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Use of water-soluble polymers in cleaning compositions, and water-soluble polymers for such use

Verwendung von wasserlöslichen Polymeren in Reinigungsmittelzusammensetzungen und für solche Anwendungen geeignete wasserlösliche Polymere

Utilisation de polymères hydrosolubles dans des compositions de nettoyage et polymères hydrosolubles à cet effet

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References cited:
EP-A- 0 132 792
EP-A- 0 239 379
GB-A- 2 104 091
GB-A- 2 203 163
US-A- 4 784 789


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Description

The present invention is concerned with the use of polymers comprising, as polymerized units, (a) one or more monomer selected from C₃-C₆ monoethylenically unsaturated carboxylic acids, and alkali metal and ammonium salts thereof, (b) one or more aminoacryloyl derivative, and (c) optionally, one or more monomer polymerisable with (a) and (b), as additives for cleaning formulations such as hard surface cleaner formulations and particularly automatic machine dishwashing detergent formulations. The polymers improve the spotting and filming characteristics (i.e. reduce spotting and filming) of cleaning formulations such as automatic machine dishwashing detergents. The present invention is also concerned with polymers containing, as polymerized units, (a) one or more monomer selected from C₃-C₆ monoethylenically unsaturated carboxylic acids, and alkali metal and ammonium salts thereof, (b) one or more aminoacryloyl derivative, and (c) one or more monomer polymerisable with (a) and (b).

Polymeric additives are used in automatic machine dishwashing detergent formulations as phosphate substitutes, builders, thickeners, processing aids, film-control agents and spot-control agents. Unlike many other detergent formulations, it is critical that automatic machine dishwashing detergents are low foaming systems. Foam interferes with the mechanical washing action of the water which is sprayed in the machine. This requirement limits the types of polymeric additives and surfactants which can be used in an automatic machine dishwashing detergent formulation.

GB-B-2,104,091 discloses amphoteric copolymers containing as polymerized units cationic vinyl monomers and anionic vinyl monomers for use in detergent compositions. The mole ratio of cationic vinyl monomer to anionic vinyl monomer is from 1:99 to 99:1, and is preferably 20:80 to 80:20. The molecular weight of the polymers is from 1,000 to 3,000,000. All of the examples employ copolymers having a 1:1 molar ratio of cationic vinyl monomer to anionic vinyl monomer. The polymers are disclosed to be useful for enhancing the foaming power of surfactant-based liquid detergent compositions.

US-A-4,784,769 to Jeschke et al. discloses the use of certain copolymers for use in liquid hard-surface cleaner formulations to provide an anti-static finish on the surfaces. The polymers described therein are those taught by GB-B-2,104,091, discussed above, which contain at least one mole of nitrogen-containing acrylic acid derivative per mole of acrylic acid.

US-A-4,075,131 to Sterling discloses the use of zwitterionic copolymers for use in shampoos. The copolymers disclosed therein have a molar ratio of basic monomer to acidic monomer in the range of from 0.6:1 to 1.5:1.

US-A-4,534,892 to Suzuki et. al discloses the use of crosslinked copolymers of acidic and basic monomers as dispersants for water-insoluble fine powders in liquid detergents. It further discloses that the copolymers effectively disperse the solids without interfering with the foaming properties of the detergent compositions.

Japanese Patent Application 59-135293A discloses terpolymers comprising at least 10 mole percent of each of (1) an anionic vinyl monomer, (b) a cationic vinyl monomer, and (c) a nonionic vinyl monomer, wherein the molar ratio of anionic vinyl monomer to cationic vinyl monomer is from 1:2 to 2:1. It further discloses that the polymers increase the detergency of detergent compositions, especially when used with surfactants.


Other patents which include polymeric materials in dishwashing detergents are EP-A-0,132,792, DE-A-3627773, and GB-A-2,203,163. EP-A-0,132,792 teaches certain cleaning compositions for washing dishes in automatic dishwashers. The compositions contain from 1 to 8 weight percent of a polycarboxylic acid having a molecular weight of 12,000 to 40,000. In addition, the detergent contains surfactants and standard additives such as bleaching agents, biocides, perfumes, foaming-inhibitors, and/or solubilizers. The polymer can be poly(acrylic acid), poly(methacrylic acid), or polymers of maleic acid or fumaric acid and ethylene or propylene.

The present invention provides a method of enhancing the spotting and filming control of cleaning compositions, e.g. automatic machine dishwashing detergent formulations. The present invention also provides novel water-soluble polymers and a method for their preparation.

According to the present invention there is provided a method of improving the spotting and filming characteristics of cleaning compositions, e.g. automatic machine dishwashing detergents, which comprises adding to a cleaning composition, e.g. an automatic dishwashing detergent formulation, one or more water-soluble polymer comprising, as polymerized units:

(a) from 30 to 95 percent by weight of one or more monomer selected from C₃-C₆ monoethylenically unsaturated carboxylic acids, and alkali metal and ammonium salts thereof; and

(b) from 5 to 50 percent by weight of one or more aminoacryloyl derivative selected from:
wherein:

\( R_1 \) is selected from hydrogen and methyl;
\( A \) is selected from \( O \) and \( NH \);
\( R_2 \) and \( R_3 \) are each independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl; or \( R_2 \) and \( R_3 \), together with the carbon to which they are both attached, form a \( C_3-C_7 \) aliphatic ring;
\( M \) is equal to 0, 1, or 2 with the proviso that when \( M \) is equal to 0, a C-N bond appears in place of the \( (CH_2)_M \) group; and
\( R_4 \) and \( R_5 \) are each independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl; or \( R_4 \) and \( R_5 \), together with the carbon to which they are both attached, form a \( C_3-C_7 \) aliphatic ring; and

\( (ii) \)

wherein:

\( R_1, A, R_2, R_3, R_4, R_5 \) and \( M \) are as defined above;
\( R_6 \) is selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl;
and \( X \) is any suitable counterion such as a halogen, hydroxide, sulfate, hydrosulfate, phosphate, formate or acetate; and

(c) optionally, 3 to 25 percent by weight of one or more monoethylenically unsaturated monomer polymerisable with (a) and (b), with the proviso that, if (c) comprises one or more \( C_3-C_6 \) monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof, then said monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof is not the same as (a); in an amount effective to improve the spotting and filming characteristics.

In one aspect of the method of the present invention, the one or more water-soluble polymer comprises, as polymerized units and based on the weight of the polymer, from 95 to 60, preferably from 90 to 70, and most preferably from 90 to 75, percent by weight of the monomer(s) (a), and from 5 to 40, preferably from 10 to 30, and most preferably from 10 to 25, percent by weight of the aminocacyloyl derivative(s) (b). For example, the water-soluble polymer(s) may contain no monoethylenically unsaturated monomer(s) (c). In this aspect of the present invention, the relative amounts of components (a) and (b) are preferably in the molar ratio of from 4:1 to 150:1. More preferably, the molar ratio of component (a) to component (b) is from 1:10 to 100:1, and most preferably from 10:1 to 50:1.

In another aspect of the method of the present invention, the one or more water-soluble polymer comprises, as polymerized units and based on the weight of the polymer, from 92 to 30, preferably from 85 to 40, and most preferably from 80 to 50, percent by weight of the monomer(s) (a), from 5 to 50, preferably from 5 to 40, and most preferably from 10 to 30, percent by weight of the aminocacyloyl derivative(s) (b), and from 3 to 25, preferably from 3 to 20, and most
preferably from 5 to 20, percent by weight of the polymerisable monoethylenically unsaturated monomer(s) (c). In this aspect of the present invention, the relative amounts of components (a) and (b) are preferably in the molar ratio of from 2:1 to 100:1. More preferably, the molar ratio of component (a) to component (b) is from 2.5:1 to 90:1, and most preferably from 3.1 to 50.1.

