252-99. AU 165 EX
7-23-74 OR 3,825,498

United States Patent Office 3,825,498
Patented July 23, 1974

3,825,498

DISHWASHING DETERGENT COMPOSITION FOR USE IN DISHWASHING MACHINES

Theodor Altenschopfer, Dusseldorf-Holthausen, and Heimold Batka, Dusseldorf-Reisholz, Germany, assignors to Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, Frankfurt am Main, Germany

No Drawing. Filed Jan. 13, 1972, Ser. No. 217,649
Claims priority, application Germany, Jan. 14, 1971, P 21 01 508.7
Int. Cl. C11d 7/54
U.S. Cl. 252—99
18 Claims

ABSTRACT OF THE DISCLOSURE

A dishwashing detergent composition for use in dishwashing machines, said composition consisting essentially of (a) about 90%–5% by weight of a water soluble alkali silicate, and (b) about 5%–90% by weight of a polyhydroxycarboxylic acid containing carboxyl or carboxylate groups and hydroxyl groups, as well as specified polymer units. The composition can contain various other ingredients.

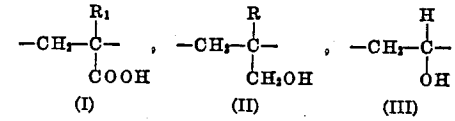
This invention relates to a dishwashing detergent composition for use in a dishwashing machine. More particularly, it relates to a dishwashing detergent composition containing a water soluble alkali silicate and a polyhydroxycarboxylic acid.

Dishwashing detergent compositions for use in automatic dishwashing machines are usually alkaline mixtures of certain cleaning agents, such as polyphosphates, silicates, alkali carbonates or alkali hydroxides. The dishwashing detergents containing the phosphates generally produce aqueous solutions having an alkaline pH. These detergents have good cleansing power, but are slightly corrosive when some sensitive objects to be washed are contacted with them. Furthermore, they have not proved entirely satisfactory for cleansing objects soiled with burnt food scraps or starch-containing deposits. The burnt food scraps are generally found on pots and pans used as cooking utensils. Additionally, there presently exists uncertainty as to the environmental effects of the phosphate containing detergents. For example, it has been alleged that the use of phosphate detergents is responsible in large part for the pollution of water supplies. Although this question has not been completely resolved, a few states are considering measures to be taken to prohibit the use of phosphate-containing detergent compositions.

On the other hand, strongly alkaline cleansing agents which generally contain the alkali carbonates or alkali hydroxides exhibit relatively strong cleansing power, but also exhibit an increased corrosion effect on glass and decorated utensils. For example, glass or ceramic dishes, cups, plates, etc. are frequently decorated with a glaze which is subject to attack by the strongly alkaline detergents.

Thus, there exists a need for a dishwashing detergent composition for use in dishwashing machines having increased cleansing power and useful on the difficult-to-remove food residues, such as burnt foods, protein containing food scraps, starches, and stains from tea leaves and coffee grounds. The dishwashing detergent should be less corrosive than at least some of the prior art compositions. The detergent should either be free of phosphates or have a greatly reduced phosphate content.

Accordingly, this invention provides a dishwashing detergent composition for use in dishwashing machines wherein the composition consists essentially of about 90%–5% by weight of a water soluble alkali silicate and about 5%–90% by weight of a polyhydroxycarboxylic acid containing carboxyl or carboxylate groups and hydroxyl groups. The alkali silicate and polyhydroxycarboxylic acid are in a weight ratio of about 1/0.5–1/18. The acid is a cross-linked or non-cross-linked polymer having predominantly C—C bonds in a main polymer chain. If the polymer chain contains side chains, at least some of the side chains contain vinyl or carbonyl groups. The polymers are built predominantly from units of formulas I and II and/or III.

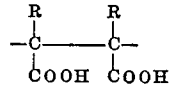


(I) (II) (III)

Units of these formulas are the main components of the polymer. Any units of formulas I, II and III present in the polymer can be arranged in any desired sequence. In these formulas, each R and R_1 in each unit is independently selected from hydrogen and a C_1–C_6 alkyl radical (i.e. an alkyl radical having 1–6 carbon atoms). Also, at least one R_1 can be a halogen atom. The average frequency of all such units in the polymer is such that the molar ratio of carboxyl or carboxylate groups in the polymer to hydroxyl groups in the polymer is about 1.1/1–16/1, preferably about 2/1–9/1. The degree of polymerization of the polymer is about 3–5,000, preferably about 3–600.

As used herein, the term "polyhydroxycarboxylic acid" means a solid cross-linked or non-cross-linked hydroxycarboxylic acid polymer.

Another preferred dishwashing detergent composition contains a polymer having a small number (relative to units of I, II and III) of units of formula IV.



(IV)

In formula IV each R radical in each unit is independently selected from hydrogen or a C_1–C_6 alkyl radical. Any units of formulas I, II, III and IV present in the polymer can be arranged in any desired sequence. The degree of polymerization and the molar ratio of carboxyl or carboxylate groups to hydroxyl groups is the same as that specified above.

In any of the aforementioned compositions, it is preferred that each R and each R_1 in each unit is independently selected from hydrogen or a methyl radical. It is also preferred that the dishwashing detergent composition contain a polymer having at least one unit of formula I in which at least one R_1 is chlorine. The units of formulas I and IV can be present as free acids or in the form of water soluble salts.

