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(54) Liquid cleaning compositions containing water-soluble polymer.

(57) The present invention is concerned with alkaline, cleaning concentrates, and cleaning solutions, comprising (i) alkali metal hydroxide, (ii) active chlorine source, (iii) water-soluble copolymer comprising monomer units of monoethylenically unsaturated dicarboxylic acid and at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids and carboxyl-free monoethylenically unsaturated monomers, and, optionally, (iv) alkali metal silicate. These cleaning concentrates/solutions are useful for the cleaning of food soils, and more specifically are useful for the removal of milk soils from cold and hot surfaces without the use of phosphate builders.

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The present invention is concerned with alkaline, aqueous cleaning concentrates and cleaning solutions comprising such concentrate. These cleaning concentrates/solutions are useful for the cleaning of food soils, and more specifically, are useful for the removal of milk soils from cold and hot surfaces without the use of phosphate builders.

Dairy soils are composed of two components, the soil left behind from the milk processing operation and the soil left behind at the end of the cleaning operation. The soil resulting from the milk processing operation can vary widely in composition depending on, for example, the breed of cows, the time of year and the cow's food source. Additionally, if the surface contacting the milk is a heated surface, as used in pasteurization, it may be soiled with certain components in the milk which can be denatured, degraded, caramelized, or concentrated, thereby making soil removal even more difficult.

The second soil results from the interaction between the milk soil residues and the chemicals in the cleaning solution. The problem can be compounded by poor rinsing and poor cleaning of the equipment, resulting in a substantial buildup of residual soil on the surfaces. This can lead to bacterial growth capable of causing a serious health risk when additional milk is processed through the equipment. Also, hardness ions naturally present in the water source used for rinsing or for preparing the concentrate or cleaning solution, can further compound the cleaning problem because of their tendency to react with the cleaning solution and inactivate the builder components of the cleaning solution.

Sodium polyphosphates have been used as the builder of choice in previous aqueous cleaning solutions, but because of the increased use of liquid detergents, where sodium tripolyphosphate has a limited solubility, and increased environmental concerns on the use of phosphorous containing builders, alternative compositions have been investigated. However, with the decrease in phosphate use, performance of the cleaners has also decreased.

US-A-4,579,676 claims a composition which purportedly avoids a decrease in the cleaning performance of phosphate free cleaning compositions through the use of a polyacrylic acid in combination with a soil-dispersing amount of a phosphinopolycarboxylic acid. The wash solutions are disclosed to be useful in the cleaning of cleaned-in-place food-processing equipment fouled with greasy or oily soils. However, the composition disclosed in US-A-4,579,676 continues to use the ecologically undesirable phosphorus in the form of phosphinopolycarboxylic acid.

Another patent, Belgium Patent 762,816, also discloses the use of a reduced amount of phosphorus in a cleaning solution. The solution described contains from 0 to 0.4 wt. % of a low level of alkali metal hydroxide, a sequestering agent containing amino and carboxyl groups, from 0.02 to 1 wt. % of condensed phosphate, from 0 to 0.3 wt. % alkali metal silicate and from 0.001 to 0.05 wt. % nonionic surfactant. This composition is supposedly useful for cleaning, with high efficiency and less susceptibility to contamination, heat exchangers used for pasteurizing milk and other dairy and food industry equipment.

A third patent, EP-B-0,268,873, discloses a cleaning composition based on a quaternary ammonium compound, an alkyl ether carboxylic acid, an alkali metal hydroxide, and a complex-forming aminopolycarboxylic acid. This cleaning composition is purportedly useful for the food industry, especially dairies, does not foam, and also has some disinfectant properties.

The present invention is directed to an aqueous cleaning concentrate, formulated as a water-dilutable aqueous concentrate, comprising (i) an alkali metal hydroxide, (ii) an active chlorine source, (iii) a water-soluble copolymer comprising units of a monoethylenically unsaturated dicarboxylic acid and at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids and carboxyl-free monoethylenically unsaturated monomers and, optionally, (iv) an alkali metal silicate. The present invention is also directed to aqueous cleaning solutions that do not contain any phosphorus, are suitable for the removal of food soils, and perform effectively at high water hardness levels.