The present invention also provides water-soluble polymers comprising, as polymerized units and based on the weight of the polymer,

(a) from 92 to 30, preferably from 85 to 40, and most preferably from 80 to 50, percent by weight of one or more monomer selected from C3-C6 monoethylenically unsaturated carboxylic acids, and alkali metal and ammonium salts thereof;
(b) from 5 to 50, preferably from 5 to 40, and most preferably from 10 to 30, percent by weight of one or more aminoacryloyl derivative selected from

\[
\begin{align*}
R_1 & \quad \text{(i)} \\
R_2 & \quad \text{(ii)} \\
R_3 & \quad \text{wherein:}
R_1, R_2, R_3, R_4, R_5, R_6, A, R_6, M & \quad \text{as defined above;}
R_6 & \text{selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl; and}
X & \text{is any suitable counterion such as a halogen, hydroxide, sulfate, hydrosulfate, phosphate, formate or acetate; and}
\end{align*}
\]

(c) from 3 to 25, preferably from 3 to 20, and most preferably from 5 to 20, percent by weight of one or more monoethylenically unsaturated monomer polymerisable with (a) and (b), with the proviso that, if (c) comprises one or more C3-C6 monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof, then said
monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof is not the same as (a).

In the above polymers according to the invention, which comprise monomers (a), (b), and (c), the relative amounts of components (a) and (b) are preferably in the molar ratio of from 2:1 to 100:1. More preferably, the molar ratio of component (a) to component (b) is from 2.5:1 to 90:1, and most preferably from 3:1 to 50:1.

The present invention further provides a method of making a polymer as defined in the preceding two paragraphs, which comprises contacting a mixture of monomers (a), (b) and (c) with an initiator in an amount effective to polymerize said mixture, and maintaining the mixture at an elevated temperature to produce the polymer product. The method may further comprise utilizing one or more solvents, for example, water. In the method, one or more of (a), (b) and (c) may be fed to a reactor at an elevated temperature.

Component (a) is one or more monomer selected from C3-C6 monoethylenically unsaturated carboxylic acids, and alkali metal and ammonium salts thereof. Suitable carboxylic acids include monoethylenically unsaturated monocarboxylic acids and monoethylenically unsaturated dicarboxylic acids. Examples of suitable monoethylenically unsaturated carboxylic acids include, but are not limited to, acrylic acid (AA), methacrylic acid (MAA), \( \alpha \)-ethacrylic acid, \( \beta \)-dimethylacrylic acid, methylenemalonic acid, vinylacetic acid, allylacetic acid, ethylideneacetic acid, propylideneacetic acid, crotonic acid, maleic acid (MALAC), maleic anhydride (MALAN), fumaric acid, itaconic acid, citraconic acid, mesaconic acid, and alkali metal and ammonium salts thereof. Preferably, the monoethylenically unsaturated carboxylic acid(s) is/are selected from acrylic acid, methacrylic acid, and alkali metal and ammonium salts thereof. More preferably, the monoethylenically unsaturated carboxylic acid(s) is acrylic acid or methacrylic acid.

Component (b) is one or more aminoacryloyl derivative selected from:

(i)

![Diagram](attachment:diagram.png)

wherein:

- \( R_1 \) is selected from hydrogen and methyl;
- \( A \) is selected from O and NH;
- \( R_2 \) and \( R_3 \) are each independently selected hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl; or \( R_2 \) and \( R_3 \), together with the carbon to which they are both attached, form a C3-C7 aliphatic ring;
- \( M \) is equal to 0, 1, or 2 with the proviso that when \( M \) is equal to 0, a C-N bond appears in place of the \((CH_2)_M\) group; and
- \( R_4 \) and \( R_5 \) are each independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl; or \( R_4 \) and \( R_5 \), together with the carbon to which they are both attached, form a C3-C7 aliphatic ring.

(ii)

![Diagram](attachment:diagram.png)

wherein:

- \( R_1, A, R_2, R_3, R_4, R_5 \) and \( M \) are as defined above.
Component (c) is one or more monoethylenically unsaturated monomer which is polymerisable with components (a) and (b), with the proviso that, if (c) comprises one or more C₃₋₆ monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof, then said monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof is not the same as (a). Preferably, (c) is at least partially soluble in water or the reaction solvent, or in the other monomers if no water or solvent is used. Suitable monomers include any of the C₃₋₆ monoethylenically unsaturated carboxylic acids and their alkali metal and ammonium salts used for component (a), with the proviso that, if (c) comprises one or more C₃₋₆ monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof, then said monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof is not the same as (a); C₁₋₄ alkyl esters of acrylic acid and methacrylic acid such as methyl acrylate, ethyl acrylate (EA), butyl acrylate (BA), methyl methacrylate (MMA), and butyl methacrylate (BMA); C₁₋₄ hydroxyalkyl esters of acrylic acid and methacrylic acid such as hydroxyethyl acrylate (HEA), hydroxpropyl acrylate (HPA), and hydroxyethyl methacrylate (HEMA); acrylamide (AM); alkyl substituted acrylamides, such as methacrylamide (MAM), N-t-butylacrylamide (t-BAM) and N-t-octylacrylamide (t-BAM) and N-1-octylacrylamide; N,N-dialkyl substituted acrylamides, such as N,N-dimethyl acrylamide and piperidinacrylamide; styrene; sulfonated styrene; sulfonated alkyl acrylamides, such as 2-acrylamidomethylpropanesulfonic acid (AMPSA); vinylsulfonates; vinylsulfonic acid; allylsulfonic acid; methallylsulfonic acid; vinylphosphonic acid; vinylacetate; allyl alcohols; sulfonated allyl alcohols; acrylonitrile; N-vinylpyrrolidone; N-vinylformamide; N-vinylimidazole; N-vinylpyrrolidone; N-vinyl-2-methylimidazoline. In one embodiment of the invention, the monomer is acrylamide, C₃₋₆ monoethylenically unsaturated carboxylic acids or alkali metal or ammonium salts thereof, C₁₋₄ alkyl esters of acrylic acid or methacrylic acid, or C₁₋₄ hydroxyalkyl esters of acrylic acid. In another embodiment of the invention, component (c) is selected from methyl methacrylate, butyl methacrylate, butyl acrylate, ethyl acrylate, t-butyl acrylamide, styrene and 2-acrylamido methylpropane sulfonic acid.

The polymers useful in the present invention can be made by methods of polymerization well known to those skilled in the art. They can be prepared by aqueous polymerization, solvent polymerization or bulk polymerization. Preferably, they are prepared by aqueous polymerization. Furthermore, the polymerization can be conducted as a batch, cofeed, heelp, semi-continuous or continuous process. Preferably, the polymerization is conducted as a cofeed or continuous process.

When the polymers are prepared by a cofeed process, the initiator and monomers are generally introduced into the reaction mixture as separate streams which are fed linearly (i.e. at constant rates). If desired, the streams can be staggered so that one or more of the streams are completed before the others. If desired, a portion of the monomers or initiators may be added to the reactor before the feeds are begun. The monomers can be fed into the reaction mixture as individual streams or combined into one or more streams. Preferably, the monomer stream containing component (b) is not combined with the monomer stream containing component (a).