The detergent compositions of this invention can also contain the customary detergent additives, such as alkalies, slightly foaming non-ionic surfactants, chlorine separating compounds, enzymes, complexing agents, etc. The preferred formulas for detergent compositions are set forth below.

A particularly preferred dishwashing detergent composition has about the following formula:

(a) 5–90% by weight of the polyhydroxycarboxylic acid or its water soluble salts,
(b) 90–5% by weight of the soluble alkali silicate,
(c) 0–5% by weight of an alkali hydroxide or alkali carbonate,
(d) 0–10% by weight of a slightly foaming, non-ionic surfactant selected from the group consisting of alkylene oxide adducts of higher fatty alcohols or alkyl phenols having about 10–18 carbon atoms, preferably 12–18

carbon atoms, or alkylene oxide adducts of polypropylene glycol having a molecular weight of about 900–4000,

(e) 0–10% by weight of an active chlorine releasing compound,

(f) 0–5% by weight of an enzyme or enzyme mixture selected from the group consisting of hydrolases, preferably amylases, proteases and lipases, and

(g) 0–10% by weight of a complexing agent selected from the group consisting of the hydroxy polycarboxylic acids, amino polycarboxylic acids, amino polyphosphonic acids and hydroxy alkane phosphonic acids, as well as their water soluble salts and further in which the ratio of alkali silicate to polyhydroxycarboxylic acid is about 1/0.5–1/18.

The detergent composition of this invention can be adapted to the various purposes and requirements of use. A composition which develops a particularly strong cleaning effect against protein containing burnt scraps of food has about the following composition:

(a) 5–80% by weight of a polyhydroxycarboxylic acid or its water soluble salts,

(b) 18–48% by weight of a soluble alkali silicate,

(c) 0–5% by weight of an alkali hydroxide or alkali carbonate,

(d) 1–5% by weight of a slightly foaming nonionic surfactant selected from the group consisting of alkylene oxide adducts of higher fatty alcohols having about 12–18 carbon atoms, alkylene oxide adducts of alkyl phenols with 12–18 carbon atoms, or alkylene oxide adducts of polypropylene glycol having a molecular weight of about 900–4000, and

(e) 1–5% by weight of an active chlorine releasing compound, and further in which the ratio of alkali silicate to polyhydroxycarboxylic acid is about 1/1.2–1/4.

For an enzyme-containing composition particularly effective for removing starch-containing residues, the following composition is preferred:

(a) about 60–90% by weight of the polyhydroxycarboxylic acid or its water soluble salts,

(b) about 5–38% by weight of the soluble alkali silicate,

(c) about 0–5% by weight of an alkali hydroxide or alkali carbonate,

(d) about 1–5% by weight of a slightly foaming non-ionic surfactant from the group of alkylene oxide adducts of higher fatty alcohols or alkyl phenols with 12–18 carbon atoms, or polypropylene glycol having a molecular weight of about 900–4000,

(e) about 1–5% by weight of an enzyme or enzyme mixture selected from the group consisting of hydrolases, preferably amylases, proteases and lipases,

(f) about 0–10% by weight of a complexing agent selected from the group consisting of the hydroxypolycarboxylic acids, amino-polycarboxylic acids, amino polyphosphonic acids and hydroxy alkane phosphonic acids, as well as their water soluble salts,

and wherein the ratio of alkali silicate to polyhydroxycarboxylic acid is about 1/4–1/18.

While the compositions of above mentioned formulas are generally solid, lumpy or powdery cleaning agents, a liquid, slurry or paste mixture which can be dosed automatically can be used. A preferred formula consists essentially of:

(a) about 10–50% by weight of the polyhydroxycarboxylic acid or its water soluble salts,

(b) about 2–30% by weight of the soluble alkali silicate,

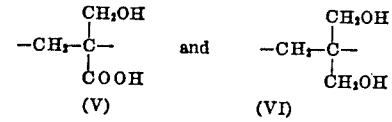
(c) about 2–20% by weight of an alkali hydroxide,

(d) about 30–86% by weight of water, and wherein

the ratio of alkali silicate to polyhydroxycarboxylic acid is about 1/0.5–1/18.

The polyhydroxycarboxylic acids suitable for use in this invention are described in German published application 1,904,941 (U.S. Application S.N. 7,251, filed Jan. 30, 1970 now U.S. Pat. No. 3,686,145). The polyhydroxycarboxylic acids can be produced by known methods. For example, they can be obtained by capolymerizing acrolein, acrylic acid or substituted acrylic acids in the presence of radical catalysts or redox catalysts and by subsequent conversion according to a Cannizzaro reaction. Also, they can be obtained by copolymerizing substituted or unsubstituted acrylic acids with allyl alcohol. They can also be produced by saponification of copolymers of acrylic acid esters and esters of vinyl alcohol or their derivatives such as acrylonitrile. Also, they can be produced by the oxidation of copolymers of acrolein with allyl alcohol or its derivatives, or with vinyl alcohol derivatives. They can also be produced by the cyclopolymerization of allyl acrylate, the cyclopolymerization of allyl acrylate with acrylic acids and simultaneous saponification, as well as the partial oxidation of polyacrolein, or its homo- or copolymerizates and subsequent conversion according to a Cannizzaro reaction. Basically, all polymerization processes are suitable, for example, precipitation, solution polymerization, bulk polymerization, etc.

