Copolymers of polyamino acids formed by reaction of polysuccinimide with alkyl, alkenyl, aromatic amines or alkyl and alkenyl polyamines are useful as inhibitors of mineral scale deposition. Such compounds may be used in high volume water applications such as boiler, cooling, oil well, agricultural sprays and irrigation water. They are also useful in preventing scale formation on fabrics when formulated with laundry detergents and in preventing scale formation on glassware when formulated in dishwashing detergents.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
<td>BR</td>
<td>Brazil</td>
<td>BY</td>
<td>Belarus</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>CA</td>
<td>Canada</td>
<td>CB</td>
<td>Central African Republic</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>CG</td>
<td>Congo</td>
<td>CH</td>
<td>Switzerland</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>CM</td>
<td>Cameroon</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>CN</td>
<td>China</td>
<td>CS</td>
<td>Czechoslovakia</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>CO</td>
<td>Colombia</td>
<td>CZ</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>DE</td>
<td>Germany</td>
<td>DK</td>
<td>Denmark</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>ES</td>
<td>Spain</td>
<td>FI</td>
<td>Finland</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>FR</td>
<td>France</td>
<td>GA</td>
<td>Gabon</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>KP</td>
<td>Democratic People's Republic</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KR</td>
<td>Republic of Korea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KZ</td>
<td>Kazakhstan</td>
<td>LI</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>LV</td>
<td>Latvia</td>
<td>MC</td>
<td>Monaco</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>MD</td>
<td>Republic of Moldova</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>MG</td>
<td>Madagascar</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>MV</td>
<td>Montenegro</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>MY</td>
<td>Malaysia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MN</td>
<td>Mongolia</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MW</td>
<td>Malawi</td>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>NL</td>
<td>Netherlands</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>NZ</td>
<td>New Zealand</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>PT</td>
<td>Portugal</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
<td>RU</td>
<td>Russian Federation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>SD</td>
<td>Sudan</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>SI</td>
<td>Slovenia</td>
<td>SK</td>
<td>Slovakia</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>SN</td>
<td>Senegal</td>
<td>TD</td>
<td>Chad</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>TJ</td>
<td>Tajikistan</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UA</td>
<td>Ukraine</td>
<td>US</td>
<td>United States of America</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UZ</td>
<td>Uzbekistan</td>
<td>VN</td>
<td>Viet Nam</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.
COPOLYMERS OF POLYAMINO ACIDS AS SCALE INHIBITION AGENTS

FIELD OF THE INVENTION

This invention relates to the use of copolymers of polyamino acids and their salts as scale inhibition agents.

DESCRIPTION OF RELATED ART

U.S. Pat. 3,846,380 discloses the preparation and composition of copolymers of polyamino acids with primary or secondary aliphatic amines, followed by alkaline hydrolysis to provide surface active agents. Emphasis is placed on long chain alkylamines having eight to twenty carbon atoms. The products formed are said to have good solubilizing ability, emulsifying and dispersing properties, as well as good foaming properties. They are useful as foaming agents, solubilizing agents, dispersing agents, emulsifying agents, rust-proofing agents, fiber-treating agents, level dyeing agents and retarding agents.

U.S. Pat. Application 07/926,242, filed August 7, 1992, by Louis L. Wood, incorporated herein by reference, discloses methods of preparation of copolymers of amino acids wherein polyamines are reacted to form a polymer network. These materials are excellent inhibitors of metal scale deposition.

Summary of the Invention

We have discovered that polypeptide materials that have a general formula of

\[
\frac{R'}{\text{CH}-\text{CO}-\text{NH}-} \quad \text{and} \quad \frac{R'}{\text{CH}-\text{CO}-\text{NH}-}
\]

\[
\frac{\text{CH}_2\text{-CO}-\text{NH}-}{R''} \quad \frac{\text{CH}_2\text{-CO}-\text{N}}{R''}
\]

wherein \(R'\) is a hydrogen or an alkyl or alkenyl group having 1 to 20 carbons and \(R''\) is an alkyl or alkenyl group having 2 to 20 carbons, together with at least one of the groups

\[
\frac{\text{CH}-\text{COOZ}}{\text{CH}_2\text{-CO}-\text{NH}-} \quad \text{and} \quad \frac{\text{CH}_2\text{-COOZ}}{\text{CH}_2\text{-CO}-\text{NH}-}
\]

wherein \(Z\) represents a hydrogen atom, an alkali metal or an alkaline earth metal or ammonium ion, as a repeating unit have useful properties of inhibition of mineral scale deposition.

One object of this invention is to provide methods useful in inhibition of metal scale formation in hard water, boiler water, cooling water, oil well waters, agricultural sprays and irrigation water.

Another object is to provide a method of preventing deposition of metal salts in clothing.

Another object is to prevent deposition of scale on glassware washed in an automatic dishwasher.

A final object is to provide methods for preventing scale formation which are effective, low in cost, and environmentally benign.
DEFINITIONS

Polysuccinimide is the imide form of polyaspartic acid and is also known as anhydropolyaspartic acid.

