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(54) Scratch inhibiting agent.

(57) A scratch inhibiting agent for inhibiting the generation of scratches on the surface of a siliceous inorganic product caused by an alkaline detergent comprising, as a main ingredient, at least one compound selected from the group consisting of (A) aliphatic hydroxydicarboxylic acids having a functional group ratio (OH/COOH) of 1.0 to 2.0 and the alkali metal salts thereof and (B) polycarboxylic acids having a molecular weight of 5000 to 20000 and the alkali metal salts thereof.

This scratch inhibiting agent can effectively prevent the generation and expansion of scratches on the surfaces of the siliceous inorganic products without decreasing the washing power of aqueous alkaline solutions at a washing step.

EP 0 235 961 A1

0235961

SCRATCH INHIBITING AGENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a scratch inhibiting agent for inhibiting scratches generated or expanded on the surfaces of siliceous inorganic products (or articles) such as glass bottles, substrates of electric devices, and tableware.

2. Description of the Related Art

Siliceous inorganic products such as glass bottles are generally recycled after washing with hot aqueous alkaline solutions at a recovery step. However, fine flaws are generated on the surfaces of the glass bottles by impingement and friction during the recovery step. These portions are further attacked at an alkali washing step to generate scratches (i.e., the generation of whitened portions on the surfaces of the bottles). The scratches are expanded with the increase in the number of times the glass bottles are recycled, and as a result, the fine appearance of glass bottles is impaired and the commercial value of bottled beverages is decreased.

Various attempts have been made to inhibit or suppress the generation of scratches. For example, Japanese Unexamined Patent Publication (Kokai) No. 57-179053 discloses a method for coating a water-resistant silicone resin on the surface of a glass bottle. Furthermore, it is known that a washing solution containing a small amount of sodium gluconate as a scratch inhibiting agent in an aqueous alkaline solution can be used (see Senjyo of Shokuhin Kogyo (i.e., Washing in Food Industries), Chapter 5, bottle washing method, pages 120-160).

However, the former method is disadvantageous in that the process becomes complicated because of the necessity for an additional step for coating the surfaces

of glass bottles with water-resistant silicon resins, and because the chemical agent cost becomes high due to the use of the expensive silicon resins.

On the other hand, the latter method is disadvantageous in that the effect of sodium gluconate for inhibiting scratches on the surface of glass bottles is low and the possible number of times the bottle can be reused is small, although the washing process is simple and the chemical agent cost is not expensive.

SUMMARY OF THE INVENTION

An object of the present invention is to eliminate the above-mentioned disadvantages in the prior art and to provide a novel scratch inhibiting agent suitable for effectively inhibiting the generation of scratches on the surfaces of siliceous inorganic products, without decreasing the detergent power of an aqueous alkaline solution. Another object of the present invention is to provide a novel method for washing a siliceous inorganic product such as a glass bottle.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided a scratch inhibiting agent for inhibiting the generation of scratches on the surface of a siliceous inorganic product caused by an alkaline detergent comprising, as a main ingredient, at least one compound selected from the group consisting of (A) aliphatic hydroxydicarboxylic acids having a functional group ratio (OH/COOH) of 1.0 to 2.0 and the alkali metal salts thereof and (B) polycarboxylic acids having a molecular weight of 5000 to 20000 and the alkali metal salts thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, the rate of increase in the scratch area can be decreased to approximately one third of that caused by using the conventional sodium gluconate, when the present scratch inhibiting

agent is used as an additive for preventing the generation or expansion of scratches at a washing step for siliceous inorganic products such as glass bottles. Thus, the number of times that the inorganic products can be reused is increased approximately 3-fold when compared to the case of a sodium gluconate wash.

Although the mechanism of the remarkable scratch inhibiting effect obtained from the use of the present scratch inhibiting agent has not been clearly elucidated, it is believed that the above-mentioned compound (A) and/or (B) is reacted with a metal ion such as calcium or magnesium, which is considered to be the scratch causing substance, to form water-insoluble substances by chelating or ion crosslinking. Thus, the resultant water-insoluble substances are selectively adsorbed on the surface of, for example, a glass bottle, to form a protective film and prevent the attack by alkali on the silica network.

