.1% to 20% of other auxiliary and supplementary substances.

The detergent substances can consist of up to 100%, preferably from 5% to 70%, of compounds of the sulfonate and/or the sulfate type, up to 100%, preferably from 5% to 40% of the nonionic polyglycolether type, and up to 100%, preferably from 10% to 50% of soaps. The builders can consist of up to 100%, preferably from 25% to 95%, of alkali metal triphosphates and their mixtures with alkali metal pyrophosphates, up to 100%, preferably from 5% to 50%, of an alkali salt of a complexing agent from the class of polyphosphonic acids, nitrilotriacetic acid, ethylenediaminetetraacetic acid, and up to 100%, preferably from 5% to 75% of at least one compound of the class of alkali metal silicates, alkali metal carbonates and alkali metal borates.

To the additional auxiliary and supplementary substances belong, in addition to the optical brighteners, especially the foam inhibitors which can be present in the agents according to the invention in an amount of up to 5%, preferably from 0.2% to 3%; also the enzymes which can be present in an amount up to 5%, preferably from 0.2% to 3%; and the greying-inhibitors which can be present in an amount up to 5%, preferably from 0.2% to 3%.

The poly-(N-alkyldicarboxylic acid) - alkyleneimines and their salts impart to the washing, cleansing and bleaching agents, according to the invention, a high washing and cleansing power, as well as improved dirt-carrying power. They are effective stabilizers for peroxide compounds and are less attacked by peroxide compounds than known complexing agents. They are, therefore, suitable for the stabilization of liquid bleaching detergents, such as those containing hydrogen peroxide and compounded liquid bleaching agents. The preparation of such agents has failed so far because of the low storage-stability of the peroxide compounds. The new compounds protect, in addition, the oxygen-sensitive ingredients of washing agents, particularly the optical brighteners and enzymes effectively against oxidative destruction. In contrast to many known oxidation inhibitors they do not diminish the bleaching power of the agents. The agents can be easily degraded biologically and have the advantage that they can replace completely or partially the polymeric phosphates which have previously necessarily

been present in washing agents, so that because of a lesser amount of phosphate ions in the sewage they do not promote the growth of algae in rivers and lakes.

The following examples are illustrative of the practice of the invention without being limitative. In the following, some recipes are given which have proven particularly good in practice.

EXAMPLES

(A) Powdery, low-foaming washing agent

3% to 16% of a sulfonate basic washing component from the class of alkylbenzene sulfonates, olefin sulfonates and n-alkane sulfonates (sodium salts)

0.5% to 5% of an alkylpolyglycolether (alkyl C_{12} to C_{18}) or alkylphenolpolyglycolether (alkyl C_8 to C_{14}) with 5 to 10 oxyethylene groups

0 to 5% of a C_{12} to C_{18} soap (sodium salt)

0.2% to 5% of foam inhibitors from the class of tri-alkylmelamines and saturated fatty acids with 20 to 24 carbon atoms, or their alkali metal soaps

10% to 50% of a condensed alkali metal phosphate from the class of the pyrophosphates or the tripolyphosphates

0.1% to 25% of poly-(N-alkyldicarboxylic acid)-alkyleneimine or its alkali metal salt

1% to 5% of sodium silicate

10% to 35% of sodium perborate tetrahydrate

0 to 5% of enzymes

0.05% to 1% of at least one optical brightener from the class of diaminostilbenedisulfonic acid or diarylpyrazoline derivatives

0.1% to 30% of an inorganic alkali metal salt from the class of the carbonates, bicarbonates, borates, sulfates and chlorides

0 to 4% of magnesium silicate

0.5% to 3% of sodium celluloseglycolate

(B) Powdery foaming fine washing agent

1% to 30% of a sulfonate basic washing component (sodium salt)

0.5% to 10% of alkylpolyglycolether sulfate (alkyl C_8 to C_{16} , 1 to 5 oxyethylene groups)

0 to 20% of an alkylpolyglycolether (alkyl C_{10} to C_{18}) or alkylphenolpolyglycolether (alkyl C_8 to C_{12}), with 5 to 12 oxyethylene groups

0.2% to 25% of poly-(N-alkyldicarboxylic acid)-alkyleneimine or its alkali metal salt

0 to 5% of a higher fatty acid ethanolamide or diethanolamide

0 to 20% of sodium tripolyphosphate

0 to 1% of a brightener from the class of the diarylpyrazoline derivatives and its mixtures with polyester brighteners

