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 from 0.1% to 50%, by weight, of a polyethyleneimine selected from the group consisting of (1) branched poly-(N-acetic acid)-polyethyleneamines having an average molecular weight of from 2,000 to 200,000 wherein from about 50% to 100% of the primary and secondary amine groups in the polyethyleneimine molecule are carboxymethylated and (2) their alkali metal, ammonium and organic ammonium salts.

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 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 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.

In the German Auslegeschriften 1,060,849, as stabilizing agents for perborates or for washing and bleaching agents containing perborates are suggested, in addition to DTPA, also such complexing agents as are obtained by the reaction of ethylene chloride with ammonia and a subsequent carboxymethylation of the resulting polyamines. This reference teaches that the carboxymethylation products of the polyamine should contain up to 11 ethyleneimine groups which corresponds to a maximum molecular weight of 1220. Contrary to the assertion in the German Auslegeschrift 1,060,849, these complexing agents are also considerably oxidized by peroxide compounds and also their cleaning properties in the washing agents is lower than that of EDTA.

OBJECTS OF THE INVENTION

An object of the present invention is the obtaining of washing, bleaching and cleansing agents which have incorporated therein complexing aminopolycarboxylic 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 from 0.1% to 50%, by weight, of a polyethyleneimine selected from the group consisting of (1) branched poly-(N-acetic acid)-polyethyleneamines having an average molecular weight of from 2,000 to 200,000 wherein from about 50% to 100% of the primary and secondary amine groups in the polyethyleneimine molecule are carboxymethylated and (2) their alkali metal, ammonium and organic ammonium salts.

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 branched poly-(N-acetic acid)-ethyleneimine having an average molecular weight of from 2,000 to 200,000 wherein from about 50% to 100% of the primary and secondary amine groups in the polyethyleneimine molecule are carboxymethylated 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 a polyethyleneimine selected from the group consisting of (1) branched poly-(N-acetic acid)-polyethyleneamines having an average molecular weight of from 2,000 to 200,000 wherein from about 50% to 100% of the primary and secondary amine groups in the polyethyleneimine molecule are carboxymethylated and (2) their alkali metal, ammonium and organic ammonium salts.

The preparation of the branched polymeric-N-acetic acid-ethyleneamines is executed according to known procedures, for example, by reaction of polyethyleneamines of an average molecular weight of 1200 to 120,000 in an aqueous alkaline medium with alkali metal salts of chloroacetic or bromoacetic acid. By treatment with ion-exchange resins, the alkali metal salts obtained are converted to the free acids or, by subsequent neutralization with ammonia or organic amines, such as mono-, di-, and triethanolamine, morpholine and N-methylmorpholine, to the corresponding ammonium salts.

The molecular structure of the branched poly-(N-acetic acid)-ethyleneamines is partially illustrated as follows:

\[ \begin{align*}
\text{CH}_2 & \text{CH}_2 \text{N-CH}_2 \text{CH}_2 \text{N}\cdots \text{CH}_2 \text{CH}_2 \text{N} & \\
\text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{N} & \\
\text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{N} & & & \\
\text{H} & \text{N-CH}_2 & \text{CH}_2 & \text{N} & & & \\
\text{CH}_2 & \text{CH}_2 & \text{N} & & & & \\
\text{CH}_2 & \text{CH}_2 & \text{N} & & & & \\
\text{CH}_2 & \text{CH}_2 & \text{N} & & & &
\end{align*} \]

where A represents the \( \text{CH}_2 \text{COOH} \) radical. According to the degree of alkylation the polymers can also contain unsubstituted primary or secondary amine groups. In products with a high degree of alkylation also quaternary ammonium groups can be present. For the use according to the invention primarily such products are suitable in which the primary and secondary amine groups contained in the starting material are carboxymethylated to from about 50% to 100%, preferably from 60% to 98%.