According to the present invention there is provided a cleaning concentrate which comprises:

(a) about 0.25 to 20% by weight of water-soluble copolymer comprising monomer units of about 5 to 70% by weight, based on total monomers, of monoethylenically unsaturated dicarboxylic acid or salt or anhydride thereof, and about 95 to 30% by weight, based on total monomers, of at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids and carboxyl-free monoethylenically unsaturated monomers, and wherein said copolymer has a molecular weight of about 4000 to 100,000;

(b) about 2.5 to 35% by weight of alkali metal hydroxide;

(c) active chlorine source to provide the concentrate with about 1 to 5% by weight available chlorine; and, optionally,

(d) alkali metal silicate.

All percentages recited herein in connection with the present invention are percentages by weight unless specified otherwise.

The present invention enables the provision of cleaning concentrates/solutions that do not contain any

phosphorus, are suitable for the removal of food soils, and perform effectively at high water hardness levels, this being achieved by the use of the stated copolymers in an alkaline, chlorine-containing composition, with said copolymer aiding in the complete removal of residual fatty and oily soil.

Most milk soils are composed of a protein-calcium-fat complex. Although the mechanism of the process set forth herein is not fully understood, it is believed that the copolymer contained in the detergent composition of this invention interacts with the protein-calcium-fat complex on the surface of stainless steel food processing equipment, removing the calcium, and thereby enabling other detergent components to react with the fat and the protein. When the fat and the protein are in the sodium or ionized form, sodium hydroxide can saponify the fat, and chlorine can break the protein into water soluble fragments. This conjecture is supported by the fact that when non-fat milk is used as the soil source, no cleaning problem existed as measured by the test procedure herein described. Also, the copolymers used in this invention have a greater affinity for calcium as compared to previously described acrylic homopolymers. Furthermore, since there is not enough polymer in the detergent bath to sequester all the hardness ions, especially at high hardnesses, the polymer must be interacting with the calcium at a specific location, such as the substrate surface, and not improving the cleaning by dispersing more soil or by interacting with the calcium in the aqueous media. The theory of this invention is presented here as a possible explanation of the surprising results obtained, and in no way is intended to limit the scope of this invention.

Substitution of the copolymer used in this invention for phosphorus-containing compounds should be considered in any area where the use of phosphates is restricted. Since most food soils contain fats, proteins and minerals, this invention is applicable to the cleaning of any hard surface, such as glass or metal, where food soils have to be removed. Some specific applications of this invention would include automatic dishwasher detergents and institutional and industrial warewash detergents.

Additionally, because of the stability of the copolymers, used in this invention, to available chlorine, these copolymers could be applicable to any situation where a soil removal aid in an alkaline, chlorinated liquid is needed.

The copolymer used in this invention contains, as copolymerized monomer units, from 5 to 70% by weight of the monoethylenically unsaturated dicarboxylic acid or salt or anhydride thereof, and from 95 to 30% by weight of the comonomer(s), e.g. the monoethylenically unsaturated monocarboxylic acid. The preferable range is from 10 to 30% by weight of the monoethylenically unsaturated dicarboxylic acid or salt or anhydride thereof and from 90 to 70% by weight of the comonomer(s), e.g. the monoethylenically unsaturated monocarboxylic acid, and the more preferable range is from 15 to 25% by weight of the monoethylenically unsaturated dicarboxylic acid or salt or anhydride thereof and from 85 to 75% by weight of the comonomer(s), e.g. the monoethylenically unsaturated monocarboxylic acid.

Suitable monoethylenically unsaturated dicarboxylic acids include those containing from 4 to 6 carbon atoms per molecule, their salts, e.g. their alkali metal and ammonium salts, and the anhydrides of the cis dicarboxylic acids. Examples of suitable monomers include maleic acid, itaconic acid, mesaconic acid, fumaric acid, citraconic acid and the anhydrides of cis dicarboxylic acids, such as maleic anhydride. Maleic anhydride is the more preferred of these monomers.