(A) Examples of the aliphatic hydroxydicarboxylic acids having a functional ratio, i.e., OH/COOH ratio of 1.0 to 2.0, and the alkali metal salts thereof are as follows:

(1) Aliphatic hydroxydicarboxylic acids having a functional ratio of 1, and the alkali metal salts thereof, such as tartaric acid and the alkali metal salts thereof

(2) Aliphatic hydroxydicarboxylic acids having a functional ratio of 1.5, and the alkali metal salts thereof, such as trioxyglutaric acid and the alkali metal salts thereof

(3) Aliphatic hydroxydicarboxylic acids having the functional ratio of 2, and the alkali metal salts thereof, such as allogalactaric acid and the alkali metal salts thereof

(B) Examples of polycarboxylic acids having a molecular weight of 5000 to 20000, and the alkali metal salts thereof, such as;

Acrylic acid homopolymers
Methacrylic acid homopolymers
Acrylic acid - methacrylic acid copolymer
Acrylic acid - maleic anhydride copolymers
Methacrylic acid - maleic anhydride copolymers
Acrylic acid - fumaric acid copolymers
Methacrylic acid - fumaric acid copolymers
Acrylic acid - itaconic acid copolymers
Methacrylic acid - itaconic acid copolymers

As shown in the Comparative Examples below, (1) when aliphatic hydroxy polyhydriccarboxylic acids having structures similar to those of the present invention but having a functional group ratio (OH/COOH) of outside the range of 1.0 to 2.0, such as tartron acid, malic acid (i.e., OH/COOH = 0.5), and citric acid (i.e., OH/COOH = 0.3) are used, (2) when aliphatic hydroxycarboxylic acids having the similar functional ratio but having structures different from those of the present dicarboxylic acid, such as glyceric acid (i.e., OH/COOH = 2), lactic acid, hydroacrylic acid, α-oxybutyric acid (i.e., OH/COOH = 1) are used, (3) when aliphatic carboxylic acids having both the functional group ratio and structure different from those of the present hydroxy dicarboxylic acids, such as gluconic acid, oxalic acid, and succinic acid are used, (4) when aromatic hydroxycarboxylic acids such as α-oxybenzoic acid, gallic acid, mandelic acid, and tropic acid are used, (5) when amino carboxylic acids such as ethylenediaminetetraacetic acid, nitrilotriacetic acid, and diethylenetriaminepentaacetic acid are used, (6) when polyphosphoric acid compounds such as pyrophosphoric acid triployphosphoric acid, and hexametaphosphoric acid are used, (7) when polycarboxylic acids having a molecular weight of less than 5000 are used, or (8) when polycarboxylic acids having a molecular weight of more than 20000 are used, the desired scratch inhibiting effects cannot be obtained. Although the reasons why these compounds

shown in (1) to (8) do not exhibit the desired scratch inhibiting effects are not clear, it is believed that these compounds do not have sufficient capability to caption (or chelate) metal ions such as calcium and magnesium ions, which are considered to be scratch causing substances, or that, if the above-mentioned compounds can caption said metal ions by chelating, the resultant reaction product cannot form a firm protective film capable of preventing the attack on the surface of siliceous inorganic products by alkali, since the resultant reaction product is water-soluble unlike those of the present invention, so that the absorption degree thereof on the surface of the siliceous product is small.

The siliceous inorganic products, for which the scratch inhibiting agent of the present invention is used for preventing the generation or expansion of scratches during the alkali washing, include, for example, glass products such as glass bottles and glass tableware, and ceramics such as the ceramic substrates of electric devices or parts (special glass, rock crystal), and ceramic tableware.