The preferred polyhydroxycarboxylic acids are those that can be produced by the oxidative polymerization of acrolein, and subsequent treatment of the resulting polymerizate with a strong base according to a Cannizzaro reaction. Preferred strong bases are the alkali hydroxides. The preferred polyhydroxycarboxylic acids can optionally contain small quantities of units of the formulas V and VI:



(V) (VI)

Polyhydroxycarboxylic acids containing unts of these formulas are obtained when conversion is carried out in the presence of formaldehyde and according to the Cannizzaro reaction.

The water soluble salts of the polyhydroxycarboxylic acids can also be used in the novel dishwashing detergent of this invention. The preferred salts are the alkali salts. Sodium salts and ammonium salts are particularly preferred.

The polymers can have vinyl or carbonyl groups in sidechains in minor amounts relative to the amounts of the units identified as (I), (II) and (III) above.

In all cases, it is necessary to select the polymerization and reaction conditions, and in particular the amount of the oxidizing agent, in such a manner that the ratio of carbonyl or carboxylate groups to hydroxyl groups in the final product is as defined above and, furthermore, in such a manner that the minimum degree of polymerization is about 3. In other words, there must be the required number of different units as defined above.

As oxidation agents, peroxides or peracids may be used. Preferred is the oxidation with H_2O_2. In case of the oxidation polymerization, it is possible to adjust the ratio of carboxyl to carbonyl groups by the ratio of oxidizing agent to amount of acrolein. The higher this ratio, the larger will be the number of carboxyl groups in the final polymer, and conversely. Since the peroxide compound also acts as chain-regulating agent, it will be understood that the degree of polymerization will be controlled also by the amount of oxidizing agent. The degree of polymerization decreases with an increasing amount of oxidizing agent and conversely. For instance, with a ratio of H_2O_2 to acrolein of 1:1, it is possible to obtain an average polymerization degree of 3.2 and a COOH/C=O-ratio of 5:1. On the other hand, if under otherwise the same conditions, the ratio employed is 0.7:1, the degree of polymerization will be 13 and the ratio between carboxyl group and C=O group will be 3.2:1.

The oxidation polymerization of the acrolein can also be carried out in the presence of other copolymerizable monomers in virtually any desired amounts. The use of acrylic acid is preferred since this will directly influence the contents of carboxyl groups in the polymer. Besides, the acrylic acid content in the starting product also affects the degree of polymerization in that this degree increases with the content of acrylic acid.

The homo- or copolymerization of the acrolein can be carried out, depending on the desired contents of carboxyl groups in the final polymer, both in solution and as precipitation polymerization and, preferably, in an aqueous medium. If peroxy compounds are used as oxidation agents, it is preferred, first, to introduce these compounds and, if desired, the comonomer or a part thereof into an aqueous solution or suspension, and to add the acrolein and, if desired, the residual comonomer only at an increased temperature of, for instance, between 50 and 100° C.

In case of a solution polymerization, the polymers obtained can be used, if desired, directly for further reactions preferably after concentration of the solution. It is advisable in this case to destroy any residual amounts of oxidizing agent that may be present in the solution, for instance by addition of small amounts of MnO_2 or activated carbon. It is, however, also possible to precipitate the solution polymers from the mass by means of a dilute acid, for instance hydrochloric acid. In this operation the remaining monomers can be recovered, for instance by distillation, directly from the reaction mass. The distillation residue in this case constitutes a highly concentrated, aqueous solution of the polymer which can be used for further reaction.

It is, however, also possible to go through with the distillation up to dryness, and thus to obtain the pure polymer in solid form.

If the polymerization is carried out as a precipitation polymerization, it is easy to separate the polymers by filtration. The residual monomers in the filtrate can then be used for further purposes in the form in which they are present in the filtrate. The precipitation polymer can be purified with water or, if desired, by passing air therethrough.

The thus-obtained polyaldehydro-carboxylic acids can be further reacted in an aqueous solution or suspension with a strong base, in the presence of formaldehyde if desired. This can be carried out by using the formaldehyde in about the stoichiometric amount relative to the aldehyde groups which are present in the polymer and by stirring for an extended period of time at room temperature or at an elevated temperature up to about 100° C. After 2 hours, the yield is already about 60–70%, and within 24 hours will increase to 90–100%. The Cannizzaro reaction may be carried out much more rapidly by selecting suitable conditions, and this particularly in the case of the reaction with water-soluble polyaldehydocarboxylic acids.

The reaction in solution results in solutions which, in addition to the salts of the hydroxycarboxylic acid polymers, contain an excess of a base. They can be concentrated by evaporation to dryness. The thus-obtained salt can be used directly as complexing agent. By precipitation from the reaction mass, for instance with methanol, the salts are obtained in a particularly pure form. However, the solution may also be neutralized prior to evaporation with a dilute acid such as hydrochloric acid, or the free acid may be precipitated. Likewise, the course of the Cannizzaro reaction may be controlled in such a manner that eventually virtually neutral salt solutions are obtained. This can be accomplinhed by selecting the amount of added base in such a manner that the excess of base decreases with continuing reaction, and finally, at the end of the reaction, just reaches zero.

The neutralization of the excess base should be effected only with a type of acid of which the salts do not interfere in the use of the polymers. Such acid is, for instance, carbon dioxide. However, it is preferred to carry out the neutralization with the hydroxycarboxylic acid polymers themselves in pure form or directly with the reaction products of the first reaction stage, that is the polyaldehydro-carboxylic acids or the solution or suspensions thereof. In this manner, there are obtained pure, neutral solutions of the salts of the hydroxycarboxylic acid polymers from which the latter can easily be isolated by evaporation of the water. The hydroxycarboxylic acids which are used for the neutralization can, for instance, be precipitation polymers obtained as described above. They can easily be precipitated from the solutions obtained in the reactions by means of a dilute acid.