The initiators suitable for making the polymers are any of the conventional water-soluble free-radical initiators and redox initiators. Suitable free-radical initiators include, but are not limited to, peroxides, persulfates, peresters, and azo initiators. Suitable redox initiators include but are not limited to peroxides, such as hydrogen peroxide, and persulfates, such as sodium persulfate. Also, mixed initiator systems can be used such as a combination of a free radical initiator and a redox initiator. The level of initiator is generally from 0.1 to 20 percent by weight based on the total amount of polymerisable monomers. Preferably, the initiator is present at a level of from 1 to 15 percent, and most preferably at a level of from 2 to 10 percent, by weight based on the total amount of polymerisable monomer.
In addition to the initiator, one or more promoters may also be used. Suitable promoters include water-soluble salts of metal ions. Suitable metal ions include iron, copper, cobalt, manganese, vanadium, and nickel. Preferably, the one or more promoters are water-soluble salts of iron or copper. When used, the one or more promoters are present at levels of from 1 to 100 ppm based on the total amount of polymerisable monomer. Preferably, the one or more promoters are present at levels of from 3 to 20 ppm based on the total polymerisable monomers.

It is generally desirable to control the pH of the polymerizing monomer mixture especially when using thermal initiators such as persulfate salts. The pH of the polymerizing monomer mixture can be controlled by a buffer system or by the addition of a suitable acid or base and is preferably designed to maintain the pH of the system from between 3 and 8, and most preferably from between 4 and 6.5. Similarly, when redox couples are used there will be an optimum pH range in which to conduct the polymerization depending on the choice of the components of the redox couple. The pH of the system can be adjusted to suit the choice of the redox couple by the addition of an effective amount of a suitable acid or base.

When the polymerization is conducted as a solution polymerization employing a solvent other than water, the reaction should be conducted up to 70 percent by weight, preferably from 40 to 60 percent by weight of polymerisable monomers based on the total reaction mixture. Similarly, when the polymerization is conducted as an aqueous polymerization, the reaction should be conducted up to 70 percent by weight, preferably from 40 to 60 percent by weight of polymerisable monomers based on the total reaction mixture. In general, it is preferred to conduct the polymerizations as aqueous polymerizations. The solvents or water, if used, can be introduced into the reaction vessel as a heel charge, or can be fed into the reactor either as a separate feed stream or as a diluent for one of the other components being fed into the reactor.

The temperature of the polymerization reaction will depend on the choice of initiator, solvent and target molecular weight. Generally, the temperature of the polymerization is up to the boiling point of the system although the polymerization can be conducted under pressure if higher temperatures are used. Preferably, the temperature of the polymerization is from 50 to 95 °C and most preferably from 60 to 80 °C.

The polymers useful in the present invention are water-soluble. This limits the maximum molecular weight of the polymers. Furthermore, the limit of the molecular weight will vary depending upon the relative amounts, and the hydrophilicity, of the monomer components incorporated into the polymer. If desired, chain regulators or chain transfer agents may be employed to assist in controlling the molecular weight of the polymers. Any conventional water-soluble chain regulator or chain transfer agent can be used. Suitable chain regulators include, but are not limited to, mercaptans, hypophosphites, isoascorbic acid, alcohols, aldehydes, hydrosulfites and bisulfites. If a chain regulator or chain transfer agent is used, preferred mercaptans are 2-mercaptoethanol and 3-mercaptopropionic acid; a preferred bisulfite is sodium metabisulfite. Generally, the weight average molecular weight (Mw) of the polymers is from 500 to 100,000, preferably from 750 to 30,000, and most preferably from 1,000 to 25,000, as measured by aqueous gel permeation chromatography relative to a poly(acrylic acid) standard.

The polymerisation of polymer in a detergent composition, and particularly an automatic machine dishwashing detergent composition, is preferably from 0.2 to 10 percent by weight of the composition, and more preferably from 0.5 to 7 percent by weight. The concentration of the polymer in the detergent composition is dependent on the amount of other additives in the detergent composition which have an impact on the desired performance characteristics. For example, if a phosphate containing compound is present in the detergent composition, the effective amount of polymer necessary to achieve the desired performance may be lower than if no phosphate containing compound is present.

The detergent composition of this invention can be in the form of either a powder or liquid. As used herein, "liquid" also refers to a gel or a slurry. The detergent composition of this invention may include conventional machine dishwashing detergent additives well known to those skilled in the art, in conventional use amounts. For example, the detergent composition of this invention may contain an alkali metal silicate at a concentration of from 0 to 50 percent, more preferably from 1 to 20 percent, by weight of the detergent composition. The alkali metal silicates which may be used in the composition of the current invention generally have an SiO₂/M₂O ratio (where M₂O represents the alkali metal oxide portion of the silicate) of from 1:1 to 3:5:1. More preferably, the alkali metal silicates are potassium and sodium silicates.

While the alkali metal silicates are an optional component of the present invention, highly alkaline dishwashing detergents containing no silicates may attack aluminum pots and pans and other metal utensils. Therefore, silicates are beneficial when corrosion inhibition of metal parts is desired.

The detergent compositions of this invention may optionally include a builder. The level of builder can be from 0 to 90 percent, and more preferably from 20 to 90 percent, by weight of the detergent composition. However, the builder concentration is dependent on whether the detergent is a liquid or a powder. Generally, a liquid composition will contain less builder than a powder composition. By way of example, builders which may be employed in combination with the polymers useful in the present invention include water soluble inorganic builder salts such as alkali metal polyphosphates, i.e., tripolyphosphates and pyrophosphates, alkali metal carbonates, borates, bicarbonates, and hydroxides and water soluble organic builders such as polycarboxylates including nitrotriacetic acid, citrates, tartarates and succinates. Also, zeolite may be added as a builder in amounts from 0 to 40 percent, and more preferably from 5 to 20.
Polymeric additives can also be used in the detergent formulations. Conventional polymeric additives include, but are not limited to water-soluble homopolymers of acrylic acid, and copolymers of acrylic acid with a suitable comonomer such as maleic anhydride, and the salts of these polymers. When used, the polymeric additives are present in the detergent formulation at levels of from 0.2 percent to 15 percent, and preferably at a level of from 0.2 to 10 percent, and most preferably from 0.5 percent to 8 percent, by weight of the detergent formulation.

Although optional, the detergent compositions of this invention will generally contain a low-foaming water soluble surfactant. Low-foaming surfactants are preferred for the detergent compositions of the present invention since foam reduces the mechanical efficiency of the wash spray as discussed previously. Certain low-foaming water soluble anionic, nonionic, zwitterionic, amphoteric surfactant or combinations thereof should be employed. The quantity of surfactant used in the detergent formulation will depend on the surfactant chosen and will generally be from 0.1 to 10 percent, and more preferably from 1 to 5 percent, by weight of the detergent composition.

Examples of suitable anionic surfactants include soaps such as the salts of fatty acids containing 9 to 20 carbon atoms, e.g. salts of fatty acids derived from coconut oil and tallow; alkylbenzenesulfonates - particularly linear alkylbenzenesulfonates in which the alkyl group contains from 10 to 16 carbon atoms; alcohol sulfates; ethoxylated alcohol sulfates; hydroxyalkylsulfonates; alkenyl and alkyl sulfates and sulfonates; monoglyceride sulfates and acid condensates of fatty acid chlorides with hydroxyalkylsulfonates. Because anionic surfactants tend to produce foam, it is preferred that the level of anionic surfactant is kept to a minimum and may require the use of a foam suppressant. If used, the level of anionic surfactant is preferably below 5 percent, and most preferably below 3 percent, by weight of the formulation.

Examples of suitable nonionic surfactants include alkylene oxide (e.g. ethylene oxide) condensates of mono and polyhydroxy alcohols, alkylphenols, fatty acid amides, and fatty amines; amine oxides; sugar derivatives such as sucrose monopalmitate; long chain tertiary phosphine oxides; dialkylsulfites; block copolymers of poly(ethylene oxide) and propylene oxide; hydrophilically modified poly(ethylene oxide) surfactants and fatty acid amides, (e.g., mono or diethanolamides of fatty acids containing 10 to 18 carbon atoms). The hydrophilically modified poly(ethylene oxide) surfactants are the preferred nonionic surfactants.