Although the scratch inhibiting agent according to the present invention may be used alone prior to the alkali washing of the siliceous inorganic products, the present scratch inhibiting agent is generally or preferably added to an aqueous alkaline solution to be used at an alkali washing step. Although the present scratch inhibiting agent may be added over a wide range of addition to the aqueous alkali solution, the preferable addition amount of the present scratch inhibiting agent is 1.0% to 20% by weight, more preferably 5% to 15% by weight, based on the amount of the alkali (e.g., sodium hydroxide). Although any aqueous alkali solution conventionally used in the alkali washing can be used, the preferable aqueous alkali solutions are those containing, for example, sodium hydroxide, potassium

hydroxide, sodium phosphate, sodium silicate, sodium carbonate, and potassium carbonate. In view of the washing power and economical advantages, the use of sodium hydroxide or sodium carbonate is most preferable. Although there are no critical limitations to the alkali concentration of the aqueous alkaline solution, the preferable alkali concentration is 0.5% to 10% by weight, more preferably 1% to 6% by weight.

Also, there are no critical limitations to the alkali washing techniques and conditions, but the so-called dipping washing capable of washing a large amount of the siliceous inorganic products in a relatively short time is preferably used. The preferable washing temperature is 60°C to 100°C, more preferably 70°C to 90°C, to increase the decomposition power by alkali of animal and vegetable oils.

As mentioned above, the scratch inhibiting agent according to the present invention can effectively prevent the generation and expansion of scratches on the surfaces of siliceous inorganic products, without decreasing the washing power of the aqueous alkali solutions. Thus, the number of times that the siliceous inorganic products can be reused is greatly increased.

Furthermore, in the case of glass bottles, iron rust generated from, for example, crown caps is adhered to the bottles. This rust is not completely removed by the alkali washing with the aqueous alkaline solution containing the present scratch inhibiting agent. However, it has been found that, when the glass bottle is first washed with a first aqueous alkaline solution containing the present scratch inhibiting agent, followed by washing with a second aqueous alkaline solution containing gluconic acid and/or the alkali metal salt thereof, the iron rust adhered to the cap portion of the glass bottle can be effectively removed as shown in Examples 6 and 7 below.

In the first washing step, first aqueous alkaline

solutions containing, for example, 0.5% to 10% by weight, preferably 1% to 6% by weight, of an alkali (e.g., sodium hydroxide or sodium carbonate) and 1% to 20% by weight, preferably 5% to 15% by weight, based on the weight of the alkali, of the scratch inhibiting agent are used for preventing the generation or expansion of the scratch areas.

In the second washing step, second aqueous alkaline solutions containing, for example, 0.4% to 7% by weight, preferably 0.4% to 4% by weight, of an alkali (e.g., sodium hydroxide or sodium carbonate) and 1% to 20% by weight, preferably 5% to 15% by weight, based on the weight of the alkali, of the gluconic acid or the salt thereof are used. The alkali concentration of the second washing solution is preferably less than that of the first washing solution, particularly 0.2 to 0.7 times of that of the first washing solution to obtain good results.

The glass bottle washing can be carried out in any conventional manner, except that the first and second aqueous alkaline solutions are used. That is, in the conventional glass bottle washing process, glass bottles are washed consecutively with the same kind of a washing solution in a plurality of washing baths. In the practice of the present washing system, glass bottles are first washed in, for example, 1 to 5 consecutive washing baths with the first washing solution, and then washed in, for example, 1 to 5 consecutive washing baths with the second washing solution. Thus, according to the present invention, the generation and expansion of the scratches are effectively prevented and also the iron rust in the cap portions of the glass bottles are effectively removed.

EXAMPLES

The present invention now will be further illustrated by, but is by no means limited to, the following Examples and Comparative Examples.

Example 1: Effects of Various Scratch Inhibiting Agent

Test pieces of glass bottles having a size of 3 cm in length x 5 cm in breadth were cut from glass bottles having a thickness of 4 mm. The test pieces were rubbed together to form fine flaws within a definite area on the surfaces of the test pieces. The test pieces were then dipped in a water bath filled with an aqueous washing solution containing 4% by weight of sodium hydroxide and 0.4% by weight (i.e., 10% by weight based on the alkali) of a scratch inhibiting agent listed in Table 1. The test pieces were washed at a constant temperature of 80°C for 60 minutes.