3% to 70% of sodium sulfate

(C) Liquid washing agent

0.5% to 10% of a sulfonate basic washing component (potassium salt)

0 to 10% of alkylpolyglycolether sulfate (alkyl C_8 to C_{16} , 1 to 5 oxyethylene groups)

0.2% to 25% of poly-(N-alkyldicarboxylic acid)-alkyleneimine or its alkali metal salts

0.1% to 5% of fatty amide-glycolether condensate, alkyl C_{10} to C_{18} , 1 to 10 oxyethylene groups)

1% to 10% of solution aids from the class of the alkali metal salts of benzene, toluene, or xylene sulfonic acids.

0 to 30% of neutral or acid potassium pyrophosphate.

0 to 10% of organic solvent media from the class of the C_2 to C_3 alcohols and ether alcohols

0 to 1% of optical brighteners from the class of the diaminostilbene disulfonic acids and diarylpyrazoline derivatives

0 to 5% of hydrogen peroxide

Residue: Water, perfumes, dyes, preservatives

(D) Steeping and pre-washing agent

- 0.5% to 5% of sulfonate basic washing component (sodium salt)
 0 to 3% of compounds from the class of alkylpolyglycol-ethers (alkyl C₁₂ to C₁₈) and alkylphenolpolyglycol-ethers (alkyl C₈ to C₁₂ with 5 to 12 oxyethylene groups)
 0.1% to 10% of poly-(N-alkyldicarboxylic acid)-alkyleneimine or its alkali metal salts
 10% to 50% of sodium carbonate
 1% to 5% of water glass
 0 to 5% of magnesium silicate
 0 to 5% of enzymes

(E) Dishwashing-machine washing agents

- 0.1% to 3% of compounds from the class of the alkylpolyglycolether (alkyl C₁₂ to C₁₈), alkylphenolpolyglycolether (alkyl C₈ to C₁₄) with 5 to 30 oxyethylene groups and 5 to 30 oxypropylene groups, and ethoxylated polypropyleneglycols.
 0.2% to 25% of poly-(N-alkyldicarboxylic acid)-alkyleneimine or its alkali metal salts
 45% to 95% of pentasodium triphosphate
 1% to 40% of sodium silicate (Na₂O:SiO₂=1:1 to 1:3)
 0 to 5% of potassium dichloroisocyanurate
 0 to 2% of foaming inhibitors

(F) Liquid rinsing and cleansing agent

- 5% to 30% of a sulfonated basic washing component (potassium salt)
 2% to 15% of alkylpolyglycolether sulfate (alkyl C₈ to C₁₆, 1 to 5 oxyethylene groups)
 0.2% to 10% of alkali metal salts of poly-(N-alkyldicarboxylic acid)-alkyleneimine
 0 to 20% of organic solvents from the class of C₂ to C₄ alcohols and ether alcohols
 1% to 10% of solution aids such as sodium toluene sulfonate, sodium xylene sulfonate and urea.

Residue: Water, perfumes, dyes, preservatives

(G) Bleaching agents

- 0.2% to 25% of poly-(N-alkyldicarboxylic acid)-alkyleneimine or its alkali metal salts
 10% to 95% of percompounds
 0 to 50% of alkaline reacting compounds from the class of alkali metal hydroxides, carbonate, silicates and phosphates
 0 to 50% of bleaching activators
 0 to 5% of an ionic and/or nonionic detergents
 0 to 10% of other ingredients, such as, corrosion inhibitors, optical brighteners, neutral salts, magnesium silicate

(H) Alkaline cleansers

- 0.1% to 25% of poly-(N-alkyldicarboxylic acid)-alkyleneimine or its alkali metal salts
 0.5% to 50% of sodium silicate (Na₂O:SiO₂=1:1 to 1:3)
 0.5% to 80% of sodium hydroxide
 0 to 40% of trisodium phosphate
 0 to 40% of condensed alkali metal phosphates
 0 to 40% of sodium carbonate
 0 to 10% of hydroxyethane diphosphonate (sodium salts)
 0 to 5% of anionic and/or nonionic detergents

(I) Scouring agent

- 1% to 10% of anionic and/or nonionic basic washing components
 0.1% to 5% of alkali metal salts of poly-(N-alkyldicarboxylic acid)-alkyleneimine
 80% to 95% of abrasive agents
 0 to 10% of cleansing salts of the class of alkali metal polyphosphates, alkali metal silicates, alkali metal borates, and alkali metal carbonates
 0 to 10% of alkali metal dichloroisocyanurate