The polymers of the invention, as already pointed out, predominantly have carbon-to-carbon bonds in the main chain. The polymers predominantly consist of the above-identified units (I) and (II) and/or (III). These units are the main portion of the main chain which is predominantly formed by carbon-to-carbon bonds. They are in part formed when the polyaldehydrocarboxylic acid is subjected to the Cannizzaro reaction. In this reaction, there may however also be formed intermolecular aldol condensation between the active CH groups which are α-oriented relative to the aldehyde groups in the polyaldehydrocarboxylic acid and, on the other hand, the carbonyl groups of one or several adjacent chains. In this way there result cross-linking connections.

In case of the use also of further comonomers in addition to acrolein and possibly an acrylic acid such as maleic acid and/or vinyl alcohol derivatives and/or allyl alcohol units of the type (III) and (IV), as defined above, may be present in minor amounts in the main chain. The amount may be up to 50 mol percent. These units can be used to control the water solubility and/or the acidity and thus the use of the complexing agents in extreme pH ranges.

Units of the type (V) and (VI) form if the reaction of the polyaldehydrocarboxylic acids is carried out with a strong base by the Cannizzaro method in the presence of formaldehyde. The amount of aldehyde in this case will control the degree of cross-linking.

The polyhydroxycarboxylic acids used in the detergent composition of this invention are substitutes for the phosphates used in conventional detergents. It will, of course, be understood that the polyhydroxycarboxylic acids can be replaced in part by alkali phosphates or alkali polyphosphates to reduce the cost of the detergent composition. Sodium hexametaphosphate or pentasodium-triphosphate are typical of the phosphate substitutes which can be used in the composition of this invention. These phosphates are customarily used in detergents.

The detergent composition of this invention also contains a water soluble alkali silicate. Sodium or potassium metasilicates are preferred water soluble alkali silicates. When using sodium or potassium metasilicates, it is particularly preferred that the ratio of alkali oxides to silicon dioxide is of 1/0.5–1/3.5. Alkali hydroxide or alkali carbonates can be used along with or in place of some of the soluble alkali silicates. Sodium hydroxide, potassium hydroxide and their corresponding carbonates are preferred. However, not more than 30 percent by weight of the alkali silicate is to be replaced by an alkali hydroxide since the more strongly alkaline solutions obtained exhibit a more corrosive effect on the objects being cleaned.

The wetting effect of the detergent composition can be improved by the addition of a slightly foaming nonionic surfactant. Among the preferred surfactants are ethylene oxide adducts of higher molecular weight polypropylene glycols having molecular weights of about 900–4000, adducts of ethylene oxide or ethylene oxide and propylene oxide with higher fatty alcohols, such as dodecyl alcohol, palmityl alcohol, oleoyl alcohol and their mixtures, as well as alcohols having chain lengths of C_{12}–C_{18} pro-

duced synthetically as for example by oxosynthesis, as well as the corresponding alkylene oxide adducts of nonyl phenol. Production of the surfactants is well known in the art. For example, a quantity of alkaline catalyst is reacted with about three times as much alkaline oxide at an elevated temperature and with the optional use of elevated pressure. Examples of compounds suitable for the addition reaction are the adduct of 10%–30% by weight ethylene oxide and a polypropylene glycol having a molecular weight of about 1,750, the adduct of 20 moles ethylene oxide or 9 moles ethylene oxide and 10 moles propylene oxide with nonyl phenol, the adduct of 5–12 moles ethylene oxide and a fatty alcohol mixture having chain lengths of C_{12}–C_{18}, containing about 30% by weight oleoyl alcohol, and the like.

It has been found that certain residues on objects to be cleaned are particularly difficult to remove. For example, it has been found that an active chlorine releasing compound or enzymes should be used in the detergent composition to remove burnt scraps of food, lipstick and tea stains. Preferred chlorine releasing compounds include the alkali salts of isocyanuric acids, for example potassium dichloroisocyanurate, the alkali hypochlorites, for example lithium or sodium hypochlorite, and complex salts containing hypochlorite, for example, the so-called chlorinated phosphates.

Among the enzymes suitable for use in the detergent composition are those derived from animal or plant materials, especially digestive ferments, yeasts and strains of bacteria. In most instances they represent a complex mixture of various enzymatic agents. Enzymes or enzyme mixtures selected from the group of hydrolases are preferred. Particularly preferred are the amylases, protease and lipases which cleave starch, albumin or fats. The enzymes can be produced from strains of bacterial fungi, yeasts, or animal organs by methods well-known in the art. Enzyme mixtures have been found to be particularly effective against starch and albumin-containing food deposits. Enzymes obtained from *Bacillus subtilis* are particularly suitable for use in the dishwashing detergents. Such enzymes are relatively stable in the presence of alkalis, and retain their activity at temperatures between about 45°–70° C.

Complexing agents can be used as buffering agents and water softening agents. Typical of the complexing agents which can be used are hydroxycarboxylic acids, such as citric acid and tartaric acid, the amino polycarboxylic acids, such as amino triacetic acid, ethylene diamino tetracetic acid, amino tri-(methylene phosphonic acid), ethylene diaminotetra-(methylene phosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid as well as the higher homologues of the above-mentioned polyphosphonic acids. It will of course be understood that the water soluble salts, such as the potassium and sodium salts, can be used instead of the free acids.