After washing, the test pieces were taken from the water bath and washed with water. After drying, the scratch areas generated by the alkali washing were determined by using an industrial linear camera analyzer, and the rate of increase (%) of the scratch area was calculated from the formula (1):

(1) Rate of increase (%) of scratch area $= \frac{B - A}{A} \times 100$

wherein A: Scratch area (cm^2) before washing treatment

B: Scratch area (cm^2) after washing treatment

Furthermore, the washing power of the alkali washing was evaluated by washing test pieces having about 130 mg of soybean oily soil adhered to the surface of each piece. After washing, the remaining oil was guantitatively determined by a Soxhelt extractor. The removal efficiency of the oily soil was calculated according to the formula (2).

(2) Removal efficiency (%) of oily soil $= \frac{W_1 - W_2}{W_1} \times 100$

wherein W_1: Adhered oil amount (g)

before the washing treatment

W_2: Adhered oil amount (g)
after the washing treatment

The results are shown in Table 1.

Table 1

Sample No.		Scratch Inhibiting Compound	No. of OH	No. of COOH	OH/COOH	Rate of Increase of Scratch Area (%)	Removal Efficiency of Oily Soil (%)
Present Invention	1	Sodium tartrate	2	2	1	20	100
	2	Sodium trioxyglutarate	3	2	1.5	25	"
	3	Sodium polyacrylate (Mw = 5000)				100	"
	4	Sodium polyacrylate (Mw = 10000)				40	"
	5	Sodium polyacrylate (Mw = 20000)				50	"
	6	Sodium polymethacrylate (Mw = 10000)				40	"
	7	Sodium acrylate-co-sodium methacrylate (Mw = 10000)				40	"
	8	Sodium acrylate-co-sodium fumarate (Mw = 10000)				40	"
	9	Sodium acrylate-co-sodium itaconate (Mw = 10000)				40	"
Comparative	10	Sodium tartonate	1	2	0.5	420	"
	11	Sodium malate	1	2	0.5	460	"
	12	Sodium citrate	1	3	0.3	550	"
	13	Sodium glycerate	2	1	2.0	300	"
	14	Sodium lactate	1	1	1.0	580	"
	15	Sodium hydroxyacrylic acid	1	1	1.0	430	"
	16	Sodium α-oxybutyrate	1	1	1.0	410	"

0235961

Table 1 (Continued)

Sample No.		Scratch Inhibiting Compound	No. of OH	No. of COOH	OH/COOH	Rate of Increase of Scratch Area (%)	Removal Efficiency of Oily Soil (%)
Comparative	17	Sodium gluconate	5	1	5.0	290	100
	18	Sodium oxalate	0	2	0	860	"
	19	Sodium succinate	0	2	0	750	"
	20	Sodium α-oxybenzoate	1	1	1.0	290	"
	21	Sodium gallate	3	1	3.0	290	"
	22	Sodium mandelate	1	1	1.0	300	"
	23	Sodium tropate	1	1	1.0	310	"
	24	Sodium ethylenediamine tetraacetate				610	"
	25	Sodium nitrilotriacetate				590	"
	26	Sodium polyacrylate (Mw = 1000)				420	"
	27	Sodium polyacrylate (Mw = 2000)				330	"
	28	Sodium polyacrylate (Mw = 50000)				380	"
	29	Sodium polyacrylate (Mw = 1000000)				400	"
	30	CMC (Mw = 10000)				350	"

Example 2

The effects of the amount of sodium tartaric acid and sodium polyacrylic acid having a molecular weight of 10000 added to the alkali solution were evaluated in the same manner as in Example 1.

The results are shown in Table 2.

Table 2

Addition amount*	Sodium tartrate		Sodium polyacrylate (Mw = 10000)	
	Rate of Increase (%) of Scratch Area	Removal Efficiency (%) of Oily Soil	Rate of Increase (%) of Scratch Area	Removal Efficiency (%) of Oily Soil
0	650	100	650	100
2	200	"	250	"
5	25	"	60	"
10	20	"	40	"
15	100	"	120	"
20	150	"	230	"
30	310	"	380	"
50	470	"	590	"

* % by weight based on the weight of the alkali

Example 3

The effects of the alkali concentration were evaluated in the same manner as in Example 1 when sodium tartrate or sodium polyacrylate (Mw = 10000) was added to the alkali solution in an amount of 10% by weight based on the weight of alkali.