Examples of suitable zwitterionic surfactants include derivatives of aliphatic quaternary ammonium compounds such as 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate.

Examples of suitable amphoteric surfactants include betaines, sulfobetaines and fatty acid imidazole carboxylates and sulfonates.

The detergent may also contain up to 20 percent by weight of a bleaching agent, and preferably from 0.5 to 15 percent by weight. Suitable bleaching agents include the halogen, peroxide and peracid bleaches. Examples of suitable bleaches include sodium chlorite, potassium chlorite, sodium hypochlorite, potassium hypochlorite, sodium dichloroisocyanurate, sodium perborate, potassium perborate and sodium percarbonate.

The detergent may also contain up to 5 percent by weight of conventional adjuvants such as perfumes, colorants, foam suppressants, enzymes and bacterial agents. When the detergent composition is in the liquid form, from 0 to 5 percent by weight of stabilizers or viscosity modifiers, such as clays and polymeric thickeners, can be added.

Inert diluents may be used in the cleaning compositions, e.g. the detergent compositions, of the present invention. For example, inert diluents such as alkali metal chlorides, sulfates, nitrates and nitrites, may be used in the detergent compositions. Examples of such diluents which may be incorporated into the detergent compositions are sodium or potassium chloride, sodium or potassium sulfate and sodium or potassium nitrate. In addition, if the detergent composition is in the liquid form, water can be used as a diluent. The amount of diluent used is generally an amount to bring the total amount of the additives in the detergent composition up to 100% by weight.

The detergent composition of this invention may be used in machine dishwashers as an aqueous solution at a concentration of 0.2 to 1.5 percent, more preferably from 0.4 to 1 percent, by weight of the aqueous solution. The water temperature during the washing process should be about 37.8°C to 65.6°C (about 100°F to 150°F), and more preferably from about 43.3°C to 57.2°C (about 110°F to 135°F).

**Test Method**

The dishwashing tests were performed using a modified version of A.S.T.M. method D 3556-85, Standard Test Method for Deposition on Glassware During Mechanical Dishwashing. This test method covers a procedure for measuring performance of household automatic dishwashing detergents in terms of the buildup of spots and film on glassware. Glass tumblers were given three cycles in a dishwasher, in the presence of food soils, and the levels of spotting and thin film allowed by the detergents under test were compared visually.

A Kenmore dishwashing machine was used to perform the washing tests. The bottom rack of the dishwasher was randomly loaded with 14-18 dinner plates and the top rack was randomly loaded with several beakers and cups. Four
new 113.4 g (10 ounce) tumblers were placed randomly on the top racks as the test glasses. Soil used in the test was a mixture of 80% Parkay Margarine and 20% Carnation Non-fat Dry milk. The amount of soil used for each test was usually 40 grams for the first wash.

When a test was ready to be started, the desired amount of soil was smeared across the plates on the bottom rack, the detergent for the first cycle was placed in the detergent dispenser cup, and the machine was started. A normal cycle consisted of a wash, a rinse, a second wash, and two more rinses followed by a heat-drying cycle. At the beginning of the second wash, the machine was opened and a second detergent aliquot added. Soil was not added when a second detergent dose was added. The temperature of the supply water was maintained at 48.9°C (120° F) unless noted otherwise. Tap water with a measured hardness of 200 ppm and a Ca++ to Mg++ ratio of 2.0:1 was used as supply water unless noted otherwise. The machine was then allowed to complete the normal cycle including the drying time. This procedure was followed for a total of three complete cycles for each set of glasses.

When the final drying cycle was completed, the door was opened and the four glasses were removed and evaluated for filming and spotting. The test glasses were evaluated by placing them in light box equipped with a fluorescent light. The glasses were ranked according to the following scale and the average rating for the four glasses is reported below in Table 1:

<table>
<thead>
<tr>
<th>Filming</th>
<th>Spotting</th>
</tr>
</thead>
<tbody>
<tr>
<td>0  No film</td>
<td>0  No spots</td>
</tr>
<tr>
<td>1  Barely perceptible</td>
<td>1  Random</td>
</tr>
<tr>
<td>2  Slight</td>
<td>2  1/4 of glass</td>
</tr>
<tr>
<td>3  Moderate</td>
<td>3  1/2 of glass</td>
</tr>
<tr>
<td>4  Heavy</td>
<td>4  Complete spotting</td>
</tr>
</tbody>
</table>

**Table 1: Detergent Compositions Tested (by weight solids)**

<table>
<thead>
<tr>
<th>DETERGENT A</th>
<th>20% sodium carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12.5% sodium citrate-2H2O</td>
</tr>
<tr>
<td></td>
<td>7.5% zeolite</td>
</tr>
<tr>
<td></td>
<td>5% perborate-4H2O</td>
</tr>
<tr>
<td></td>
<td>7% RU Silicate (SiO2:Na2O 2.4:1)</td>
</tr>
<tr>
<td></td>
<td>2% Olin Poly-Tergent SLF-18 surfactant</td>
</tr>
<tr>
<td></td>
<td>4% polymer (unless specifically stated otherwise)</td>
</tr>
<tr>
<td></td>
<td>diluted to 100% with sodium sulfate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DETERGENT B</th>
<th>20% sodium carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12.5% sodium citrate-2H2O</td>
</tr>
<tr>
<td></td>
<td>7.5% zeolite</td>
</tr>
<tr>
<td></td>
<td>5% perborate-4H2O</td>
</tr>
<tr>
<td></td>
<td>7% RU Silicate (SiO2:Na2O 2.4:1)</td>
</tr>
<tr>
<td></td>
<td>4% Olin Poly-Tergent SLF-18 surfactant</td>
</tr>
<tr>
<td></td>
<td>4% polymer (unless specifically stated otherwise)</td>
</tr>
<tr>
<td></td>
<td>diluted to 100% with sodium sulfate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DETERGENT C</th>
<th>20% sodium carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30% sodium citrate-2H2O</td>
</tr>
<tr>
<td></td>
<td>20% BRITESIL H2O Polysilicate (SiO2:Na2O 2.0:1)</td>
</tr>
<tr>
<td></td>
<td>7.5% perborate-4H2O</td>
</tr>
<tr>
<td></td>
<td>4% Olin Poly-Tergent SLF-18 surfactant</td>
</tr>
<tr>
<td></td>
<td>4% polymer (unless specifically stated otherwise)</td>
</tr>
<tr>
<td></td>
<td>diluted to 100% with sodium sulfate</td>
</tr>
</tbody>
</table>

The polymer syntheses which follow are representative of the cofeed process suitable for preparing polymers of, and polymers useful in, the present invention. Methods of preparing the polymers of, and polymers useful in, the present
invention are not limited to this procedure.

COPOLYMER SYNTHESIS 80 AA / 20 APTAC

350.0 grams of deionized water and 12.0 grams of 0.15 percent FeSO₄·7H₂O in deionized water were added to a 3-litre round bottom flask equipped with a stirrer, thermometer, condenser, heater, and inlets for monomer, and initiator solutions. The stirrer was turned on and the water was heated to 70 °C. A solution of 1.95 grams sodium metabisulfite dissolved in 5.0 grams of deionized water was added to the flask. Three feed solutions were prepared: a monomer solution of 480.0 grams glacial acrylic acid and 200.0 grams of 60 percent APTAC in deionized water; an initiator solution of 2.86 grams of sodium persulfate dissolved in 60.0 grams of deionized water; and a chain regulator solution of 32.25 grams sodium metabisulfite dissolved in 100 grams of deionized water. These solutions were fed into the flask linearly and separately over two hours (except the chain regulator solution which was fed for 105 minutes) while maintaining the mixture at 70 °C. After the feeds were completed, the mixture was maintained at 70°C for ten minutes. The data for this copolymer appear as Examples 16 and 17 in Table 1 below.