The cleaning properties of the polymers increase with increasing molecular weight and, therefore, such polymers are preferably used which have an average mo-
The polymeric N-acetic-acid-ethyleneimines can be added to the washing, bleaching, and cleaning agents in forms of salts or the free acid, if in the latter case, the substrate contains sufficient amounts of alkaline reacting compounds so that on dissolving the agents in water a neutralization of the free acid groups takes place.

The agents according to the invention contain at least one water-soluble component, such as nonionic, anionic and amphoteric surface-active materials, inorganic or organic builders, oxygen-containing bleaching agents, as well as other conventional washing and cleansing ingredients.

Among the surface-active materials present as a component in the washing, bleaching and cleaning agents of the invention are, in the case where little foaming is essential, nonionic compounds, such as the polyalkylene-glycol ether derivatives of alcohols, fatty acids and alkylphenols which contain 3 to 30 alkyleneoxycarbonyl groups and 8 to 20 carbon atoms in the hydrocarbon radical. Particularly suitable are the polyalkyleneoxycarbonyl derivatives in which the number of oxycarbonyl 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 with 6 to 16 carbon atoms. By the addition of 3 to 15 mols of propylene oxide to the last-named polyalkylene-glycol ethers, or by converting them into acetals, detergents are obtained which are distinguished by a specially low foaming power.

Other suitable nonionic basic washing components are the water soluble polyethylene oxide adducts, adducted to polypropylene glycol, ethylenediamine-propylene glycol and alkylpolyethylene glycol with 1 to 10 carbon atoms in the alkyl chain. Preferably, these adducts contain from 20 to 250 oxycarbonyl groups and 10 to 100 oxypropylene groups in the molecule. The named compounds contain usually 1 to 5 oxypropylene units per oxypolypropylene unit. Also nonionic compounds of the type of aminooxides and sulfoxides 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 obtained from 3 to 15 mols of propylene oxide to the last-named polyalkylene glycol ethers, or by converting them into acetals, detergents are obtained which are distinguished by a specially low foaming power.

As anionic basic washing components, alkylamines and, particularly, alkyldialkylamines are suitable, for example, 3-(N,N-dimethyl-N-alkylammonium)-propene-1-sulfonate and 3-(N,N-dimethyl-N-alkylammonium)-2-propene-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 carbon atoms should 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.

Appropriate mixture ingredients in addition to the above are also inorganic builders, particularly condensed phosphates, such as, pyrophosphates, tripolyphosphates, 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 tripolyphosphates 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 aminophosphonic acids, particularly amino-tri-(methylene phosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, methylene diphosphonic acid, ethylene diphosphonic acid as well as the higher homologs of the named phosphonic acid, as well as the alkali metal or ammonium salts of low-molecular-weight aminopolycarboxylic acids, such as, as well as the sodium or potassium salt, or as salts of organic bases, such as mono, di, and triethanolamine.

Fibers used in the washing agents of the invention are those of the diaminostilbene disulfonic acid type of the formula:

\[
\text{SO} \quad \text{in which X and Y have the following meanings: } \text{NH, NH-CH}_3, \text{NH-CH-CHOH}
\]

As much as 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 of double bonds or the amount of sulfur in the hydrocarbon. Synergistically effective mixtures of inorganic and organic builders can also be used or combined with the preceding named mixtures.

Depending upon their respective use, the washing agents of the invention can contain oxygen-releasing bleaching compounds, such as, hydrogen peroxide, alkali metal perborates, alkaline metal percarbonates, alkaline metal perphosphates, urea hydrogen peroxide and alkali metal persulfates or active-chlorine compounds, such as, alkali metal hypochlorites, 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 diamino-diphenyl disulfonic acid type of the formula:

\[
\text{X} \quad \text{in which X and Y have the following meanings: } \text{NH}_2, \text{NH-CH}_3, \text{NH-CH}_2-\text{CH}_2\text{OH}
\]
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:

\[
\text{Ar}-\text{C}-\text{CH}_2\text{OH}, \text{ N(CH-CH}_2\text{O)}_2, \text{ morpholino, dimethylmorpholino, N-CH}\text{5}, \text{ NH-CHSO}_3\text{H, OCH, Cl where X and Y can be thymol or not. Particularly suitable are those compounds in which X is an anilino and Y is a diethylamino, or a morpholino group.}
\]