In addition to the aforementioned compounds, the detergent composition can contain other components, especially inorganic salts such as sodium sulphate or sodium chloride which act as detergent agents. Other possible additives include substances which have a buffering effect, dyes, perfumes, enzyme activating additives, such as ammonium chloride, etc.

When the dishwashing detergent composition of this invention is in the form of a solid or powder, it can be finished by grinding or mixing the various components by methods well known in the art. In order to obtain an intimate mixture of powdery components, it is preferable to spray the powder during or after the mixing process with an aqueous solution of crystallizing salts. For example, sodium sulphate or one of the aforementioned nonionic surfactants can be used. Such a treatment also improves the dusting characteristics of the powdery detergent composition.

The dishwashing detergent composition can be used in liquid form by dissolving the individual components in water and mixing the resulting solution. Dissolution of some components, particularly the organic components, can be aided by the use of other solvents, such as ethanol, propynol or isopropynol. When the detergent composition is used in paste or slurry form, the viscosity can be adjusted with water soluble polymeric compounds, such as methyl cellulose, carboxymethylcellulose, or polyacrylates. The liquid or paste-like detergent compositions are preferably sold as commercial concentrates having about 14%–70% by weight solid substances, preferably about 20%–50% by weight.

The dishwashing detergent composition can be used in domestic dishwashers as well as in commercial dishwashing machines. Addition of the detergent to the machine can be made by hand or by means of suitable dosing devices. Liquid concentrates are particularly suitable for use in automatic liquid dosing devices conventionally used. When a solid or powdery detergent composition is used, the concentration of detergent in water during the washing cycle should be about 0.5–10 g./liter, preferably 2–5 g./liter. When liquid detergent compositions are used, the amount employed should be sufficient to provide about 6–10 g./liter. The cleaning liquors should have a pH of about 7–12, preferably about 8–11. The machine washing cycle is generally followed by a few rinsing cycles using clear water. During the rinsing cycle, conventional rinsing agents can be used. After drying, clean dishes and utensils having excellent hygienic qualities are obtained.

The dishwashing detergent composition of this invention exhibits excellent cleaning capacity. It is particularly suitable for removing protein-containing burnt scraps of food, traces of lipstick, tea stains, and coffee grounds. The compositions containing enzymes or enzyme mixtures are excellent for removing starch from the surfaces of dishes and cooking utensils, and prevent the development of starch coatings. The low corrosive effect of the compositions of this invention make them particularly suitable for use on utensils having a porcelain glaze. Finally, water pollution problems attributable to the use of phosphates in detergents are minimized because of the greatly reduced, or in some cases the total absence, of phosphates.

This invention will be more clearly understood by reference to the following examples. All parts, proportions and percentages are by weight unless otherwise indicated. The detergent compositions contain polyhydroxycarboxylic acids, which can be prepared according to Preparation I or analogous methods. The carboxyl and hydroxyl content of the acids is expressed as a percentage, and refers to the number of COOH or OH groups per 100 monomer units in the polymer molecule.

PREPARATION I

Polyhydroxycarboxylic Acid A

(a) 520 ml. of distilled water and 260 ml. of 30% hydrogen peroxide are heated to 60° C. Beginning with 50° C., 400 ml. of freshly distilled acrolein are added drop by drop within 2½ hours. During this time a white flaky polymer will already have been obtained. After completion of the addition of acrolein, this mixture is stirred for another 2 hours at 60° C. with a slight reflux, which finally stops completely. Then this is diluted with 500 ml. of distilled water. The reaction mixture is allowed to cool and is filtered off after standing for a few hours. The deposit is washed with distilled water until odorless, and is dried over NaOH in a vacuum at 50° C. There is obtained 186 g. polyaldehyde carboxylic acid with a medium molecular weight of 7500; degree of polymerization: about 120; carboxyl content: 44%; carbonyl content: 27%.

(b) 100 g. polyaldehyde carboxylic acid, produced according to (a), are dissolved in 400 ml. of distilled water, and 100 ml. of a 40% formaldehyde solution are added. 125 ml. of 40% NaOH is allowed to flow into the mixture while stirring and within 40 minutes. 10 minutes after the

beginning of the NaOH addition, the reaction mixture becomes highly viscous and is diluted with 400 ml. distilled water. After addition of 60 ml. of the NaOH quantity provided, a strong drop in the viscosity occurs. A clear, highly fluid bright yellow solution is obtained. After standing for a few hours it is precipitated by allowing 280 ml. of an aqueous 20% HCl solution to flow in. This is allowed to settle for 15 minutes, it is decanted from the deposit, and the deposit is washed with distilled water. After preliminary drying, preliminary grinding, washing and final drying, one will obtain 66 g. polyhydroxycarboxylic acid A with a carboxyl content of 58% and a hydroxyl content of 31% (COOH:OH ratio 1.85).

(c) 3 g. of the polyhydroxycarboxylic acid A produced according to (b) are dissolved in 120 ml. distilled water, and 15 ml. of 1 N sodium hydroxide solution are allowed to run into this while stirring. The pH 15 minutes afterwards is 7. It is filtered off from undissolved parts, and it is steamed until dry. There is obtained 3.5 g. of the Na salt of polyhydroxycarboxylic acid A.

The following polyhydroxycarboxylic acids are produced using the method of Preparation I: (P=average degree of polymerization):

B—Product from reaction of acrolein and acrylic acid in a ratio of 7:1, P=10. COOH:OH ratio 3.6.