Suitable monoethylenically unsaturated monocarboxylic acids contain from 3 to 6 carbon atoms per molecule and include acrylic acid, methacrylic acid, vinyl acetic acid, crotonic acid and acryloxypropionic acid. The more preferred monoethylenically unsaturated monocarboxylic acid is acrylic acid.

Suitable carboxyl-free monoethylenically unsaturated monomers include alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic or methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide; methacrylamide; N-tertiary butyl acrylamide; N-methyl acrylamide; N,N-dimethyl acrylamide; acrylonitrile; methacrylonitrile; allyl alcohol; allyl sulfonic acid; allyl phosphonic acid; vinyl-phosphonic acid; dimethylaminoethyl acrylate; dimethylaminoethyl methacrylate; phosphoethyl methacrylate; N-vinyl pyrollidone; N-vinylformamide; N-vinylimidazole; ethylene glycol diacrylate; trimethylolpropane triacrylate; diallyl phthalate; vinyl acetate; styrene; vinyl sulfonic acid and its salts; and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and its salts. The concentration of carboxyl-free monoethylenically unsaturated monomers can be from 0 to about 80% by weight of the total monomer concentration. The concentration is typically up to 35% by weight and is dependent upon the solubility of the particular monomer in the reaction mixture.

These copolymers may be made by a heel charge process whereby the monoethylenically unsaturated dicarboxylic acid is placed in a reactor, to which a feed of initiator and comonomer(s), e.g. monoethylenically unsaturated monocarboxylic acid, is added, or a co-feed process, whereby the monoethylenically unsaturated dicarboxylic acid is fed into the reactor concurrently with the comonomer(s), e.g.

the monoethylenically unsaturated monocarboxylic acid. This co-feed process is disclosed in European Patent Application No. 90305346.0.

The range of molecular weights, Mw, for the copolymer, as measured by aqueous gel permeation chromatography (GPC), is from about 4,000 to 100,000, preferably from about 10,000 to 30,000, and more preferably from about 10,000 to 25,000.

The alkali metal hydroxide can be any type commonly used in the art such as sodium hydroxide, potassium hydroxide or mixtures thereof. Also, the chlorine source can be either organic or inorganic including alkali metal and alkaline earth metal hypochlorites, hypochlorite addition products, chloramines and chlorimines, chloramides and chlorimides. Typically these compounds include sodium hypochlorite, potassium hypochlorite, monobasic calcium hypochlorite, dibasic magnesium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium dichloroisocyanurate, trichlorocyanuric acid, sodium dichloroisocyanurate dihydrate, 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, Chloramine T, Dichloramine T, Chloramine B, Dichloramine B, chlorine gas or mixtures thereof. The more preferred source of chlorine is sodium hypochlorite.

The cleaning concentrate of the present invention contains: from 2.5 to 35% alkali metal hydroxide, preferably from 5 to 15%, and more preferably 10%; from 1 to 5% available chlorine, preferably from 2 to 4%, and more preferably 3%; from 0.25 to 20% polymer solids, preferably from 3 to 15%, and more preferably 5.1%; and the remainder is water or other components commonly known to those skilled in the art. Optionally, alkali metal silicate, e.g. sodium silicate, may be used, e.g. at a level of up to 10%, preferably from 2 to 7%, and more preferably 4.7%, as alkali metal, e.g. sodium, silicate solids.

Other components that may be contained in the cleaning concentrate and/or cleaning solution of the present invention are any of the usual adjuvants found in detergents of this type such as inorganic phosphates, citrates, ethylenediaminetetraacetic acid, nitrilotriacetic acid, carboxyalkylamines, surfactants, and homopolymers of polyacrylic acid. To form the cleaning solution of the present invention, the cleaning concentrate may be diluted to about 0.1 to 10% with water.

The present invention will now be further illustrated by way of the following Example which is for illustrative purposes only and is not to be construed as imposing any limitation on the scope of the invention. The Example provides a representative procedure for the synthesis of the polymers used in the formulations of the present invention and all percentages recited are percentages by weight unless specified otherwise.