EXAMPLES 1 to 8

The cleaning action of washing agents that contained one part by weight of an anionic basic washing component (Na-n-dodecylbenzene sulfonate) and two parts by weight of builder components were compared. With these washing agents, cotton cloth which had been soiled with a synthetic soil containing soot, iron oxide and cutaneous fat was washed in a laboratory washing machine where the washing liquor was heated from 20° C. to 90° C. within 15 minutes and kept at 90° C. for another 15 minutes. The washing agent concentration was 3 gm./l. The water hardness was 16° dH. The weight ratio of textile to liquor was 1:12. Subsequently, the washed cloth was rinsed with water four times, centrifuged and dried. The percent of whiteness was determined with a photometer (soiled cloth 0%, original cloth 100%) and is shown in the following Table III as well as the composition of the washing agents.

For the preparation of the polymeric (N-succinic acid)-ethyleneimine, first dibutyl maleate and aziridine in a mol ratio of 1:2 were heated in the presence of 1 mol percent of sodium methylate for 24 hours at 30° to 40° C. The N-(dibutyl succinate)-aziridine was then isolated by fractionate distillation (B.P. 122° C./0.4 mm. Hg) from the reaction mixture. After addition of 1 mol percent of diethyl sulfate, the monomer was polymerized in an inert atmosphere at a temperature not higher than 40° C. for a period of 5 to 10 hours depending on the average molecular weight desired. The polymer was dissolved in methanol and treated with an equivalent amount of a 20% aqueous sodium hydroxide solution. The solution was heated to 80° to 85° C., and the methanol was removed by distillation. After heating for 5 hours, with water being added several times, the saponification was completed. The sodium salt of the polymerizate was isolated by spray drying.

For the preparation of the polymers according to Examples 4 to 8, either dimethyl itaconate, or dimethyl α-methyleneglutarate was heated with ethyleneimine in a mol ratio of 1:1 in the presence of 1 mol percent of sodium methylate for 24 hours at 20° to 30° C. On stepwise addition of 1 mol percent of diethyl sulfate, the monomeric ethyleneimine derivative was polymerized in an inert atmosphere for 5 to 48 hours at a temperature not higher than 50° C. The polymer was dissolved in methanol and treated with the equivalent amount of a 20% aqueous sodium hydroxide solution. The solution was heated from 80° to 85° C., and the methanol removed by distillation. After 5 hours of heating of the methylenesuccinic acid derivative or, 15 hours of heating of the methyleneglutaric acid derivative with water being repeatedly added, the saponification was completed. The respective sodium salts were then isolated by spray drying.

The results of the washing tests of Table III show that the polymeric (N-alkyldicarboxylic acid)-ethyleneimines are superior to the other known builders, among them the pentasodium triphosphate which is known as being very effective, in the cleaning property.

TABLE III

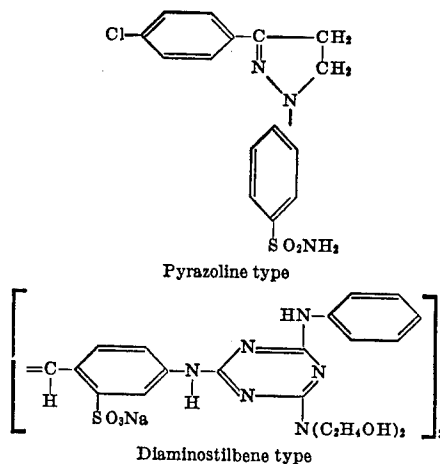
Example	Complexing agent (Na salt)	Average molecular weight	Percent brightening
1	Poly-(N-succinic acid)-ethyleneimine	1,230	78.4
2		1,720	78.5
3		5,000	79.0
4	Poly-(N-methylenesuccinic acid)-ethyleneimine	730	76.6
5		1,500	76.7
6		2,070	78.4
7	Poly-(N-methyleneglutaric acid)-ethyleneimine	1,220	78.9
8		3,050	79.6
	Pentasodium triphosphate		77.8
	Na ethylenediaminetetraacetate		75.4

EXAMPLES 9 TO 12

A washing agent of the following composition was used (data in percent by weight):