Table 3

Sodium hydroxide (%)	Sodium tartrate		Sodium polyacrylate (Mw = 10000)	
	Rate of Increase (%) of Scratch Area	Removal Efficiency (%) of Oily Soil	Rate of Increase (%) of Scratch Area	Removal Efficiency (%) of Oily Soil
2	20	100	40	100
4	20	"	40	"
5	20	"	40	"
6	20	"	40	"
8	20	"	40	"

Example 4

Test pieces having a size of 3 cm in length x 5 cm in breadth were cut from glass cups having a thickness of 2 mm. The test pieces were rubbed together to form fine flaws within a definite area on the surfaces of the test pieces. The test pieces were then dipped in a water bath filled with aqueous alkali washing solution containing 2% by weight of sodium hydroxide and 0.2% by weight (i.e., 10% by weight based on the alkali) of a scratch inhibiting agent listed in Table 4. The test pieces were washed at a constant temperature of 80°C for 60 minutes.

The test pieces after treatment were evaluated in the same manner as in Example 1. The results are shown in Table 4.

Table 4

Sample No.		Scratch Inhibiting Agent	Rate of Increase (%) of Scratch Area	Removal Efficiency (%) of Oily Soil
Present Invention	1.	Sodium tartrate	10	100
	2.	Sodium trioxyglutarate	15	"
	3.	Sodium polyacrylate (Mw = 5000)	50	"
	4.	Sodium polyacrylate (Mw = 10000)	20	"
	5.	Sodium polyacrylate (Mw = 20000)	15	"
Comparative	6.	Sodium gluconate	150	"
	7.	Sodium oxalate	420	"
	8.	Sodium polyacrylate (Mw = 500000)	180	"

Example 5

Test pieces having a size of 3 cm in length x 5 cm in breadth were cut from siliceous substrates for electric devices having a thickness of 1 mm. The test pieces were then dipped in a water bath filled with an aqueous alkali washing solution containing 1% by weight of sodium hydroxide and 0.1% by weight (i.e., 10% by weight based on the alkali) of a scratch inhibiting agent listed in Table 5. The test pieces were washed at a constant temperature of 70°C for 60 minutes.

The test pieces after treatment were evaluated in the same manner as in Example 1. The results are shown in Table 5.

Table 5

Sample No.		Scratch Inhibiting Agent	Rate of Increase (%) of Scratch Area	Removal Efficiency (%) of Oily Soil
Present Invention	1.	Sodium tartrate	5	100
	2.	Sodium trioxyglutarate	10	"
	3.	Sodium polyacrylate (Mw = 5000)	30	"
	4.	Sodium polyacrylate (Mw = 10000)	18	"
	5.	Sodium polyacrylate (Mw = 20000)	10	"
Comparative	6.	Sodium citrate	120	"
	7.	Sodium oxalate	250	"
	8.	Sodium polyacrylate (Mw = 1000000)	120	"

Example 6

Fifteen steel plates having a size of 25 mm x 75 mm x 1 mm were dipped in 700 ml of tap water at a temperature of 60°C for 2 days to generate rust on the plates. The rust was centrifugally concentrated to obtain an aqueous rust liquid. A 0.2 ml amount of the resultant liquid was uniformly coated on the surface of a slide glass, followed by air drying.

The liquid on the slide glass was further dried at a temperature of 105°C for one hour, and after allowing to cool, the weight of the slide glass was measured.

The rusted slide glass was placed in a Leenuts washing power tester, which is generally used in a detergent power test for food detergent. The slide glass having rust soil thereon was washed in 700 ml of washing solutions at 250 rpm at a temperature of 80°C for one hour. The first aqueous washing solution contained 4.0% by weight of sodium hydroxide and 0.4% by weight of the additive listed in Table 6 and the second aqueous washing solution contained 2.0% by weight of sodium hydroxide and 0.2% by weight of the additive listed in Table 6. Furthermore, 3000 ppm, in terms of aluminum, of sodium aluminate was added to the washing solutions so that the effect of aluminum caused by an aluminum label, which may be used in actual bottles, was obviated.