EXAMPLE

Polymer Preparation

To a two liter, four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 190 grams of deionized water, 6 grams of a 0.15% by weight solution of copper (II) sulfate pentahydrate dissolved in deionized water and 42.4 grams of maleic anhydride. This solution was heated to reflux at which time 200 grams of glacial acrylic acid, an initiator solution of 40 grams of deionized water and 12.5 grams of sodium persulfate, and a neutralizing solution of 217 grams of 50% sodium hydroxide, 75 equivalent percent based on the monomers, were fed into the flask linearly and separately over 2 hours while maintaining reflux. When the addition was complete the system was held at reflux for twenty minutes, then cooled to 60 $^{\circ}$ C and the solution pH was adjusted with the addition of 52 grams of a 50% solution of NaOH in water.

The resultant pH 6.7 polymer solution had a solids content of 46.0%. Based on gel permeation chromatography (GPC), the weight average molecular weight (Mw) was 15,200 and the number average molecular weight (Mn) was 7440. Residual maleic acid content was 0.2% by weight and residual acrylic acid content was 0.01% by weight, the percentages being based on the total theoretical weight of solids.

Detergent Testing

A detergent formulation utilized for the testing of this invention had the following composition: 10% sodium hydroxide, 3% available chlorine, and 5.1% polymer solids. Sodium hydroxide levels of 14% were also employed in some tests to assess the effect of higher levels of alkali on the cleaning performance as compared to the use of the polymer to boost cleaning. Sodium silicate was also used in some of the testing at a level of 4.7% sodium silicate solids, which is equivalent to approximately 3.3% silicate solids (SiO_2). The performances of these detergent compositions were compared to a typical commercial product, Interest (trademark of the Diversey-Wyandotte Corporation) detergent, which is a phosphate-based com-

position.

The detergents, both those of this invention and the Interest detergent, were tested at concentrations of from about 0.1% use level (on an as is basis) to about 2% detergent concentration in the bath. The detergents were tested predominately against a multicycle-deposited cold milk soil. The substrates soiled in the testing were 304 stainless steel panels measuring 2.54 cm x 7.62 cm x 0.094 cm (1" x 3" x 0.037"). The water used for dilution of the detergent and cleaning of the panels contained from 100 ppm to 600 ppm hardness as $CaCO_3$ and 225 ppm sodium bicarbonate, regardless of the water hardness.

The cold milk soiled panels were prepared by precleaning them with methanol, immersing them in a 1% solution of Interest detergent for 15 minutes, rinsing them with deionized water and then drying them. The chemically cleaned panels (6 at a time) were then immersed in fresh whole milk (Vitamin A&D - not skim or low fat) to about 7/8ths of their total length and agitated for exactly 15 minutes. This was the soiling portion of the test.

After the 15 minute soiling process, the panels were removed, rinsed in 48.9 °C (120 °F) running tap water with a hardness of 200 ppm as $CaCO_3$. Each test panel was then cleaned in detergent solution maintained at 60 °C in a shaker bath. The detergent solution contained the water hardness and detergent concentrations listed in the Tests. The detergent solution also contained two drops of milk added as an additional stress to the test. After the panels were exposed to the agitated detergent solution for ten minutes, the test panels were removed and rinsed in 48.9 °C (120 °F) running tap water. This constituted one cycle.

The panels were then placed back in the milk bath to start the second cycle of soiling and cleaning. In all, each panel was exposed to five complete soiling, cleaning and rinsing cycles.

After the panels were rinsed in tap water for the final time, they were immersed in a 1% protein dye solution for 2 to 3 minutes (the protein dye used was Safranine O). The dye solution immediately attached to any milk soil present that had not been removed by the detergent solutions. Depending on the amount of milk soil remaining on the panel, varying degrees of red stain resulted, the darker the red stain the more milk soil left on the panels. The stained panels were then dried with forced hot air and graded using the following scale:

Rating	Appearance
0	Panel was clean
1	A dull film was evident but no red color
2	Some red stain was seen
3	Noticeable red color covered 50% of the panel
4	Red color covered the entire panel
5	Very deep red color covered the entire panel

The results of testing demonstrate that the detergents of this invention are useful for the removal of milk soils. The results also show that the copolymers in accordance with this invention are superior to previously described acrylic homopolymers, even at equivalent molecular weights, when higher (>300 ppm) water hardnesses are used.