The counterion, "Z" above includes, but is not limited to, the alkali and alkaline earth metals examples of which as their cations are, Na⁺, K⁺, Mg²⁺, Li⁺, and Ca²⁺, Zn²⁺, Ba²⁺, Co²⁺, Fe²⁺, Fe³⁺, and NH₄⁺.

Detailed Description of the Embodiments.

Methods of preparation of polyamino acid derivatives based upon reaction of primary or secondary amines with polysuccinimide are known as disclosed in U.S. Pat 3,846,380, incorporated herein by reference. These materials were observed to have useful properties as surface active agents having no cloud point and good solubilizing, emulsifying and dispersing abilities. Thus, their use as foaming agents, solubilizing agents, dispersing agents, emulsifying agents, rust-proofing agents, fiber treating agents, level dyeing agents and retarding agents were disclosed.

The use of these agents as inhibitors of scale deposition has hitherto been unknown. We have found that these compounds are excellent inhibitors of the formation of metal scale deposits. In particular, the types of scale in which deposition is inhibited are those exemplified by hard water, boiler water, cooling water, oil well waters, agricultural sprays and irrigation water. Further, this property makes them useful as builders in detergents, where deposition of metal salts are injurious to clothing and impart a hard crust to the textile fibers. Their use to prevent deposition of scale on glassware makes them desirable in detergents for automatic dishwashers and the like. As is pointed out in the examples, we have found that these compounds are excellent inhibitors of the formation of scale deposits.

The effective compounds are polyamides having in their molecules at least one of the groups

\[ \text{-CH-CO-N} \quad \text{and} \quad \text{-CH-CO-NH-} \]

\[ \text{CH}_2\text{-CO-NH-} \quad \text{and} \quad \text{CH}_2\text{-CO-N} \]

wherein \( R' \) is a hydrogen or an alkyl or alkenyl group having 1 to 20 carbons and \( R'' \) is an alkyl or alkenyl group having 2 to 20 carbons, together with at least one of the groups

\[ \text{-CH-COOZ} \quad \text{and} \quad \text{-CH-CO-NH-} \]

\[ \text{CH}_2\text{-CO-NH-} \quad \text{and} \quad \text{CH}_2\text{-COOZ} \]

wherein \( Z \) represents a hydrogen atom, an alkali metal or an alkaline earth metal or ammonium ion, as a repeating unit.

Preferred groups for \( R' \) and \( R'' \) are hydrogen, methyl, oleyl, stearyl, and lauryl.

EXAMPLE 1
Precipitation assay for calcium sulfate.

The material to be tested as an inhibitor of scale formation was added in appropriate quantities to a solution of 5 ml of calcium chloride solutions (21.6 g/L of CaCl₂ dihydrate and 41.4 g/L of NaCl) and 5 ml of sulfate solution (20.9 g/L of Na₂SO₄ and 41.4 g NaCl). The mixture was then placed in an oven at 160°F for 3 hours. Finally the mixture was filtered through Whatman #2 paper and dried at 160°F for 8 hours, after which the weight of precipitate was determined.

<table>
<thead>
<tr>
<th>compound</th>
<th>additive (ppm)</th>
<th>weight of precipitate (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>polyacrylate, 5000 molecular weight</td>
<td></td>
<td>46</td>
</tr>
<tr>
<td>5% stearyl α,β-polyaspartate amide/α,β-polyaspartic acid</td>
<td>5</td>
<td>34</td>
</tr>
<tr>
<td>10% stearyl α,β-polyaspartate amide/α,β-polyaspartic acid</td>
<td>5</td>
<td>31</td>
</tr>
</tbody>
</table>

It will be apparent to those skilled in the art that the examples and embodiments described herein are by way of illustration and not of limitation and that other examples may be utilized without departing from the spirit and scope of the present invention, as set forth in the appended claims.
We claim:

1. A method of inhibition of mineral scale deposition comprising the addition of an amount effective in preventing scale formation of a polyamide having in its molecule at least one of the groups

\[
\begin{align*}
\text{R'} & \quad \text{and} \quad \text{R''} \\
\text{CH}_2\text{-CO-NH-} & \quad \text{CH}_2\text{-CO-N} \\
\text{R}^- & \quad \text{R}' \\
\end{align*}
\]

wherein \( \text{R'} \) is a hydrogen or an alkyl or alkanyl group having 1 to 20 carbons or a polyamine and \( \text{R''} \) is an alkyl or alkanyl group having 2 to 20 carbons or a polyamine, together with at least one of the groups

\[
\begin{align*}
\text{-CH-COOZ} & \quad \text{-CH-CO-NH-} \\
\text{CH}_2\text{-CO-NH-} & \quad \text{CH}_2\text{-COOZ} \\
\end{align*}
\]

wherein \( \text{Z} \) represents a hydrogen atom, an alkali metal or an alkaline earth metal or a ammonia, as a repeating unit.

2. A method for preventing scale formation of claim 1 wherein the polyamide is a copolymer of stearyl \( \alpha,\beta \)-polyaspartate amide and \( \alpha,\beta \)-polyspartic acid or its salt.