In this formula \( \text{Ar} \) and \( \text{Ar}’ \) are aryl radicals, such as, phenyl, diphenyl, or naphthyl which can have further substituents, such as, hydroxy, alkoxy, hydroxalkyl, amino, alkylamino, acylamino, carboxyl, sulfonic acid, and sulfonamide groups, or halogen atoms. Preferred is a 1,3-diarylpypyrazoline derivative in which the radical \( \text{Ar} \) is a p-sulfonamidophenyl group and the radical \( \text{Ar}’ \) 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 naphthalenesulfonic acids, ethylbenzene sulfonates, ethylene-bis-hexamethylene azo, ethylene-bis-benzenoxazoles, thiophene-bis-benzenoxazoles, diallylaminocoumarin, 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 cellulosexyglucoside, 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 polymericizers of the named unsaturated carboxylic acids, or their mixed polymerizates with olefins and vinyloxethers.

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-chain, branched-chain or cyclic primary monomines or by propoxylating, or butoxyxating 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, papin, catalase and diastase. Preferably used are enzymatic active substances obtained from bacterial strains or molds, such as, Bacillus subtilis and Strepto-

\[
\text{tonyces griseus which are relatively stable against alkalis, peroxide compounds and anionic detergents and essentially not inactivated even at temperatures between 45^\circ C. and 70^\circ C.}
\]

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 benzoic, toltenic, xylene, or ethylbenzene sulfonic acids. For increasing of the foaming power and for the improvement of the skin compatibility alkylamides, such as, fatty acid mono-, or diethanolamides may, if necessary, be added. The mixture can also contain dyes or odorizing substances, bactericidal-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 containing 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 powder particles so that the mixtures do not tend to dust or separate.

The content of the washing, bleaching and cleansing agents of poly-(N-acetic acid)-ethyleneimine 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 polyglycolyloleter type, and up to 100%, preferably from 10% to 50% of nasses. The builders can consist of up to 100%, preferably from 25% to 95%, of alkali metal trisophosphates 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, nitrolitricioic acid, ethylenediaminetetraacetic acid, and up to 100%, preferably from 5% to 75% of at least one compound of the class of alkali metal carboxylates, 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 following examples are illustrative of the practice of the invention without being limiting. In the following some recipes are given which have proven particularly good in practice.

**EXAMPLES**

(A) Powdery, low-foaming washing agent

3% to 15% of a sulfona bel basic washing component from the class of alkybenzene sulfonates, olefin sulfonates and a-alkane sulfonates (sodium salts)

0.5% to 5% of an alkyl polyglycol ether (alkyl C12 to C18) or alkylphenolpolyglycol ether (alkyl C6 to C14) with 5 to 10 oxyethylene groups

0 to 5% of a C12 to C18 soap (sodium salt)
0.2% to 5% of foam inhibitors from the class of trialkylmelamines 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-acetic acid)-ethyleneimine or its alkali metal salt
1% to 5% of sodium silicate
10% to 25% of sodium perborate tetrahydrate
0 to 5% of enzymes
0.05% to 1% of at least one optical brightener from the class of dianinostibenedisulfonic acid or diarylpyrazoline derivatives
0.1% to 3% 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 cellulose glycolate