The copolymers appearing in Table 1, below, were prepared in a similar manner as the copolymer synthesis above with the monomer compositions as noted. Compositions are listed as percent by weight of the monomer mix.
The data in Table 1 shows the effectiveness of the copolymers for enhancing the spotting and filming properties of automatic machine dishwashing detergents containing them.

**TERPOLYMER SYNTHESIS 75 AA/ 20 DMAPA /5 BA**

250.0 grams of deionized water and 12.0 grams of 0.15 percent FeSO$_4$·7H$_2$O in deionized water were added to a 3-litre round bottom flask equipped with a stirrer, thermometer, condenser, heater, and inlets for monomer, and initiator solutions. The stirrer was turned on and the water was heated to 70 °C. A solution of 1.8 grams sodium metabisulfite dissolved in 10.0 grams of deionized water was added to the flask. Four feed solutions were prepared: a monomer solution of 450.0 grams glacial acrylic acid and 30.0 grams butyl acrylate; a monomer solution of 120.0 grams of DMAPA; an initiator solution of 3.32 grams of sodium persulfate dissolved in 20.0 grams of deionized water; and a chain regulator solution of 30.0 grams sodium metabisulfite dissolved in 75 grams of deionized water. These solutions were fed into the flask linearly and separately over two hours (except the chain regulator solution which was fed for 105 minutes) while maintaining the mixture at 70 °C. After the feeds were completed, the mixture was maintained at
70°C for ten minutes. The data for this terpolymer appears as Example 5 in Table 2 below. The terpolymers appearing in Table 2, below, were prepared in a similar manner as the terpolymer synthesis above with the monomer compositions as noted. Compositions are listed as percent by weight of the monomer mix.

<table>
<thead>
<tr>
<th>Example</th>
<th>Composition</th>
<th>M_w</th>
<th>Spot</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative 13</td>
<td>Acusol 445N^1</td>
<td>4500</td>
<td>3.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Comparative 14</td>
<td>Acusol 445N</td>
<td>4500</td>
<td>2.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Comparative 15</td>
<td>Acusol 445N^5</td>
<td>4500</td>
<td>2.7</td>
<td>0.8</td>
</tr>
<tr>
<td>18</td>
<td>68 AA/5 DIMAPA/7 BA</td>
<td>4220</td>
<td>3.0</td>
<td>0.6</td>
</tr>
<tr>
<td>19</td>
<td>83 AA/10 DIMAPA/7 BA</td>
<td>4010</td>
<td>2.5</td>
<td>0.7</td>
</tr>
<tr>
<td>20</td>
<td>78 AA/15 DIMAPA/7 BA</td>
<td>4510</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>21</td>
<td>75 AA/20 DIMAPA/5 BA</td>
<td>4450</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>22</td>
<td>75 AA/20 DIMAPA/5 BA^5</td>
<td>4800</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>23</td>
<td>80 AA/15 DIMAPA/5 BA</td>
<td>4080</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>24</td>
<td>60 AA/15 DIMAPA/5 STY</td>
<td>6510</td>
<td>1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>25</td>
<td>83 AA/10 DIMAPMA/7 BA</td>
<td>4180</td>
<td>2.5</td>
<td>0.6</td>
</tr>
<tr>
<td>26</td>
<td>80 AA/15 DIMAPMA/5 BA</td>
<td>4180</td>
<td>3.5</td>
<td>0.0</td>
</tr>
<tr>
<td>27</td>
<td>80 AA/15 DIMAPMA/5 STY</td>
<td>6560</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>28</td>
<td>75 AA/15 DIMAPMA/10 MMA</td>
<td>4790</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>29</td>
<td>70 AA/15 DIMAPMA/15 MMA</td>
<td>4790</td>
<td>3.2</td>
<td>0.0</td>
</tr>
<tr>
<td>30</td>
<td>75 AA/20 DIMAPMA/5 STY</td>
<td>6010</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>31</td>
<td>75 AA/20 DIMAPMA/5 BA</td>
<td>6490</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>32</td>
<td>80 AA/15 DMAEMA/5 BA</td>
<td>5120</td>
<td>1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>33</td>
<td>75 AA/20 DMAEMA/5 IBAM</td>
<td>5330</td>
<td>3.0</td>
<td>0.0</td>
</tr>
<tr>
<td>34</td>
<td>75 AA/20 DMAEMA/5 STY</td>
<td>5480</td>
<td>3.0</td>
<td>0.0</td>
</tr>
<tr>
<td>35</td>
<td>75 AA/20 DMAEMA/5 BA</td>
<td>4420</td>
<td>1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>36</td>
<td>75 AA/20 DMAEMA/5 EA</td>
<td>4260</td>
<td>2.5</td>
<td>0.0</td>
</tr>
<tr>
<td>37</td>
<td>60 AA/15 t-BAEMA/5 BA</td>
<td>4020</td>
<td>3.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

^1 Example 18 was tested in a detergent composition containing only 2% by weight surfactant. Acusol 445N is a fully neutralized poly(acrylic acid) having M_w 4,500. Acusol is a trademark of Rohm and Haas Company.

^5 These compositions were tested at a hardness of 300 ppm wherein the ratio of Ca^{2+}:Mg^{2+} was 3.5:1.
TABLE 2 (continued)

<table>
<thead>
<tr>
<th>Example</th>
<th>Composition</th>
<th>$M_w$</th>
<th>Spot</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>74 AA/21 DMAPMA/5 BA</td>
<td>5210</td>
<td>0</td>
<td>0.3²</td>
</tr>
<tr>
<td>39</td>
<td>75 AA/20 APTAC/5 BA⁵</td>
<td>3970</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>40</td>
<td>55 AA/40 APTAC/5 BA³</td>
<td>4660</td>
<td>0</td>
<td>3.2²</td>
</tr>
<tr>
<td>41</td>
<td>75 AA/20 DMAEA/5 BA</td>
<td>5120</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>42</td>
<td>55 AA/20 MALAC/20 APTAC/5 AMPSA⁴</td>
<td>6270</td>
<td>0</td>
<td>0.2²</td>
</tr>
<tr>
<td>43</td>
<td>3% Example 21 / 1% Acusol 445N</td>
<td>0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>2% Example 21 / 2% Acusol 445N</td>
<td>0</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>2% Example 22 / 2% Acusol 445N⁵</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>1% Example 21 / 3% Acusol 445N</td>
<td>0</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

² These compositions were tested at a cycle temperature of 57.2°C (135°F) and hardness of 300 ppm wherein the ratio of Ca°²:Mg²⁺ was 3.5:1.
³ Dilute sulfuric acid solution was added during polymerization to maintain pH between 1.0 and 3.5.
⁴ Prepared by a thermal process using mixed initiator system of 4.8 weight percent sodium persulfate based on active monomer and 4.0 percent hydrogen peroxide based on active monomer. Dilute NaOH was added during the polymerization to maintain in-process pH between 3.5 and 7.0.
⁵ These compositions were tested at a hardness of 300 ppm wherein the ratio of Ca²⁺:Mg²⁺ was 3.5:1.

The data in Table 2 shows the effectiveness of the polymers of the present invention for enhancing the spotting and filming properties of automatic machine dishwashing detergents (Detergent B) containing them. "Acusol", "Poly-Tergent" and "BRITESIL" are trademarks which may be registered in one or more of the designated countries.