C—Product from reaction of acrolein, acrylic acid and formaldehyde in a ratio of 1:2.5:0.5, P=320, COOH content 62.8, OH content 13.5; COOH:OH ratio 4.6.

D—Product from reaction of acrolein and acrylic acid in a ratio of 1:0.9, P=60, COOH:OH ratio 2.3.

E—Product from reaction of acrolein, acrylic acid and maleic acid in a ratio of 1:0.5:0.1, P=65, COOH:OH ratio 4.9.

F—Product from reaction of acrolein, P=18, COOH content 58%, OH content 7%, COOH:OH ratio 8.3.

The preceding products as well as additional suitable products can be produced in accordance with the examples of German published application 1 904 941 (U.S. Application S.N. 7,251 filed Jan. 30, 1970).

Example 1

To check the cleaning results of the cleaning mixtures claimed, glass dishes with burnt scraps of food, milk, chocolate pudding and minced meat are treated in a household dishwasher with 3 g. detergent per liter of washing liquor in the cleaning cycle. The food deposits are selected in such a way that their removal is possible only with detergents which have an especially high cleaning power. Washing is accomplished with a detergent having the following composition:

(a) 40% sodium metasilicate with a ratio of sodium oxide to silicon dioxide of 1:1, and
(b) 60% sodium salt of polyhydroxycarboxylic acid A.

In the clean rinsing cycle, 0.4 g./liter of a commercial clear rinsing agent adjusted to an acid value is used. After completion of the entire washing cycle, evaluation of the cleaning capacity of the cleaning mixtures is made. For the individual evaluation, a point system from 0 to 10 is used, whereby 0 designates "without recognizable cleaning effect" and 10 indicates "complete elimination of the food deposits in the test." From this a number of intermediate values result which make possible a graduated evaluation. In the example of the above-mentioned cleaning mixture, the following result is achieved:

Removal of burnt milk: 10
Removal of burnt chocolate pudding: 9
Removal of burnt minced meat: 8

With a good commercial cleaning powder having a phosphate base used similarly, the following cleaning values are obtained:

Removal of burnt milk: 8
Removal of burnt chocolate pudding: 7
Removal of burnt minced meat: 6

Example 2

Washing is accomplished under the conditions of Example 1 with 3 g./liter of the following cleaning mixture:

(a) 40% sodium metasilicate having a ratio of sodium oxide to silicon dioxide of 1:1,
(b) 40% sodium salt of the polyhydroxycarboxylic acid B, and
(c) 20% pentasodium triphosphate.

The cleaning result corresponds to that of Example 1.

Example 3

Washing is accomplished as in Example 1 with 3 g./liter of the following composition:

(a) 40% sodium metasilicate having a ratio of sodium oxide to silicon dioxide of 1:2.75,
(b) 30% sodium salt of the polyhydroxycarboxylic acid B,
(c) 29% pentasodium triphosphate, and
(d) 1% of an adduct of 30 mole percent of ethylene oxide with a polypropylene glycol having a molecular weight of 900.

The following cleaning result is achieved:

Removal of burnt milk: 10
Removal of burnt chocolate pudding: 9
Removal of burnt minced meat: 8

Example 4

Washing is accomplished as in Example 1 with 3 g./liter of the following cleaning composition:

(a) 40% sodium metasilicate having a ratio of sodium oxide to silicon dioxide of 1:1.25,
(b) 59% sodium salt of the polyhydroxycarboxylic acid C, and
(c) 1% of an adduct of 5 moles ethylene oxide with an unsaturated fatty alcohol mixture with chain lengths of C_{12}–C_{18}.

The cleaning result corresponds to that in Example 3.

Example 5

A cleaning mixture of the following composition is used in a household dishwasher at a concentration of 3 g./liter:

(a) 30% sodium metasilicate having a ratio of sodium oxide to silicon dioxide of 1:1.35,
(b) 27% calcined soda,
(c) 40% sodium salt of the polyhydroxycarboxylic acid F,
(d) 2% potassium dichloroisocyanurate, and
(e) 1% of an adduct of 5 moles ethylene oxide with an unsaturated fatty alcohol mixture with chain lengths of C_{12}–C_{18}.

Cups and glasses with tea stains and remnants of lipstick were washed completely clean while protecting the decorative patterns well.

Example 6

The following cleaning mixture is used in a commercial dishwasher in a concentration of 3 g./liter:

(a) 27% sodium metasilicate having a ratio of sodium oxide to silicon dioxide of 1:0.95,
(b) 10% caustic soda,
(c) 60% sodium salt of the polyhydroxycarboxylic acid E,
(d) 2% potassium dichloroisocyanurate, and
(e) 1% of an adduct of 5 moles ethylene oxide with an unsaturated fatty alcohol mixture with chain lengths of C_{12}–C_{18}.

In the actual washing operation of a canteen in a plant, an excellent cleaning result is obtained. Even burnt scraps of food are completely removed.

Example 7

The washing is accomplished with 3 g./liter of the following cleaning composition:

(a) 57% sodium salt of polyhydroxycarboxylic acid A,
(b) 40% sodium metasilicate having a ratio of sodium oxide to silicon dioxide of 1:1.35,
(c) 2% potassium dichloroisocyanurate, and
(d) 1% of an adduct of 5 moles ethylene oxide with an unsaturated fatty alcohol mixture having chain lengths of C_{12}–C_{18}.