	Percent
Na n-dodecylbenzene sulfonate	8
Sodium soap of C ₁₂ to C ₂₂ fatty acids	5
Oleyl alcohol polyethyleneglycolether (10 oxyethyl-ene groups)	3
Pentasodium triphosphate	40
Sodium silicate (Na ₂ O·3.3SiO ₂)	5
Magnesium silicate	2
Sodium cellulose glycolate	1
Sodium perborate-tetrahydrate	25
Water	8
Brightener of the pyrazoline type	0.8
Brightener of the diaminostilbene type	0.2

The brighteners had the following structures:



To this agent were added each time 2% by weight of sodium salt of the poly-(N-alkyldicarboxylic acid)-ethyleneimine listed in the following Table IV. For comparative purposes, a washing agent was used which, instead of the polymers according to the invention, 2% of sodium nitrilotriacetate (NTA) or 2% of Na ethylenediamine tetraacetate (EDTA) was added.

With these agents, textiles of polyamide fiber ("Perlon" registered trademark) were washed in a laboratory washing machine where the washing liquor was heated from 20° C. to 60° C. within 15 minutes and was kept at this temperature for additional 15 minutes. The washing agent concentration was 5 gm./l. and the weight ratio of textiles to liquor was 1:30. The water used had a hardness of 16° dH as well as a copper ion content of 10⁻⁵ mols per liter. The degree of whiteness of the four times rinsed and then dried wash was determined by photometer. The results are summarized in Table IV. These results demonstrate the superiority of the use of the polymers of the present invention.

TABLE IV

Ex.	Poly-(N-alkyldicarboxylic acid)-ethyleneimine (2%)	Molecular weight	Degree of whiteness after—	
			1 washing	5 washings
9	Poly-(N-succinic acid)-ethyleneimine.	1,720	107	115
10	Poly-(N-methylenesuccinic acid)-ethyleneimine.	5,000	108	115
11	Poly-(N-methylenesuccinic acid)-ethyleneimine.	1,500	107	115
12	Poly-(N-methyleneglutaric acid)-ethyleneimine.	3,050	108	115
	NTA		100	104
	EDTA		103	110

EXAMPLES 13 AND 14

Cotton fabric soiled with tea as well as textile samples of unbleached cotton cloth are washed by using the washing agents listed in the Examples 9 to 12 with addition

of 2% by weight of polymeric (N-alkyldicarboxylic acid)-ethyleneimines for 30 minutes at a temperature of 90° C. The concentration of the washing agent was 5 gm./l. The weight ratio of textile to washing liquor was 1 to 10 and the hardness of the tap water was 16° dH. The reflection values of the three times rinsed and dried samples, determined photometrically, are summarized in the following Table V.

TABLE V

Ex.	Addition	Molecular weight	Percent reflection	
			Cotton fabric	Unbleached cotton cloth
13	Na-poly-(N-methylenesuccinic acid)-ethyleneimine.	1,500	85.9	77.1
14	Na-poly-(N-methyleneglutaric acid)-ethyleneimine.	3,050	86.0	77.3
20	Na ethylenediamine		85.7	75.8
	Na nitrilotriacetate		86.4	76.8

EXAMPLE 15

An aqueous solution containing 0.62 gm./l. of sodium perborate was prepared from a bleaching agent consisting of 154 gm. of sodium perborate and 124 gm. of the sodium salt of a poly-(N-succinic acid)-ethyleneimine having an average molecular weight of 5000. The pH of the solution was adjusted to 10 by addition of dilute sodium hydroxide. The decrease in the active-oxygen content of this solution at 90° and 100° was determined every 30 minutes by iodometric titration. For comparison the determination was repeated with equal amounts of known perborate stabilizers. The results are summarized in the following Table VI. They show the superiority of the polymeric agent according to the invention.

TABLE VI

Stabilizer	Percent active oxygen after—				
	30 min.	60 min.	90 min.	120 min.	150 min.
45 Poly-(N-succinic acid)-ethyleneimine (M.W.=5,000) at—					
90° C.	75	60	48	33	25
100° C.	70	48	26	13	8
Ethylenediaminetetraacetate at—					
90° C.	52	26	10	3	
100° C.	28	0			
50 Diethylenetriaminepentaacetate at—					
90° C.	40	15	5	2	
100° C.	10	0			
Without addition at—					
90° C.	35	18	8	4	
100° C.	30	18	6	3	