Claims

1. A method of improving the spotting and filming characteristics of cleaning compositions, which comprises adding to a cleaning composition one or more water-soluble polymer comprising, as polymerized units:

   (a) from 95 to 30 percent by weight of one or more monomer selected from C₃-C₆ monoethylenically unsaturated carboxylic acids, and alkali metal and ammonium salts thereof;
   (b) from 5 to 50 percent by weight of one or more aminoacyrloyl derivative selected from:

   (i)

   \[
   \text{CH}_2\text{A}\text{C}\text{O} \quad \text{(CH}_2\text{M} \quad \text{N} \quad \text{R}_4 \quad \text{R}_5
   \]

   wherein:

   $R_1$ is selected from hydrogen and methyl;
   $A$ is selected from O and NH;
   $R_2$ and $R_3$ are each independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl; or $R_2$ and $R_3$, together with the carbon to which they are both attached, form a C₃-C₇ aliphatic...
EP 0 560 519 B1

ring;
M is equal to 0, 1, or 2 with the proviso that when M is equal to 0, a C-N bond appears in place of the
(CH2)M group; and
R4 and R5 are each independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl,
an isobutyl; or R4 and R5, together with the carbon to which they are both attached, form a C3-C7 aliphatic
ring;
and

(ii)

wherein:
R1, A, R2, R3, R4, R5 and M are as defined above;
R6 is selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and isobutyl;
and X is any suitable counterion, for example, a halogen, hydroxide, sulfate, hydrosulfate, phosphate,
formate or acetate; and (c) optionally, from 3 to 25 percent by weight of one or more monoethylenically
unsaturated monomer polymerizable with (a) and (b); with the proviso that if (c) comprises one or more
C3-C6 monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof, then said
one or more monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof is
not the same as (a); in an amount effective to improve the spotting and filming characteristics.

2. A method as claimed in claim 1, wherein (a) is selected from: acrylic acid, methacrylic acid, α-ethacrylic acid, β-
β-dimethylacrylic acid, methenemalonic acid, vinylacetic acid, allylactic acid, ethylideneacetic acid, propyldiene-
acetic acid, crotonic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, citraconic acid, mesaconic
acid, and alkali metal and ammonium salts thereof.

3. A method as claimed in claim 1 or claim 2, wherein (b) is selected from: N,N-dimethylaminoethyl acrylate, N,N-
dimethylaminoethyl methacrylate, N-[3-(dimethylamino)propyl] acrylamide, N-[3-(dimethylamino)propyl] methacry-
lamide, tert-butylaminoethyl methacrylate, (3-acrylamidopropyl)trimethylammonium chloride, (3-methacrylamido-
propyl)trimethylammonium chloride, and N-[3-(dimethylamino)-2,2-dimethylpropyl]acrylamide.

4. A method as claimed in any preceding claim, wherein the weight average molecular weight of the polymer is from
500 to 100,000.

5. A method as claimed in any preceding claim, wherein the one or more water-soluble polymer comprises, as po-
lymerized units, from 95 to 60 percent by weight of (a), and from 5 to 40 percent by weight of (b).

6. A method as claimed in claim 5, wherein (a) is present at a level of from 70 to 90 percent by weight.

7. A method as claimed in claim 5 or claim 6, wherein (b) is present at a level of from 10 to 30 percent by weight.

8. A method as claimed in any of claims 1 to 4, wherein the one or more water-soluble polymer comprises, as po-
lymerized units, from 92 to 30 percent by weight of (a), from 5 to 50 percent by weight of (b), and from 3 to 25
percent by weight of (c).

9. A method as claimed in claim 8, wherein (a) is present at a level of from 40 to 85 percent by weight.

10. A method as claimed in claim 8 or claim 9, wherein (b) is present at a level of from 5 to 40 percent by weight.
11. A method as claimed in any of claims 8 to 10, wherein (c) is selected from C₃-C₆ monoethylenically unsaturated carboxylic acids and alkali metal and ammonium salts thereof, C₁-C₄ alkyl esters of acrylic acid and methacrylic acid, C₁-C₄ hydroxyalkyl esters of acrylic acid and methacrylic acid, acrylamide, alkyl substituted acrylamides, N,N-dialkyl substituted acrylamides, styrene, sulfonated styrene, sulfonated alkyl acrylamides, vinyl sulfonates, vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, vinylphosphonic acid, vinylacetate, allyl alcohols, sulfonated allyl alcohols, acrylonitrile, N-vinylpyrrolidone, N-vinylformamide, N-vinylimidazole, N-vinylpyridine, and N-vinyl-2-methylimidazoline; with the proviso that if (c) comprises one or more C₃-C₆ monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof, then said one or more monoethylenically unsaturated carboxylic acid or alkali metal or ammonium salt thereof is not the same as (a).

12. A method as claimed in any of claims 8 to 10, wherein (c) is selected from methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, butyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, acrylamide, N-t-butyl acrylamide, N-t-octylacrylamide, N,N-dimethyl acrylamide, piperidine acrylamide, styrene, sulfonated styrene, vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, vinylphosphonic acid, vinylacetate, acrylonitrile, N-vinylpyrrolidone, N-vinylformamide, N-vinylimidazole, N-vinylpyridine, N-vinyl-2-methylimidazoline, and 2-acrylamido methylpropane sulfonic acid.

13. A method as claimed in any of claims 8 to 12, wherein (c) is present at a level of from 3 to 20 percent by weight.

14. A method as claimed in any preceding claim, wherein the polymer is present in the composition at a level of from 0.2 to 10 percent by weight.

15. A method as claimed in any preceding claim, wherein the cleaning composition is an automatic machine dishwashing detergent composition.

16. A cleaning composition, which comprises a water-soluble polymer as defined in any of claims 1 to 13.

17. A cleaning composition as claimed in claim 16 which is in the form of an automatic machine dishwashing detergent composition.

18. A cleaning composition as claimed in claim 17, wherein the polymer is present at a level of 0.2 to 10 percent by weight.

19. A water-soluble polymer as defined in any of claims 8 to 13.

20. A method of making a polymer as defined in any of claims 8 to 13, which comprises contacting a mixture of monomers (a), (b) and (c) with an initiator in an amount effective to polymerize said mixture, and maintaining the mixture at an elevated temperature to produce the polymer product.

21. A method as claimed in claim 20, which further comprises utilizing a solvent, for example, water.

22. A method as claimed in claim 20 or claim 21, wherein one or more of (a), (b) and (c) are fed into a reactor at an elevated temperature.

23. Use, in a cleaning composition, for example an automatic machine dishwashing composition, of one or more water-soluble polymer as defined in any of claims 1 to 13, to improve the spotting and filming characteristics of the composition.