(B) Powdery foaming fine washing agent
1% to 30% of a sulfonate basic washing component (sodium salt)
0.5% to 10% of alkylpolyglycol ether sulfate (alkyl C6 to C14, 1 to 5 oxyethylene groups)
0 to 20% of an alkylpolyglycol ether sulfate (alkyl C12 to C18) or alkylenepolyglycol ether (alkyl C8 to C12), with 5 to 12 oxyethylene groups
0.2% to 25% of poly-(N-acetic acid)-ethyleneimine or its alkali metal salt
0 to 5% of a fatty acid ethoxylamine 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 alkylpolyglycol ether sulfate (alkyl C4 to C16, 1 to 5 oxyethylene groups)
0.2% to 25% of poly-(N-acetic acid)-ethyleneimine or its alkali metal salt
0.1% to 5% of fatty amide-glycol ether condensate (alkyl C10 to C14, 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 C4 to C6 alcohols and other alcohols.
0 to 1% of optical brighteners from the class of the dianinostibenedisulfonic acid or diarylpyrazoline derivatives.
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 alkylenepolyglycol ethers (alkyl C6 to C12) with 5 to 12 oxyethylene groups
0.1% to 10% of poly-(N-acetic acid)-ethyleneimine 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 alkylpolyglycol ether (alkyl C12 to C18), alkylenepolyglycol ether (alkyl C6 to C12) with 5 to 30 oxyethylene groups, and 5 to 30 oxypropylene groups, and ethoxylated polypropylene glycols.
0.2% to 5% of poly-(N-acetic acid)-ethyleneimine or its alkali metal salts
45% to 95% of pentasodium tripolyphosphate
10% 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 sulfonate basic washing component (potassium salt)
2% to 15% of alkylypolyglycol ether sulfate (alkyl C4 to C18, 1 to 5 oxyethylene groups)
0.2% to 10% of alkali metal salts of poly-(N-acetic acid)-ethyleneimine
0 to 20% of organic solvents from the class of C2 to C3 alcohols and ether alcohols
1% to 10% of solution aids such as sodium tolulene sulfonate, sodium xylene sulfonate and urea.
Residue: Water, perfumes, dyes, preservatives

(G) Bleaching agents
0.2% to 25% of poly-(N-acetic acid)-ethyleneimine or its alkali metal salts
10% to 95% of peroxides
0 to 50% of alkaline reacting compounds from the class of alkali metal hydroxides, carbonates, silicates and phosphates.
0 to 50% of bleaching activators
0 to 5% of anionic 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-acetic acid)-ethyleneimine or its alkali metal salts
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-acetic acid)-ethyleneimine
80% to 95% of abrasive agents
0 to 10% of cleansing salts of the class of alkali metal phosphates, alkali metal silicates, alkali metal borates, and alkali metal carbonates
0 to 10% of alkali metal dichloroisocyanurate

EXAMPIES 1 TO 3

The cleaning action of washing agents that contained one part by weight of an anionic basic washing component (Na2-2-dodecylbenzenesulfonate) and two parts by weight of builders components were compared. With these washing agents gray 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 gml/L. The water hardness was 16°dH. The weight ration 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 as well as the composition of the washing agents. For the preparation of the branched poly-(N-acetic acid)-ethyleneimine, branched polyamines of average molecular weights of 2,500, 5,000 and 10,000 were heated to 80°C to 90°C, in a 20% aqueous solution each time with 80% of
the stoichiometric amount, required for a complete carbomethylation, of sodium chloroacetate. The pH of the solution was kept constant at a value between 10 to 11 by the addition of 5 N NaOH. On treating with anionic and cationic exchange resins, the reaction products were desalted or converted to the free acid and subsequently neutralized with sodium hydroxide.