3. A method for preventing scale formation of claim 1 wherein the polyamide is a copolymer of oleyl \( \alpha,\beta \)-polyaspartate amide and \( \alpha,\beta \)-polyspartic acid or its salt.

4. A method for preventing scale formation of claim 1 wherein the polyamide is a copolymer of N-methyl-N-lauryl \( \alpha,\beta \)-polyaspartate amide and \( \alpha,\beta \)-polyspartic acid or its salt.

5. A method for preventing scale formation of claim 1 wherein the polyamide is a copolymer of lauryl \( \alpha,\beta \)-polyaspartate amide and \( \alpha,\beta \)-polyspartic acid or its salt.

6. A method for preventing scale formation of claim 1 wherein the polyamide is a copolymer of lauryl \( \alpha,\beta \)-polyaspartate amide, palmityl \( \alpha,\beta \)-polyaspartate amide and \( \alpha,\beta \)-polyspartic acid or its salt.

7. A detergent composition, which comprises a scale deposition inhibition effective amount of a polyamide that has a general formula of

\[
\begin{align*}
\text{R'} & \quad \text{and} \quad \text{R''} \\
\text{CH}_2\text{-CO-NH-} & \quad \text{CH}_2\text{-CO-N} \\
\text{R}^- & \quad \text{R}' \\
\end{align*}
\]

wherein \( \text{R'} \) is a hydrogen or an alkyl or alkanyl group having 1 to 20 carbons and \( \text{R''} \) is an alkyl or alkanyl group having 2 to 20 carbons, together with at least one of the groups

\[
\begin{align*}
\text{-CH-COOZ} & \quad \text{-CH-CO-NH-} \\
\text{CH}_2\text{-CO-NH-} & \quad \text{CH}_2\text{-COOZ} \\
\end{align*}
\]
wherein Z represents a hydrogen atom, ammonia, an alkali metal or an alkaline earth metal, as a repeating unit, in combination with an acceptable detergent composition compatible with said compound.

8. A cosmetic composition, which comprises a scale deposition inhibition effective amount of a polyamide that has a general formula of

\[
\begin{array}{c}
\text{R'} \\
\text{CH}_2\text{-CO-NH}- \\
\text{CH}_2\text{-CO-N} \\
\text{R''} \\
\end{array}
\]

and

\[
\begin{array}{c}
\text{R'} \\
\text{CH}_2\text{-CO-NH}- \\
\text{CH}_2\text{-CO-N} \\
\text{R''} \\
\end{array}
\]

wherein R' is a hydrogen or an alkyl or alkenyl group having 1 to 20 carbons and R'' is an alkyl or alkenyl group having 2 to 20 carbons, together with at least one of the groups

-CH-COOZ and -CH-CO-NH-

\[
\begin{array}{c}
\text{CH}_2\text{-CO-NH}- \\
\text{CH}_2\text{-CO-N} \\
\end{array}
\]

wherein Z represents a hydrogen atom, ammonia, an alkali metal or an alkaline earth metal, as a repeating unit, in combination with an acceptable cosmetic composition compatible with said compound.

10. A water treatment composition, which comprises a scale deposition inhibition effective amount of a polyamide that has a general formula of

\[
\begin{array}{c}
\text{R'} \\
\text{CH}_2\text{-CO-NH}- \\
\text{CH}_2\text{-CO-N} \\
\text{R''} \\
\end{array}
\]

wherein R' is a hydrogen or an alkyl or alkenyl group having 1 to 20 carbons and R'' is an alkyl or alkenyl group having 2 to 20 carbons, together with at least one of the groups

-CH-COOZ and -CH-CO-NH-

\[
\begin{array}{c}
\text{CH}_2\text{-CO-NH}- \\
\text{CH}_2\text{-CO-N} \\
\end{array}
\]

wherein Z represents a hydrogen atom, ammonia, an alkali metal or an alkaline earth metal, as a repeating unit, in combination with an acceptable water treatment composition compatible with said compound.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(5) :C02F 05/12
US CL :210/698
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 210/698-701; 252/82, 174.24, 180, 546; 514/772.4,772.6; 528/322,328

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>US, A, 5,116,513 (Koskan et al) 26 May 1992, see entire document.</td>
<td>1-8 and 10</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 3,846,380 (Fujimoto et al) 05 November 1974, see entire document.</td>
<td>1-8 and 10</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,534,881 (Sikes et al) 13 August 1985, see entire document.</td>
<td>1-8 and 10</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,839,461 (Boehmke) 13 June 1989, see entire document.</td>
<td>1-8 and 10</td>
</tr>
</tbody>
</table>

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document dealing with the same subject matter as the application
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search: 10 JANUARY 1994
Date of mailing of the international search report: 19 JAN 1994

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. NOT APPLICABLE

Authorized officer: [Signature]
PETER A. HRUSKOCI
Telephone No. (703) 308-3839

Form PCT/ISA/210 (second sheet)(July 1992)*