With this the following cleaning values are achieved:

Removal of burnt milk: 10
Removal of burnt chocolate pudding: 10
Removal of burnt minced meat: 10

The cleaning performance must be considered excellent.

Example 8

Washing is accomplished with 3 g./liter of the following cleaning composition:

(a) 30% sodium salt of the polyhydroxycarboxylic acid F,
(b) 40% sodium metasilicate with a ratio of sodium oxide to silicon dioxide of 1:0.95,
(c) 27% pentasodium triphosphate,
(d) 2% potassium dichloroisocyanurate, and
(e) 1% of an adduct of 30 moles percent ethylene oxide to form a polypropylene glycol with a molecular weight of 900.

The cleaning values achieved with this are:

Removal of burnt milk: 10
Removal of burnt chocolate pudding: 10
Removal of burnt minced meat: 10

The results are excellent. With this mixture, food deposits which are very difficult to remove are completely eliminated.

Example 9

Washing is accomplished with 3 g./liter of the following cleaning composition:

(a) 40% sodium salt of polyhydroxycarboxylic acid B,
(b) 37% sodium metasilicate with a ratio of sodium oxide to silicon dioxide of 1:0.95,
(c) 15% sodium sulfate,
(d) 2% potassium dichloroisocyanurate, and
(e) 1% of an adduct of 5 moles ethylene oxide with an unsaturated fatty alcohol mixture with chain lengths of C_{12}–C_{18}.

The cleaning values are analogous to those in Example 7.

Example 10

Cups with dried tea leaves and coffee grounds are washed with 2 g./liter of a mixture of 2 parts sodium salt of polyhydroxycarboxylic acid A and one part sodium metasilicate having a ratio of sodium oxide to silicon dioxide of 1:1.25.

The cleaning values achieved with this are in all cases 10,

Example 11

A cleaning experiment is made with 9 g./liter of a liquid cleaner having the following composition:

(a) 30% sodium salt of polyhydroxycarboxylic acid D,
(b) 5% of an aqueous 50% sodium lye solution,
(c) 11% of an aqueous 30% sodium metasilicate solution, and
(d) the remainder water.

The following cleaning results are achieved:

Removal of burnt milk: 10
Removal of burnt chocolate pudding: 10
Removal of burnt minced meat: 10

The cleaning result must be designated as optimum.

Example 12

Pattern tests are conducted according to German Standard DIN 51035.

It is particularly important that dishwashing agents do not attack too strongly the glazed patterns and colors on dishes. The determination of effectiveness of washing agents is made according to German Standard 51035, "Determination of the Resistance of Fired Glazed Pattern Colors and Decorations to Alkaline Cleaning Agents." The test is accomplished by treatment with a 1% trisodium phosphate solution at boiling temperature and for 30 minutes. The attack on glazed pattern colors achieved with this test can be considered to be equivalent to about 5000 wash cycles in a dishwasher.

The results of the decor test carried out with various detergents are summarized in Table I. The test clearly shows the reduced corrosive effect of the detergents of this invention as compared to trisodium phosphate or a commercial alkaline cleaner having tripolyphosphate base.

TABLE I.—DECOR TEST ACCORDING TO DIN 51035

	Rosenthal test plate			Seltmann test plate							
Detergent	Blue	Red	Yellow	Blue	Green	Dark green	Gray	Light green	Red	Dull gold	Glossy gold
Water	—	—	—	—	—	—	—	—	—	—	—
Na_3PO_4 DIN test	—	Abrasion	Abrasion	—	Slight abrasion.	Slight abrasion.	—	Slight abrasion.	—	Spotty	—
Commercial detergent	—	—	Slight abrasion.	—	Abrasion	do	—	—	—	do	—
Mixture of example 7	—	—	—	—	—	—	—	—	—	—	—

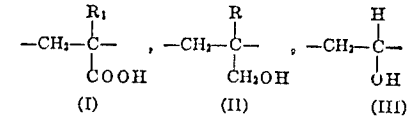
NOTE.—The dash (—) means no visible attack.

We claim:

1. A dishwashing detergent composition for use in dishwashing machines, said composition consisting essentially of:

(a) about 90–5% by weight of a water soluble alkali silicate, and

(b) about 5–90% by weight of a polyhydroxycarboxylic acid or a water soluble sodium salt thereof containing carboxyl or carboxylate groups and hydroxyl groups, the said polyhydroxycarboxylic acid being a cross-linked or noncross-linked polymer having predominantly C—C bonds in the main polymer chain and vinyl or carbonyl groups in at least some of any side chains, said polymer consisting essentially of predominantly units of formulas I and II or I and III or I and II and III:

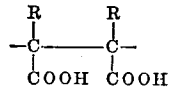


(I) (II) (III)

in which each R and each R_1 in each unit is independently selected from hydrogen and a C_1–C_6 alkyl radical, or at least one R_1 is a chlorine atom, and in which any units of formulas I, II and III present in the polymer are arranged in any desired sequence, the average frequency of all said units in the polymer corresponding to a molar ratio of carboxyl or carboxylate groups in the polymer to hydroxyl groups in the polymer of about 1.1/1–16/1, said polymer having a degree of

polymerization of about 3–5000, and further in which the alkali silicate and polyhydroxycarboxylic acid are in a weight ratio of about 1/0.5–1/18.