Patentansprüche

1. Verfahren zur Verbesserung der Fleckenbildungs- und Filmbildungseigenschaften von Reinigungszusammensetzungen, welches die Zugabe zu einer Reinigungszusammensetzung von einem oder mehreren wasserlöslichen Polymeren, umfassend als polymerisierte Einheiten

(a) von 95 bis 30 Gew.-% eines oder mehreren Monomeren, ausgewählt aus C₂-C₆ monoethylenisch unge-sättigten Carbonsäuren und Alkalimetall- und Ammoniumsalze davon,
(b) von 5 bis 50 Gew.-% eines oder mehrerer Aminoacryloylderivate, ausgewählt aus
wobei $R_1$ aus Wasserstoff und Methyl ausgewählt ist,

$A$ aus 0 und NH ausgewählt ist,

$R_2$ und $R_3$ jeweils unabhängig voneinander aus Wasserstoff, Methyl, Ethyl, Propyl, Isopropyl, Butyl, t-Butyl und Isobutyl ausgewählt sind, oder $R_2$ und $R_3$ zusammen mit dem Kohlenstoffatom, an welchem sie beide gebunden sind, einen aliphatischen C$_3$-C$_7$-Ring bilden,

$M$ gleich 0,1 oder 2 ist, mit der Maßgabe, daß, wenn $M$ gleich 0 ist, eine C-N-Bindung anstelle der (CH$_2$)$_M$-Gruppe auftritt, und

$R_4$ und $R_5$ jeweils unabhängig voneinander aus Wasserstoff, Methyl, Ethyl, Propyl, Isopropyl, Butyl, t-Butyl und Isobutyl ausgewählt sind, oder $R_4$ und $R_5$ zusammen mit dem Kohlenstoffatom, an welchem sie beide gebunden sind, einen aliphatischen C$_3$-C$_7$-Ring bilden, und

\[
\begin{align*}
(wobei R_1, A, R_2, R_3, R_4, R_5 und M wie vorstehend definiert sind, R_6 aus Wasserstoff, Methyl, Ethyl, Propyl, Isopropyl, Butyl, t-Butyl und Isobutyl ausgewählt ist, und X ein geeignetes Gegenion, beispielsweise ein Halogen, Hydroxid, Sulfat, Hydrogensulfat, Phosphat, Formiat oder Acetat, ist, und (c) gegebenenfalls von 3 bis 25 Gew.-% eines oder mehrerer monoethylenische ungesättigte, mit (a) und (b) polymerisierbarer Monomere, mit der Maßgabe, daß, wenn (c) eine oder mehrere C$_3$-C$_6$ monoethylenisch ungesättigte Carbonsäuren oder Alkalimetall- oder Ammoniumsalze davon umfaßt, die eine oder mehreren monoethylenisch ungesättigten Carbonsäuren oder Alkalimetall- oder Ammoniumsalze davon dann nicht gleich wie (a) sind, in einer wirksamen Menge zur Verbesserung der Fleckenbildungs- und Filmbildungs-Eigenschaften umfaßt.
\end{align*}
\]

2. Verfahren nach Anspruch 1, wobei (a) ausgewählt aus Acrylsäure, Methacrylsäure, α-Ethacrylsäure, β,β-Dimethylacrylsäure, Methylmalonsäure, Vinylsäure, Allylsäure, Ethylidinessigsäure, Propylidinessigsäure, Crotonsäure, Maleinsäure, Maleinsäureanhydrid, Fumarsäure, Itaconssäure, Citraconsäure, Mesaconsäure und Alkalimetall- und Ammoniumsalze davon ist.


4. Verfahren nach einem der vorstehenden Ansprüche, wobei das Gewichtsmittel des Molekulargewichts des Polymers von 500 bis 100 000 beträgt.

5. Verfahren nach einem der vorstehenden Ansprüche, wobei das eine oder die mehreren wasserlöslichen Polymere, als polymerisierte Einheiten, von 95 bis 60 Gew.-% (a) und von 5 bis 40 Gew.-% (b) umfassen.
6. Verfahren nach Anspruch 5, wobei (a) in einem Gehalt von 70 bis 90 Gew.-% vorliegt.

7. Verfahren nach Anspruch 5 oder 6, wobei (b) in einem Gehalt von 10 bis 30 Gew.-% vorliegt.

8. Verfahren nach einem der Ansprüche 1 bis 4, wobei das eine oder die mehreren wasserlöslichen Polymere, als polymerisierte Einheiten, von 92 bis 30 Gew.-% (a), von 5 bis 50 Gew.-% (b) und von 3 bis 25 Gew.-% (c) umfassen.

9. Verfahren nach Anspruch 8, wobei (a) in einem Gehalt von 40 bis 55 Gew.-% vorliegt.

10. Verfahren nach Anspruch 8 oder 9, wobei (b) in einem Gehalt von 5 bis 40 Gew.-% vorliegt.

11. Verfahren nach einem der Ansprüche 8 bis 10, wobei (c) ausgewählt aus C₃-C₆ monoethylenisch ungesättigten Carbonsäuren und Alkalimetall- und Ammoniumsalze davon, C₁-C₄-Alkylester der Acrylsäure und Methacrylsäure, C₁-C₄-Hydroxyalkylester der Acrylsäure und Methacrylsäure, Acrylamid, Alkyl-substituierte Acrylamide, N,N-Dialkyl-substituierte Acrylamide, Styrol, sulfonierte Styrol, sulfonierte Alkylacrylamide, Vinylsulfonate, Vinylsulfonsäure, Allylsulfonsäure, Methallylsulfonsäure, Vinylphosphonsäure, Vinylacetat, Allylkoholen, sulfonierte Allylkohole, Acrylonitril, N-Vinylpyrrolidon, N-Vinylformamid, N-Vinylimidazol, N-Vinylpyridin und N-Vinyl-2-methylimidazolin ist, mit der Maßgabe, daß, wenn (c) eine oder mehrere C₃-C₆ monoethylenisch ungesättigte Carbonsäuren oder Alkalimetall- oder Ammoniumsalze davon umfaßt, die eine oder mehrere monoethylenisch ungesättigten Carbonsäuren oder Alkalimetall- oder Ammoniumsalze davon nicht gleich wie (a) sind.

12. Verfahren nach einem der Ansprüche 8 bis 10, wobei (c) ausgewählt aus Methylacrylat, Ethylacrylat, Butylacrylat, Methylmethacrylat, Butylmethacrylat, Hydroxymethylacrylat, Hydroxypropylacrylat, Hydroxyethylmethacrylat, Acrylamid, N-t-Butylacrylamid, N-t-Octylacrylamid, N,N-Dimethylacrylamid, Piperidinacylamid, Styrol, sulfoniertes Styrol, Vinylsulfonsäure, Allylsulfonsäure, Methallylsulfonsäure, Vinylphosphonsäure, Vinylacetat, Acrylonitril, N-Vinylpyrrolidon, N-Vinylformamid, N-Vinylimidazol, N-Vinylpyridin, N-Vinyl-2-methylimidazolin und 2-Acrylamidomethylpropansulfonsäure ist.

13. Verfahren nach einem der Ansprüche 8 bis 12, wobei (c) in einem Gehalt von 3 bis 20 Gew.-% vorliegt.

14. Verfahren nach einem der vorstehenden Ansprüche, wobei das Polymer in der Zusammensetzung in einem Gehalt von 0,2 bis 10 Gew.-% vorliegt.

15. Verfahren nach einem der vorstehenden Ansprüche, wobei die Reinigungs zusammensetzung eine Detergens zusammensetzung für eine Geschirrspülmaschine ist.

16. Reinigungs zusammensetzung, welche ein wasserlösliches Polymer, wie in einem der Ansprüche 1 bis 13 definiert, umfaßt.

17. Reinigungs zusammensetzung nach Anspruch 16, welche in der Form einer Detergens zusammensetzung für eine automatische Geschirrspülmaschine vorliegt.

18. Reinigungs zusammensetzung nach Anspruch 17, wobei das Polymer in einem Gehalt von 0,2 bis 10 Gew.-% vorliegt.

19. Wasserlösliches Polymer, wie in einem der Ansprüche 8 bis 13 definiert.

20. Verfahren zur Herstellung eines Polymers, wie in einem der Ansprüche 8 bis 13 definiert, welches das Inkontakt bringen eines Gemisches der Monomere (a), (b) und (c) mit einem Initiator in einer wirksamen Menge zum Pol ymerisieren des Gemisches und das Halten des Gemisches bei einer erhöhten Temperatur zum Erzeugen des Polymerproduktes umfaßt.