After washing, the slide glass was dried at a temperature of 105°C for 1 hour and the efficiency of the removal of iron rust was calculated as follows:

$$\text{Removal Efficiency (\%)} = \frac{A - B}{A - C} \times 100$$

wherein A: Weight of rust-deposited slide glass before washing

B: Weight of rust-deposited slide glass after washing

C: Weight of slide glass

The results are shown in Table 6.

Table 6

Sample No.		Addition		Removal efficiency (%) of iron rust
		First solu.	Second solu.	
Comparative	1	Sodium gluconate	Sodium gluconate	100
	2	Sodium tartrate	Sodium tartrate	20
	3	Sodium gluconate	Sodium tartrate	90
Present Invention	4	Sodium tartrate	Sodium gluconate	100

As is clear from the results shown in Table 6, when sodium tartrate was used in the first washing solution and when sodium gluconate was used in the second washing solution, the desired efficiency of removal of the rust was obtained. When sodium gluconate was used both in the first and second washing solutions, the generation of scratches was not prevented to the extent required.

Example 7

The scratch inhibiting test and the rust removal test were carried out as follows.

In the scratch inhibiting test, 16 beer bottles having similar flaws were selected from the recovered bottles. Four bottles in each solution were dipped, after preheating, in a 20 liter washing bath at a temperature of 80°C for 30 minutes, while agitating. After washing, the sample bottles were taken from the bath, and while cooling, the bottles were washed with water. After drying the surfaces of the bottles, the increase in the scratch area was determined in the same manner as in Example 1. The results are shown in Table 7.

In the rust removal test, recovered beer bottles

having a similar rust adhered in the bottle mouth portion were selected. The sample bottle was dipped, upside down, in 700 ml of a washing solution at a temperature of 80°C for 30 minutes, while stirring with a magnetic stirrer, so that the mouth portion of the bottle was completely dipped in the washing solution.

After washing, the sample bottles were dried and the degree of removal of rust in the dried bottles was visually evaluated as follows:

o ... Rust completely removed.

Δ ... Small amount of rust retained.

x ... Rust substantially not removed.

The results are shown in Table 7.

The first washing solution contained 4.0% by weight of sodium hydroxide and 0.4% by weight of the additive listed in Table 6 and the second aqueous washing solution contained 2.0% by weight of sodium hydroxide and 0.2% by weight of the additive listed in Table 6. Furthermore, 3000 ppm, in terms of aluminum, of sodium aluminate was added to the washing solutions so that the effect of aluminum caused by an aluminum label, which may be used in actual bottles, was obviated.

Table 7

Sample No.		Addition		Rate of Increase (%) of Scratch Area	Removal Efficiency (%) of Iron Rust
		First soln.	Second soln.		
Comparative	1	Sodium gluconate	Sodium gluconate	2.3	o
	2	Sodium tartrate	Sodium tartrate	1.2	x
	3	Sodium gluconate	Sodium tartrate	2.0	Δ
Present Invention	4	Sodium tartrate	Sodium gluconate	1.4	o

As is clear from the results shown in Table 7, when sodium gluconate was used in the first and second washing solutions (see Sample No. 1), the expansion rate of the scratch area was large although the rust removal condition was good. When sodium tartrate was used in the first and second washing solution (see Sample No. 2), the rust removal condition worsened, although the expansion of the scratch area was extremely low. Contrary to this, when sodium tartrate was used in the first solution and when sodium gluconate was used in the second solution (see Sample No. 4), the desired results were obtained. These desired results were not obtained when sodium tartrate was used in the first solution and when sodium gluconate was used in the second solution (see Sample No. 3). As is clear from the comparison of the results of Sample No. 1 with Sample No. 4, the rate of increase (%) of the scratch area in Sample No. 4 is approximately three fifth (i.e., 3/5) of that in Sample No. 1. This means that, when the bottle No. 1 can be recycled, for example, 15 times, the bottle No. 4 washed according to the present invention can be recycled 25 times. Thus, the economical advantage of the present invention is great.