2. Dishwashing detergent composition of Claim 1 in which the polymer contains a small number of units of formula IV:



(IV)

in which each R radical in each unit is independently selected from hydrogen or a C_1–C_6 alkyl radical, and any units of formulas I, II, III and IV present in the polymer are arranged in any desired sequence, and the frequency of all units in the polymer corresponds to a molar ratio of carboxyl or carboxylate groups in the polymer to hydroxyl groups in the polymer of about 1.1/1–16/1, said polymer having a degree of polymerization of about 3–5000.

3. Dishwashing detergent composition of Claim 1 in which each R and each R_1 in each unit is independently selected from hydrogen or a methyl radical.

4. Dishwashing detergent composition of Claim 1 wherein the polymer contains at least one unit of formula I in which at least one R_1 is chlorine.

5. Dishwashing detergent composition of Claim 3 in which any units of formulas I and IV are present as free acids or in the form of water soluble sodium salts.

6. Dishwashing detergent composition of claim 3 in which the molar ratio of carboxyl or carboxylate groups to hydroxyl groups is about 2/1–9/1 and the degree of polymerization is about 3–600.

7. Dishwashing detergent composition of claim 4 in which the molar ratio of carboxyl or carboxylate groups to hydroxyl groups is about 2/1–9/1 and the degree of polymerization is about 3–600.

8. Dishwashing detergent composition of claim 1 consisting essentially of:

(a) about 5–90% by weight of the polyhydroxycarboxylic acid or its water soluble sodium salts,

(b) about 90–5% by weight of the water soluble alkali silicate,

(c) about 0–5% by weight of sodium hydroxide, potassium hydroxide, sodium carbonate or potassium carbonate,

(d) about 0–10% by weight of a slightly foaming nonionic surfactant selected from the group consisting of the adduct of 10%–30% by weight ethylene oxide and a polypropylene glycol having a molecular weight of about 1,750, the adduct of 20 moles ethylene oxide or 9 moles ethylene oxide and 10 moles propylene oxide with nonyl phenol, the adduct of 5–12 moles ethylene oxide and a fatty alcohol mixture having chain lengths of C_{12}–C_{18}, containing about 30% by weight oleoyl alcohol, an adduct of 30 mole percent of ethylene oxide with a polypropylene glycol having a molecular weight of 900, and an adduct of 5 moles ethylene oxide with an unsaturated fatty alcohol mixture with chain lengths of C_{12}–C_{18},

(e) about 0–10% by weight of an active chlorine releasing compound selected from the group consisting of alkali salts of isocyanuric acid, alkali hypochlorites and chlorinated phosphates, and

(f) about 0–5% by weight of an enzyme or enzyme mixture selected from the group consisting of amylases, proteases and lipases,

whereby the ratio of alkali silicate to polyhydroxycarboxylic acid is about 1/0.5–1/18.

9. Dishwashing detergent composition of Claim 8 consisting essentially of:

(a) about 50–80% by weight of the polyhydroxycarboxylic acid or its water soluble sodium salts,

(b) about 18–48% by weight of the water soluble alkali silicate,

(c) about 1–5% by weight of the slightly foaming nonionic surfactant, and

(d) about 1–5% by weight of the active chlorine releasing compound,

wherein the ratio of alkali silicate to polyhydroxycarboxylic acids is about 1/1.2–1/4.

10. Dishwashing detergent composition of claim 9 in which the composition is a solid or powder.

11. Dishwashing detergent composition of claim 9 in which the active chlorine releasing compound is potassium dichloroisocyanurate.

12. A solid or powdery dishwashing detergent composition of claim 8 consisting essentially of:

(a) about 60–90% by weight of the polyhydroxycarboxylic acid or its water soluble salts,

(b) about 5–38% by weight of the soluble alkali silicate,

(c) about 1–5% by weight of the slightly foaming nonionic surfactant, and

(d) about 1–5% by weight of the enzyme or enzyme mixture,

wherein the ratio of alkali silicate to polyhydroxycarboxlyic acid is about 1/4–1/18.

13. Dishwashing detergent composition of claim 12 containing an enzyme with amylolytic or proteolytic activity, said enzyme obtained from *Bacillus subtilis*.

14. A liquid dishwashing detergent composition of claim 8 consisting essentially of:

(a) about 10–50% by weight of the polyhydroxycarboxylic acid or its water soluble salts,

(b) about 2–30% by weight of the soluble alkali silicate,

(c) about 2–20% by weight of the sodium or potassium hydroxide, and

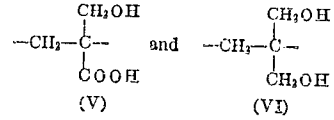
(d) about 30–86% by weight water.

15. Dishwashing detergent composition of claim 1 in which the soluble alkali silicate contains an alkali oxide and silicon dioxide in a weight ratio of about 1/0.5–1/3.5.

16. Dishwashing detergent composition of claim 1 which produces a pH value of about 7–12 in a dilute aqueous solution.

17. Dishwashing detergent composition of claim 16 in which the pH value is about 8–11.

18. Dishwashing detergent composition of claim 1 in which the polyhydroxycarboxylic acid contains a small number of units of at least one of Formulas V and VI:



(V) (VI)

References Cited

UNITED STATES PATENTS

3,544,473	12/1970	Kitchen et al.	232—99
3,686,145	8/1972	Aaschke	260—67 U
3,544,473	12/1970	Kitchen et al.	252—99
3,691,082	9/1972	Stinberg et al.	252—Dig. 12 X

MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252—95, Dig. 12; 260—67 U