At higher hardnesses all polymer formulations tended to allow the formation of a scale on the test panel. The addition of sodium silicate prevented this scale formation with the copolymers in accordance with this invention, but not with acrylic homopolymers.

Test 1

Water hardness: 100 ppm

	None*	Control	Interest	A	B	C
Stain(Rank)	1(2)	1(2)	0(1)	0(1)	0(1)	2(3)
Scale	None---------->					

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,200 Mw 80:20 acrylic:maleic, Na salt
B - 15,300 Mw 80:20 acrylic:maleic, Na salt
C - 30,000 Mw 65:35 acrylic:maleic, Na salt

* No polymer present

Test 2

Water hardness: 400 ppm

	Control	Interest	A	B
Stain (Rank)	3(3)	1(1)	2(2)	3(3)
Scale	None---------->			

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt

B - 20,000 Mw 90:10 acrylic:maleic, Na salt

Test 3

Water hardness: 400 ppm

	None*	Control	Interest	A	B	C
Stain (Rank)	3(3)	3(3)	0(1)	1(2)	3(3)	3(3)
Scale	None---------->					

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt

B - 3,390 Mw 70:20:10 acrylic:maleic:AMPS, Na salt

C - 18,000 Mw 45:35:20 acrylic:maleic:MAA, Na salt

* No polymer present

Test 4

Water hardness: 400 ppm

	None*	Control	Interest	A	B	C
Stain (Rank)	3(3)	3(3)	0(1)	1(2)	3(3)	3(3)
Scale	None---------->					

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 26,000 Mw 80:20 acrylic:maleic, Na salt
C - 20,000 Mw 80:20 acrylic:maleic, Na salt

* No polymer present

Test 5

Water hardness: 400 ppm

	Control	Interest	A	B	C	D
Stain (Rank)	3(4)	1(1)	1(1)	2(2)	2.5(3)	2.5(3)
Scale	None---------->				Light	None

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 15,200 Mw 80:20 acrylic:maleic, Na salt
C - 20,000 Mw 80:20 acrylic:maleic, Na salt
D - 30,000 Mw 65:35 acrylic:maleic, Na salt

Test 6

WATER HARDNESS: 400 ppm

	Control	Interest	A	B	C	D
Stain (Rank)	3(4)	0 (1)	2(2)	2.5(3)	3(4)	2.5(3)
Scale	None---------->				Light	None

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 9,100 Mw 80:20 acrylic:maleic, Na salt
C - 8,600 Mw 70:30 acrylic:maleic, Na salt
D- 12,000 Mw 65:35 acrylic:maleic, Na salt

Test 7

WATER HARDNESS: 400 ppm

	Control	Interest	A	B	C	D
Stain (Rank)	3(4)	0 (1)	1(2)	3(4)	3(4)	2(3)
Scale	None---------->				Light	None

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 9,100 Mw 65:35 acrylic:maleic, Na salt
C - 17,600 Mw 65:35 acrylic:maleic, Na salt
D - 19,000 Mw 80:20 acrylic:maleic, Na salt

Test 8

WATER HARDNESS: 400 ppm

	Control	Interest	A	B	C	D
Stain (Rank)	3 (4)	0(1)	0(1)	2(3)	2(3)	1(2)
Scale	None	Light	None	Med	Med	None

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 8,400 Mw 76:24 acrylic:itaconic, Na salt
C - 17,400 Mw 84:16 acrylic:itaconic, Na salt
D - 14,100 Mw 76:24 acrylic:itaconic, Na salt

Test 9

WATER HARDNESS: 400 ppm

	Control	Interest	A	B	C	D
Stain (Rank)	3(5)	0(1)	1(2)	2.5(3)	2.5(3)	3(4)
Scale	None---------->			Med---------->		

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 3,650 Mw 80:20 acrylic:maleic, Na salt
C - 3,850 Mw 80:20 acrylic:itaconic, Na salt
D - 5,700 Mw 70:20:10 acrylic:maleic:MAA, Na salt

Test 10

WATER HARDNESS: 400 ppm

	Control	Interest	A	B	C	D
Stain (Rank)	3(5)	0(1)	1(2)	1(2)	2(3)	2.5(4)
Scale	None---------->					