22. Verfahren nach Anspruch 20 oder 21, wobei eines oder mehrere von (a), (b) und (c) in einen Reaktor bei einer erhöhten Temperatur eingebracht werden.
23. Verwendung eines oder mehrerer wasserlöslicher Polymere, wie in einem der Ansprüche 1 bis 13 definiert, in einer Reinigungszusammensetzung, beispielsweise einer Zusammensetzung für eine automatische Geschirrspülmaschine, zur Verbesserung der Fleckenbildungs- und Filmbildungseigenschaften der Zusammensetzung.

Revendications

1. Procédé d'amélioration des caractéristiques anti-taches et anti-film de compositions nettoyantes, qui comprend l'addition à une composition nettoyante d'un ou plusieurs polymères hydrosolubles comprenant, sous la forme d'unités polymérisées :

   (a) de 95 à 30 % en poids d'un ou plusieurs monomères choisis parmi les acides carboxyliques en C₃ à C₆ monoéthéniquement insaturés et les sels de métal alcalin et d'ammonium de ceux-ci ;
   (b) de 5 à 50 % en poids d'un ou plusieurs dérivés aminoacryloyliques choisis parmi :

   ![Diagramme]

   où :

   R₁ est choisi parmi l'hydrogène et le groupe méthyle ;
   A est choisi parmi O et NH ;
   R₂ et R₃ sont chacun indépendamment choisis parmi l'hydrogène, les groupes méthyle, éthyle, propyle, isopropyle, butyle, t-butyle et isobutyle ; ou R₂ et R₃, avec le carbone auquel ils sont tous les deux attachés, forment un cycle aliphatique en C₃ à C₇ ;
   M est égal à 0, 1 ou 2, avec la condition que lorsque M est égal à 0, une liaison C-N apparaisse à la place du groupe (CH₂)M ; et
   R₄ et R₅ sont chacun indépendamment choisis parmi l'hydrogène, les groupes méthyle, éthyle, propyle, isopropyle, butyle, t-butyle et isobutyle ; ou R₄ et R₅, avec le carbone auquel ils sont tous les deux attachés, forment un cycle aliphatique en C₃ à C₇ ;

   (ii)

   ![Diagramme]

   où :

   R₁, A, R₂, R₃, R₄, R₅ et M sont tels que définis ci-dessus ;
   R₆ est choisi parmi l'hydrogène, les groupes méthyle, éthyle, propyle, isopropyle, butyle, t-butyle et isobutyle ;
   et X est tout contre-ion approprié, par exemple un ion halogène, hydroxyde, sulfate, hydrosulfate, phosphate, formate ou acétate ; et

   (c) facultativement, de 3 à 25 % en poids d'un ou plusieurs monomères monoéthéniquement insaturés polymérisables avec (a) et (b) ; avec la condition que si (c) comprend un ou plusieurs acides carboxyliques en
Procédé selon la revendication 1, dans lequel (a) est choisi parmi: l'acide acrylique, l'acide méthacrylique, l'acide α-éthacrylique, l'acide β,β-diméthacrylique, l'acide méthylénemalonique, l'acide vinylacétique, l'acide allylacétique, l'acide éthylidenemaléique, l'acide propylidenemaléique, l'acide crotonique, l'acide maléique, l'anhdyride maléique, l'acide fumarique, l'acide itaconique, l'acide métaconique, et les sels de métal alcalin et d'ammonium de ceux-ci.

Procédé selon la revendication 1 ou la revendication 2, dans lequel (b) est choisi parmi: l'acrylate de N,N-diméthylaminoéthyle, le méthacrylate de N,N-diméthylaminoéthyle, le N-[3-(diméthylamino)propyl]acrylamide, le N-[3-(diméthylamino)propyl]méthacrylamide, le méthacrylate de tert-butylaminoéthyle, le chlorure de (3-acrylamidopropytriméthylammonium), le chlorure de (3-méthacrylamidopropyl)triméthylammonium et le N-[3-(diméthylamino)-2,2-diméthylpropyl]acrylamide.

Procédé selon l'une quelconque des revendications précédentes, dans lequel le poids moléculaire moyen en poids du polymère est de 500 à 100 000.

Procédé selon l'une quelconque des revendications précédentes, dans lequel le ou les polymères hydrosolubles comprennent, sous la forme d'unités polymérisées, de 95 à 60 % en poids de (a) et de 5 à 40 % en poids de (b).

Procédé selon la revendication 5, dans lequel (a) est présent à une proportion de 70 à 90 % en poids.

Procédé selon la revendication 5, dans lequel (b) est présent à une proportion de 10 à 30 % en poids.

Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le ou les polymères hydrosolubles comprennent, sous la forme d'unités polymérisées, de 92 à 30 % en poids de (a), de 5 à 50 % en poids de (b) et de 3 à 25 % en poids de (c).

Procédé selon la revendication 8, dans lequel (a) est présent à une proportion de 40 à 85 % en poids.

Procédé selon la revendication 8 ou la revendication 9, dans lequel (b) est présent à une proportion de 5 à 40 % en poids.

Procédé selon l'une quelconque des revendications 10, dans lequel (c) est choisi parmi les acides carboxyliques en C₃ à C₆ monoéthéniquement insaturés et les sels de métal alcalin et d'ammonium de ceux-ci, les esters d'alkyle en C₃ à C₄ de l'acide acrylique et de l'acide méthacrylique, les esters d'hydroxyalkyle en C₃ à C₄ de l'acide acrylique et de l'acide méthacrylique, l'acrylamide, les acrylamides alkyl-substitués, les acrylamides N,N-dialyl-substitués, le styrène, le styrène sulfoné, les alkylacrylamides sulfonés, les sulfonates de vinyle, l'acide vinylsulfonique, l'acide ethylsulfonique, l'acide méthyléthylsulfonique, l'acide vinylphosphonique, l'acétylate de vinyle, les alcools alliés sulfonés, l'acrylonitrile, la N-vinylpyrrolidone, le N-vinylformamide, le N-vinyl-2,2-diméthylimidazoline ; avec la condition que si (c) comprend un ou plusieurs acides carboxyliques en C₃ à C₆ monoéthéniquement insaturés ou sels de métal alcalin ou d'ammonium de ceux-ci, alors lesdits un ou plusieurs acides carboxyliques monoéthéniquement insaturés ou sels de métal alcalin ou d'ammonium de ceux-ci ne soient pas les mêmes que (a).
14. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polymère est présent dans la composition à une proportion de 0,2 à 10 % en poids.

15. Procédé selon l'une quelconque des revendications précédentes, dans lequel la composition nettoyante est une composition détergente pour machine à laver la vaisselle automatique.

16. Composition nettoyante, qui comprend un polymère hydrosoluble tel que défini dans l'une quelconque des revendications 1 à 13.

17. Composition nettoyante selon la revendication 16, qui est sous la forme d'une composition détergente pour machine à laver la vaisselle automatique.

18. Composition nettoyante selon la revendication 17, dans laquelle le polymère est présent à une proportion de 0,2 à 10 % en poids.


20. Procédé de préparation d'un polymère tel que défini dans l'une quelconque des revendications 8 à 13, qui comprend les étapes consistant à mettre en contact un mélange des monomères (a), (b) et (c) avec un amorçeur en une quantité efficace pour polymériser ledit mélange, et à maintenir le mélange à une température élevée pour fournir le produit polymère.

21. Procédé selon la revendication 20, qui comprend en outre l'utilisation d'un solvant, par exemple de l'eau.

22. Procédé selon la revendication 20 ou la revendication 21, dans lequel un ou plusieurs de (a), (b) et (c) sont introduits dans un réacteur à une température élevée.

23. Utilisation, dans une composition nettoyante, par exemple une composition pour machine à laver la vaisselle automatique, d'un ou plusieurs polymères hydrosolubles tels que définis dans l'une quelconque des revendications 1 à 13, pour améliorer les caractéristiques anti-taches et anti-film de la composition.