EXAMPLES 16 AND 17

An aqueous solution containing 0.62 gm./l. of sodium perborate was prepared from a bleaching agent consisting of 1 mol (154 gm.) of sodium perborate and 1 monomeric unit of poly-(N-methyleneglutaric acid)-ethyleneimine (187 gm.) or poly-(N-methylenesuccinic acid)-ethyleneimine (173 gm.). The pH of the solution was adjusted to 10 with dilute sodium hydroxide. Another bleaching solution, equally adjusted to a pH of 10 with sodium hydroxide, contained, per liter, 4 millimols (0.136 gm.) of hydrogen peroxide and 4 millimols (0.69 gm.) of poly-(N-methylenesuccinic acid)-ethyleneimine or (0.75 gm.) of poly-(N-methyleneglutaric acid)-ethyleneimine. The decrease of the active-oxygen content of these solutions was determined every 30 minutes by iodometric titration. For comparison the determination was repeated with equimolecular amounts of ethylenediaminetetraacetic acid. The results are summarized in the following Table VII.

TABLE VII

Stabilizer	Percent active oxygen after—				
	30 min.	60 min.	90 min.	120 min.	150 min.
Poly-(N-methylenesuccinic acid)-ethyleneimine (mol. weight 1,500):					
NaBO ₃	70	40	28	15	10
H ₂ O ₂	78	64	32	19	12
Poly-(N-methyleneglutaric acid)-ethyleneimine (mol. weight 3,050):					
NaBO ₃	54	30	20	10	5
H ₂ O ₂	58	33	24	12	6
Ethylene diaminetetraacetate:					
NaBO ₃	28	2	-----	-----	-----
H ₂ O ₂	25	3	-----	-----	-----

EXAMPLES 18 to 20

For the preparation of branched poly-(N-succinic acid)-ethyleneimines, aqueous solutions containing 20% by weight of polyethyleneimines having average molecular weights of 5000, 25,000 and 70,000 were separately heated to 80° to 90° C. each time with 80% of the stoichiometric amount required for complete N-alkylation, of maleic acid while the pH was adjusted to 10 to 11 by addition of sodium hydroxide. The reaction product was separated by hot spray-drying. Based on free acid content, the polymers had average molecular weights respectively of 16,000, 80,000 and 220,000.

The compounds were added to the washing agent composition used in Examples 9 to 12, in place of the linear polymeric aminocarboxylic acids described there, in amounts of 2% by weight, and, subsequently the textile samples of polyamide fabric were washed and examined in the same way. The degree of whiteness of the samples is given in the following Table VIII.

Example	Molecular weight of the polymer	Degree of whiteness after—	
		1 washing	5 washings
18.....	16,000	106	113
19.....	80,000	107	114
20.....	220,000	107	115
	NTA	100	104
	EDTA	103	110

EXAMPLES 21 TO 23

For the preparation of branched poly-(N-methylene-succinic acid)-ethyleneimines, aqueous solutions containing 20% by weight of polyethyleneimines having molecular weights of 5000, 25,000 and 70,000 were separately heated to 80° to 90° C. each time with 80% of the stoichiometric amount required for complete N-alkylation, of itaconic acid, while the pH was adjusted to 10 to 11 by addition of sodium hydroxide. The reaction product was separated by hot spray-drying. Based on free acid content, the polymers had average molecular weights respectively of 17,000, 85,000, and 240,000.

The compounds were added to the washing agent compositions used in Examples 9 to 12, in place of the linear polymeric aminocarboxylic acids described there, in amounts of 2% by weight, and, subsequently the textile samples of polyamide fabric were washed and examined in the same way. The degree of whiteness of the samples is given in the following Table IX.

TABLE IX

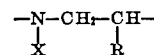
Example	Molecular weight of the polymer	Degree of whiteness after—	
		1 washing	5 washings
21.....	17,000	109	105
22.....	85,000	110	116
23.....	240,000	109	115
	NTA	100	104
	EDTA	103	110

The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients known to those skilled in the

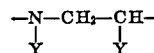
art may be employed without departing from the spirit of the invention or the scope of the appended claims.