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

### TABLE I

<table>
<thead>
<tr>
<th>Example</th>
<th>Builders</th>
<th>Average molecular weight</th>
<th>Percent Brightening</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sodium salts of branched poly-(N-acetic acid)-ethylenetrimines.</td>
<td>4,000</td>
<td>70.0</td>
</tr>
<tr>
<td>2</td>
<td>Sodium salts of branched poly-(N-acetic acid)-ethylenetetramines.</td>
<td>10,000</td>
<td>75.0</td>
</tr>
<tr>
<td>3</td>
<td>Sodium salts of branched poly-(N-acetic acid)-ethylenetetramines.</td>
<td>140,000</td>
<td>70.0</td>
</tr>
<tr>
<td>4</td>
<td>Pentasodium tripolyphosphate.</td>
<td>200</td>
<td>73.7</td>
</tr>
<tr>
<td>5</td>
<td>Sodium salt of a carbomethoxylated polyamine according to DAS 1,060,849.</td>
<td>900</td>
<td>67.2</td>
</tr>
</tbody>
</table>

### EXAMPLES 4 TO 6

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

- 8% Na n-dodecylbenzene sulfonate
- 5% sodium soap of C₁₈₂₀ to C₂₂ fatty acids
- 3% oleyl alcohol polyethylene glycol ether (10 oxyethylene groups)
- 40% pentasodium tripolyphosphate
- 5% sodium silicate (Na₂O·3.3 SiO₂)
- 2% magnesium silicate
- 1% sodium cellulose glycylate
- 25% sodium perborate-tetrahydrate
- 8% water
- 0.8% brightener of the pyrazoline type
- 0.2% brightener of the dianiminothiobene type

The brighteners had the following structures:

![Pyrazoline type](image)

![Dianiminothiobene type](image)

To this agent were added each time 2% by weight of the sodium salt of a branched poly-(N-acetic acid)-ethyleneimine which had in Example 4 an average molecular weight of 5,000, in Example 5 of 10,000, and in Example 6 of 140,000. For comparative purposes, a washing agent was used which, instead of the polymers according to the invention, 2% of sodium nitrotriureate (NTA) or 2% of Na-ethylenediaminetetraacetate (EDTA) was added.

With these agents, textiles of polyamide fiber (Perlon, 75 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 10⁻⁶ 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 the following Table II. This shows the superiority of the compounds used according to the invention.

### TABLE II

<table>
<thead>
<tr>
<th>Example</th>
<th>Degree of whiteness after—</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>5 washing 1 washing 5 washings</td>
</tr>
<tr>
<td>4</td>
<td>Na-poly-(N-acetic acid)-ethyleneimine</td>
</tr>
<tr>
<td>5</td>
<td>Na-poly-(N-acetic acid)-ethyleneimine</td>
</tr>
<tr>
<td>6</td>
<td>Na-poly-(N-acetic acid)-ethyleneimine</td>
</tr>
<tr>
<td>6</td>
<td>Na-nitrotriureate</td>
</tr>
<tr>
<td>6</td>
<td>Na-ethylenediamine tetraacetate</td>
</tr>
</tbody>
</table>

### EXAMPLES 7 AND 8

An aqueous solution containing 0.62 gm./L sodium perborate was prepared from a bleaching agent consisting of 154 gm. of sodium perborate and of 124 gm. of the sodium salt of poly-(N-acetic acid)-ethyleneimine of

Example 7, a molecular weight 4,200 Example 8, a molecular weight 15,000

prepared by reacting a branched polyethyleneimine with chloroacetic acid (1 mol of chloroacetic acid per ethyleneimine unit). The pH of the solution was adjusted to 10 by addition of dilute sodium hydroxide. The decrease of the active-oxygen content of this solution at 90° C. 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 III. This shows the superiority of the agents according to the invention.