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 56,000 Mw 80:20 acrylic:maleic, Na salt
C - 12,000 Mw 85:35 acrylic:maleic, Na salt
D - 49,000 Mw 80:20 acrylic:maleic, Na salt

Test 11

WATER HARDNESS: 600 ppm

	None*	Control	Interest	A	B	C
Stain (Rank)	3(3)	---	1(1)	1(1)	2(2)	2(2)
Scale	Slight	Heavy	None---------->			

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 12,000 Mw 65:35 acrylic:maleic, Na salt
C - 15,200 Mw 80:20 acrylic:maleic, Na salt

* No polymer present

Test 12

WATER HARDNESS: 600 ppm

	Control	Interest	A	B	B	B
Silicate (Si02)	None	---	None	None	1.7%	3.3%
Stain (Rank)	3(3)	0(1)	2(2)	2(2)	2(2)	2(2)
Scale	Med	None	None	Slight	None	None

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt

B - 14,700 Mw 80:20 acrylic:maleic, Na salt

Test 13

WATER HARDNESS: 600 ppm

	Interest	Control	Control	B	B	B
Silicate (Si02)	---	None	1.7%	None	1.7%	0.9%
Stain (Rank)	0(1)	4(5)	3(4)	1(2)	1(2)	2(3)
Scale	None	None	None	Med	None	Slight

Control:

4,500 Mw sodium Polyacrylate

Copolymers in accordance with the Present Invention:

B - 14,700 Mw 80:20 acrylic:maleic, Na salt

Test 14

WATER HARDNESS: 400 ppm

	None*	Control	Control	Control	Interest	A
Polymer level	--	X1	X2	X4	---	X1
Stain (Rank)	2(3)	2(3)	1(2)	0(1)	1(2)	0(1)
Scale	None---------->					

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt

* No polymer present

Test 15

WATER HARDNESS: 400 ppm

	Control	Interest	A	A	A	A
Polymer level	X1	---	X1	X0.75	X0.75	X0.5
Stain (Rank)	4(4)	0(1)	0(1)	2(3)	1(2)	2(3)
Scale	None---------->					

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention

A - 15,300 Mw 80:20 acrylic:maleic, Na salt

Test 16

WATER HARDNESS: 400 ppm

	Control	Interest	A	B	C	D
Stain (Rank)	1(2)	0(1)	1(2)	1(2)	1(2)	1(2)
Scale	None---------->			Med	Med	Light

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 11,600 Mw 75:25 acrylic:maleic, Na salt
C - 11,500 Mw 70:30 acrylic:maleic, Na salt
D - 14,700 Mw 80:20 acrylic:maleic, Na salt

Test 17

WATER HARDNESS: Deionized water

	Control	Interest	A	B	C	D
Stain (Rank)	0(1)	0(1)	0(1)	0(1)	0(1)	0(1)
Scale	None---------->					

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 11,600 Mw 75:25 acrylic:maleic, Na salt
C - 11,500 Mw 70:30 acrylic:maleic, Na salt
D - 14,700 Mw 80:20 acrylic:maleic, Na salt

Test 18

WATER HARDNESS: 600 ppm

	None*	Control	Interest	B	A	C
Stain (Rank)	3(3)	3(3)?	1(1)	1(1)?	1(1)	1.5(2)
Scale	None	Heavy	None	Heavy	None	------>

Control:

- 4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 18,000 Mw sodium polyacrylate
C - 14,700 Mw 80:20 acrylic:maleic, Na salt

* No polymer present

Test 19

WATER HARDNESS: 400 ppm
Detergent contains 11% NaOH

	Control	Interest	B	B	A	C
Polymer Level	X1	---	X1	X2	X1	X1
Stain (Rank)	3(5)	1(2)	2(3)	2.5(4)	0(1)	2(3)
Scale	None	None	Light	None	None	Light

Control:

4,500 Mw sodium polyacrylate

Copolymers in accordance with the Present Invention:

A - 15,300 Mw 80:20 acrylic:maleic, Na salt
B - 18,000 Mw sodium polyacrylate
C - 14,700 Mw 80:20 acrylic:maleic, Na salt