I claim:

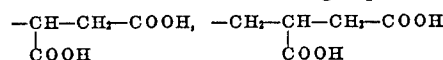
1. A washing, bleaching and cleansing agent having a content of from 50% to 99.9% by weight, of customary components of washing, bleaching and cleansing agents and from 0.1% to 50% by weight of a polyalkyleneimine selected from the group consisting of (1) poly-(N-alkyldicarboxylic acid)-alkyleneimines having an average molecular weight of from 500 to 500,000 in which at least 33⅓% to 100% of the recurring substituted alkyleneimine groups have the following formula



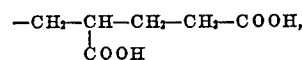
and the remainder of 0 to 66⅔% of the recurring substituted alkyleneimine groups have the following formula



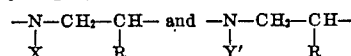
wherein, in both formulas, R represents a member selected from the group consisting of hydrogen and methyl, X represents a member selected from the group consisting of



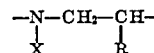
and



and Y represents a member selected from the group consisting of hydrogen,



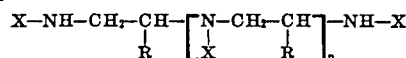
and Y' represents a member selected from the group consisting of hydrogen and



and (2) their alkali metal, ammonium and organic ammonium salts with bases selected from the group consisting of mono-, di- and triethanolamine, morpholine and N-methyl morpholine, said customary components or washing, bleaching and cleansing agents consisting essentially of from 0% to 40% by weight of at least one compound selected from the group consisting of anionic, non-ionic and amphoteric surface-active basic washing components, from 0% to 80% by weight of at least one builder selected from the group consisting of condensed inorganic phosphate builders, alkali metal silicates, carbonates, bicarbonates, borates, sulfates and chlorides, alkali metal and ammonium salts of aminophosphonic acids and low-molecular-weight aminopolycarboxylic acids, from 0% to 100% by weight of a bleaching compound selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide, alkali metal perborates, percarbonates, perphosphates, persulfates, hypochlorites, chlorinated trisodium phosphate and chlorinated cyanuric acid and its alkali metal salts, and mixtures thereof with magnesium silicates, and from 0% to 60% of other auxiliary and supplementary components of washing agents selected from the group consisting of optical brighteners, greying-inhibitors, foam-suppressors, enzymes, water-miscible solvents, water and dissolving acids, said ingredients totaling 100% by weight of said customary components.

2. The washing, bleaching and cleaning agent of claim 1 wherein said polyalkyleneimines are present in an amount of from 0.5% to 25% by weight.

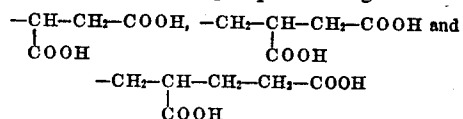
3. The washing, bleaching and cleansing agent of claim 1 wherein said polyalkyleneimines are linear poly-(N-alkyldicarboxylic acid)-alkyleneimines having the formula



wherein R represents a member selected from the group

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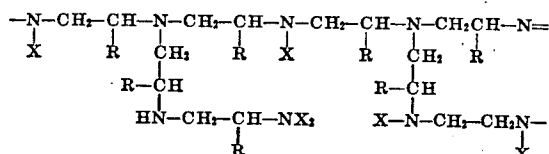
consisting of hydrogen and methyl and X represents a member selected from the group consisting of



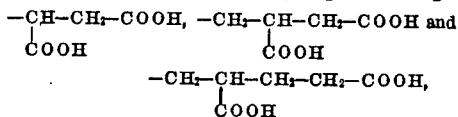
and n is an integer from 3 to 85.

4. The washing, bleaching and cleansing agent of claim 3 wherein k is hydrogen.

5. The washing, bleaching and cleansing agent of claim 1 wherein said polyalkyleneimines are branched poly-(N-alkyldicarboxylic acid)-alkyleneimines having the partial formula



wherein R represents a member selected from the group consisting of hydrogen and methyl and X represents a member selected from the group consisting of hydrogen,



and at least 50% to 100% of the primary and secondary

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amino groups in the polyalkyleneimine molecule are alkyl-dicarboxylated.

6. The washing, bleaching and cleansing agent of claim 5 wherein R is hydrogen.

7. The washing, bleaching and cleansing agent of claim 1 wherein said polyalkyleneimine is a salt of poly-(N-succinic acid)-ethyleneimine having an average molecular weight of from 500 to 300,000.

8. The washing, bleaching and cleansing agent of claim 1 wherein said polyalkyleneimine is a salt of poly-(N-methylenesuccinic acid)-ethyleneimine having an average molecular weight of from 500 to 500,000.

9. The washing, bleaching and cleansing agent of claim 1 wherein said polyalkyleneimine is a salt of poly-(N-methyleneglutaric acid)-ethyleneimine having an average molecular weight of from 500 to 500,000.

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25 MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

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