CLAIMS

1. A scratch inhibiting agent for inhibiting the generation of scratches on the surface of a siliceous inorganic product caused by an alkaline detergent comprising, as a main ingredient, at least one compound selected from the group consisting of (A) aliphatic hydroxydicarboxylic acids having a functional group ratio (OH/COOH) of 1.0 to 2.0 and the alkali metal salts thereof and (B) polycarboxylic acids having a molecular weight of 5000 to 20000, and the alkali metal salts thereof.

2. A scratch inhibiting agent as claimed in claim 1 wherein said siliceous product is a glass bottle.

3. A scratch inhibiting agent as claimed in claim 1 wherein said siliceous product is a substrate for an electric device.

4. A scratch inhibiting agent as claimed in claim 1 wherein said siliceous product is tableware.

5. A scratch inhibiting agent as claimed in claim 1 wherein said aliphatic hydroxydicarboxylic acids are aliphatic hydroxydicarboxylic acids having a functional ratio of 1 and the alkali metal salts thereof, aliphatic hydroxydicarboxylic acids having a functional ratio of 1.5 and the alkali metal salts thereof, and aliphatic hydroxydicarboxylic acids having the functional ratio of 2 and the alkali metal salts thereof.

6. A scratch inhibiting agent as claimed in claim 1 wherein said polycarboxylic acids are acrylic acid homopolymers, methacrylic acid homopolymers, acrylic acid-methacrylic acid copolymer, acrylic acid-maleic anhydride copolymers, methacrylic acid-maleic anhydride copolymers, acrylic acid-fumaric acid copolymers, methacrylic acid-fumaric acid copolymers, acrylic acid-itaconic acid copolymers, and methacrylic acid-itaoonic acid cpolymers.

7. A method for inhibiting the generation of scratches on the surface of a siliceous inorganic product caused by an alkaline detergent by incorporating thereinto a scratch inhibiting agent comprising, as a main ingredient, at least one compound selected from the group consisting of (A) aliphatic hydroxydicarboxylic acids having a functional group ratio (OH/COOH) of 1.0 to 2.0 and the alkali metal salts thereof and (B) polycarboxylic acids having a molecular weight of 5000 to 20000, and the alkali metal salts thereof.

8. A method for washing a glass bottle having iron rust adhered thereto comprising:

washing the glass bottle with a first aqueous alkaline washing solution containing at least one compound selected from the group consisting of (A) aliphatic hydroxydicarboxylic acids having a functional group ratio (OH/COOH) of 1.0 to 2.0 and the alkali metal salts thereof and (B) polycarboxylic acids having a molecular weight of 5000 to 20000 and the alkali metal salts thereof; and then

washing the glass bottle with a second aqueous alkaline washing solution containing at least one compound selected from the group consisting of gluconic acid and the alkali metal salts thereof.

9. A method as claimed in claim 8, wherein the first washing solution contains 0.5% to 10% by weight of an alkali and 1% to 20% by weight, based on the weight of the alkali, of the scratch inhibiting agent and the second washing solution contains 0.4% to 7% by weight of an alkali and 1% to 20% by weight, based on the weight of the alkali, of gluconic acid or the salt thereof.

European Patent Office

EUROPEAN SEARCH REPORT

0235961

Application number

EP 87 30 1004

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.4)
A	CHEMICAL ABSTRACTS, vol. 92, no. 16, 21st April 1980, page 322, column 2 - page 323, column 1, abstract no. 133950f, Columbus, Ohio, US; & JP - A - 79 137 020 (KOKAI TOKKYO KOHO) 24-10-1979 ---	1	C 11 D 3/37 C 11 D 1/04 C 11 D 1/08
A	CHEMICAL ABSTRACTS, vol. 103, no. 10, 9th September 1985, page 71, column 2, abstract no. 89153t, Columbus, Ohio, US; & JP - A - 60 60947 (KOKAI TOKKYO KOHO) 08-04-1985 ---	1	
A	DD-A- 207 920 (VEB AEROSOL-AUTOMAT KARL-MARX-STADT) * abstract * -----		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 11 D 3/00
C 11 D 1/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	27-04-1987	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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