Claims

1. An cleaning concentrate which comprises:
(a) about 0.25 to 20% by weight of water-soluble copolymer comprising monomer units of about 5 to 70% by weight, based on total monomers, of monoethylenically unsaturated dicarboxylic acid or salt or anhydride thereof, and about 95 to 30% by weight, based on total monomers, of at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids and carboxyl-free monoethylenically unsaturated monomers, and wherein said copolymer has a molecular weight of about 4000 to 100,000;
(b) about 2.5 to 35% by weight of alkali metal hydroxide;
(c) active chlorine source to provide the concentrate with about 1 to 5% by weight available chlorine, and, optionally,
(d) alkali metal silicate.

2. A cleaning concentrate as claimed in claim 1, wherein the monoethylenically unsaturated dicarboxylic acid is selected from maleic acid, itaconic acid, mesaconic acid, fumaric acid, citraconic acid, and the anhydrides of cis dicarboxylic acids, such as maleic anhydride.

3. A cleaning concentrate as claimed in claim 1 or claim 2, wherein the monoethylenically unsaturated monocarboxylic acid is selected from acrylic acid, methacrylic acid, vinyl acetic acid, crotonic acid, and acryloxypropionic acid, and is preferably acrylic acid.

4. A cleaning concentrate as claimed in any preceding claim, wherein the carboxyl-free monoethylenically unsaturated monomer is selected from: alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic or methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide; methacrylamide; N-tertiary butyl acrylamide; N-methyl acrylamide; N,N-dimethyl acrylamide; acrylonitrile; methacrylonitrile; allyl alcohol; allyl sulfonic acid; allyl phosphonic acid; vinylphosphonic acid; dimethylaminoethyl acrylate; dimethylaminoethyl methacrylate; phosphoethyl methacrylate; N-vinyl pyrollidone; N-vinylformamide; N-vinylimidazole; ethylene glycol diacrylate; trimethylolpropane triacrylate; diallyl phthalate; vinyl acetate; styrene; vinyl sulfonic acid and its salts; and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and its salts.

5. A cleaning concentrate as claimed in any preceding claim wherein the copolymer comprises monomer units of the monoethylenically unsaturated dicarboxylic acid, the monoethylenically unsaturated monocarboxylic acid and, optionally, the carboxyl free monoethylenically unsaturated monomer.

6. A cleaning concentrate as claimed in any preceding claim, wherein the copolymer is prepared from a monomeric mix of about 85 to 75% by weight, based on the total monomers, of the monoethylenically unsaturated monocarboxylic acid and about 15 to 25% by weight, based on total monomers, of the monoethylenically unsaturated dicarboxylic acid, for example, a monomeric mix of 80% by weight, based on total monomers, of acrylic acid, and 20% by weight, based on total monomers, of maleic acid.

7. A cleaning concentrate as claimed in any preceding claim, wherein the alkali metal hydroxide comprises sodium hydroxide, potassium hydroxide, or a mixture thereof.

8. A cleaning concentrate as claimed in any preceding claim, wherein the copolymer has a molecular weight of about 10,000 to 25,000.

9. A cleaning concentrate as claimed in any preceding claim, wherein the active chlorine source is an alkali metal hypochlorite, for example sodium hypochlorite.

10. A cleaning solution which comprises water and a cleaning concentrate as claimed in any preceding claim, the cleaning concentrate being present in an amount of 0.1 to 10%.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90308404.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US - A - 4 897 220 (WOLFGANG TRIESELT et al.) * Column 1, line 58 - column 2, line 67; column 5, lines 3-10; column 8, lines 29-54; claims *	1,2,3, 4,5	C 11 D 3/37
P,A	EP - A2 - 0 368 214 (BASF) * Page 3, line 39 - page 4, line 46; claims *	1-5	
A	EP - A2 - 0 215 251 (BASF) * Column 2, line 5 - column 4, line 35; claims 1-5 *	1-5	
D,A	US - A - 4 579 676 (SANDRA L. BULL) * Column 2, lines 13-48; table 1 *	1,7,9	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	10-12-1990	SEIRAFI

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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