### TABLE III

<table>
<thead>
<tr>
<th>Example</th>
<th>Stabilizer</th>
<th>Percent active oxygen after (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Poly-(N-acetic acid)-ethyleneimine</td>
<td>4,200</td>
</tr>
<tr>
<td>8</td>
<td>Poly-(N-acetic acid)-ethyleneimine</td>
<td>15,000</td>
</tr>
<tr>
<td>55</td>
<td>EDTA (sodium salt)</td>
<td>45</td>
</tr>
<tr>
<td>55</td>
<td>DVPFA (sodium salt)</td>
<td>45</td>
</tr>
<tr>
<td>55</td>
<td>Carboxymethylated polyamine according to DAS 1,060,849 (sodium salt)</td>
<td>45</td>
</tr>
<tr>
<td>55</td>
<td>Without addition</td>
<td>35</td>
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</table>

In the following Table IV are summarized some recipes of washing, bleaching and cleansing agents according to the invention for the following fields of application:

Example 9—foam-suppressing heavy washing agent
Example 10—cold-washing agent
Example 11—liquid washing agent
Example 12—wool-washing agent
Example 13—steeping agent
Example 14—bleaching agent
Example 15—liquid dish-rinsing agent
Example 16—cleanser for heavy soiling
Example 17—scouring agent

The ingredients a to d and f to i were present as the sodium salts, the pyrophosphate (ingredient k) was used...
in Example 9 as the potassium salt, and in all other examples as sodium salt. As enzyme (ingredient q), a preparation "Maxafase" (registered trademark), made from Bacillus subtilis, with an activity of 100,000 LVA/gm. was utilized. The foam suppressor (ingredient v) is a reaction product of 1 mol cyanuric chloride with 2.7 mols of a primary n-alkylamine with a C_6 to C_18 chain length.

Table IV

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
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<td>(a) n-dodecylbenzenesulfonate</td>
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<td>(b) C_6-C_18-olefin sulfonate</td>
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<td>(c) glycol alcohol ether sulfates (2 EO)</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>(d) Glycol alcohol polyglycol ether (10 EO)</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>(e) Glycolipid</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>(f) Glycolipid</td>
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<td>(h) Poly(N-acetic acid)-ethylenimine</td>
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<td>0</td>
<td>0</td>
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<td>(i) Triphosphate</td>
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<td>0</td>
<td>0</td>
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<td>(j) Triphosphate</td>
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<tr>
<td>(k) Sodium carbonate</td>
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<tr>
<td>(l) Sodium silicate</td>
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<td>(m) Sodium silicate</td>
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<tr>
<td>(p) Sodium carbonate</td>
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<tr>
<td>(q) Sodium carbonate</td>
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<td>(r) Enzyme</td>
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<td>(s) Enzyme</td>
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<td>(t) Sodium silicate</td>
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<td>(u) Sodium silicate</td>
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<td>(v) Sodium carbonate</td>
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<td>(w) Sodium carbonate</td>
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<td>(x) Water</td>
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<td>(y) Water</td>
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<td>(z) Coloring and odorizing agents</td>
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<td>(A) Quartz powder</td>
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</tr>
</tbody>
</table>

Note: EO = oxyethylene units.

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.

We 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 polyethyleneimine selected from the group consisting of (1) branched poly(N-acetic acid)-polyethyleneimines having an average molecular weight of from 2,000 to 200,000 wherein from about 50% to 100% of the primary and secondary amine groups in the polyethyleneimine molecule are carboxylated 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 of washing, bleaching and cleansing agents consisting essentially of from 1% to 40% by weight of at least one compound selected from the group consisting of anionic, non-ionic and amphoteric surface-acting 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 aminopolyphosphonic acids and low-molecular-weight aminopolyphosphonic acids, from 0% to 50% 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 aids, said ingredients totalling 100% by weight of said customary components.

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

3. The washing, bleaching and cleansing agent of claim 1 wherein said branched poly(N-acetic acid)-polyethyleneimines has an average molecular weight of from 4000 to 150,000 and from 60% to 98% of the primary and secondary amine groups in the polyethyleneimine molecule are carboxymethylated.

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3,424,790 1/1969 Bond et al. 260—534 E

FOREIGN PATENTS

231,499 10/1960 Astralia 252—102

MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252—186; 260—534 E