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2,976,248

BOTTLE WASHING COMPOSITION AND METHOD

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This invention relates to compositions for washing glassware and more particularly to scale inhibiting alkaline detergent compositions containing a corrosion-inhibiting agent.

It is the common practice in the bottling of carbonated beverages and dairy products to refill and reuse the glass bottles many times over during their normal span of life. When such bottles are returned to the bottler by the consumer, it is highly important that they be subjected to a vigorous and thorough washing, not only to remove residues, dirt and soil and similar contamination and thus to render them physically clean, but also to subject them to a germicidal action in order to render them sterile and free from bacterial or fungal contamination. Washing solutions of a relatively high alkaline strength have been found most suitable in practice for a washing operation of this nature. The well known alkaline detergents which can provide this high alkalinity in aqueous solution include sodium hydroxide (caustic soda), sodium carbonate (soda ash), and trisodium phosphate. These alkalis, however, do not have the same power or equal powers with respect to their ability to wet a surface, to emulsify grease and oils, to dissolve substances, to deflocculate dirt particles and with respect to their germicidal properties. Although caustic soda has poor wetting-out and rinsing action and no lime sequestering properties, it is, in general, employed as the major ingredient in most alkali washing compositions because it is a highly effective germicidal and dissolving agent and, in addition, is the most economical alkaline material for this application.

In view of the deficiencies noted for the caustic soda, other ingredients are commonly employed in limited proportions in addition to the caustic soda in order to promote the wetting, emulsifying and deflocculating action of the caustic soda. The auxiliary agents which can be added to caustic soda in order to formulate a more effective bottle washing detergent include carbonates, orthophosphates, sodium metasilicate and molecularly dehydrated phosphates such as the hexametaphosphates and tripolyphosphates. The wetting agents or surfactants which can be effectively employed include the anionics and low foaming nonionics.

When the glass bottles or beverage containers are returned to the bottling plant for washing prior to refilling, they are ordinarily passed through either soaker type, hydraulic type or hydro-soaker type washing machines. In large scale bottle washing operations, the bottles are placed upon a conveyor equipped with means for holding the bottles, these usually being pockets or hooks, and the conveyor transports the bottles through one of the above described bottle washing machines. The type of washing machine employed in any particular situation will depend upon the resistance of the soil to the alkaline detergent and whether the bottles contain labels which must be removed. In the soaker type washing machine, the bottles pass through a prerinse into a long dormant alkali soak in several compartments before entering the

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rinse stage. The hydraulic type machines operate on the principle of projecting streams of alkaline solution and rinse water through a series of spray jets at high velocity upon the inside and outside surfaces of the bottles. In the hydro-soaker type, a combination of soak tanks and spray jets is employed for cleaning the bottles.

When the conveyor and the contained glassware are contacted by a hot alkaline wash solution, they become coated with a film of alkali. This film of alkali is subsequently carried over to the rinsing step where it causes an immediate precipitation of the calcium and magnesium salts which are present in the rinse water. This precipitation also occurs when the conveyor covered by a film of rinse water containing calcium and magnesium salts enters the alkaline wash solution. These precipitated solids interfere with the proper operation of the washing equipment, deposit films on the glassware being washed and because of the intimate contact of the alkaline film on the conveyor with the rinse water tend to deposit hard scale on the conveyor. As a result, there is a continuous and ultimately serious building up of scale on the conveyor hooks, pockets and other conveyor parts.

The problem of preventing this precipitation of the calcium and magnesium salts by the caustic alkali, and thereby inhibiting the formation of hard scale on the conveyors and tanks of the bottle washing machinery, has received considerable attention by the prior art and much effort has been spent to prevent or overcome it. Thus, there have been suggestions in the art that complex polyphosphates such as sodium hexametaphosphate, tetrasodiumpyrophosphate, sodium tetrakisphosphate and sodium tripolyphosphate are suitable sequestering agents which can be effectively added to alkaline bottle washing compositions in order to minimize hard water precipitation. William C. Cooper, in U.S. 2,241,984, discloses that the phosphates can be used either along with the caustic in the alkaline wash step or used in the final washing compartment in order to try to prevent the formation of magnesium hydroxide precipitates during rinsing. It has been found, however, that the complex polyphosphates (molecularly dehydrated phosphates), are not completely effective as sequestering agents in the presence of caustic soda at elevated temperatures. W. L. McFadden in an article published in National Carbonator and Bottler, October 1943, p. 50 et seq, suggests that the extremely high pH of a caustic soda solution breaks down the soluble complex which the above type phosphates ordinarily form with calcium and magnesium ions, allowing the caustic soda to precipitate them.

Organic sequestrants falling within the class described as hydroxy carboxylic acids have now been found to be highly efficient sequestering agents in strongly alkaline solutions. These hydroxy carboxylic acids also designated as sugar acids include, for example, the fermentation acids, such as lactic, citric, gluconic, and 2-keto-gluconic as well as the aldonic and dibasic acids produced from sugars by chemical oxidation. It has been reported by C. L. Mehler et al. in an article entitled "Sequestration by Sugar Acids," Ind. Eng. Chem., 45, 2788 (1953) that the ability of sugar acids, in general, to form water-soluble complexes with metal ions stems from the capacity of their carboxyl and hydroxyl groups to bind cations in ring form by means of coordinate and covalent bonds. Dvorkovitz et al., in U.S. 2,615,846 (1952) discloses that an alkaline bottle washing composition comprising a caustic alkali such as sodium hydroxide and an alkali metal gluconate such as sodium gluconate will prevent or at least minimize (1) the formation of scale, (2) the precipitation of the hardness constituents from

hard water and (3) the attack of the caustic alkali on the glass and similar surfaces.

Although workers skilled in the art have been relatively successful in minimizing the precipitation of hard water salts and the subsequent formation of adherent scale on the bottle washing machinery by the use of hydroxy carboxylic acids, they have, in so utilizing these compositions, presented a problem which had not been encountered heretofore. The bottle washing apparatus including the conveyor system which transports the bottles through the several bottle washing compartments is, in general, fabricated from steel. Steel is an iron-carbon alloy having a carbon content less than 2.0 percent and generally below 1.5 percent. Steel has been classified into the following groups: carbon steel, alloy steel and stainless steel. Mild steel, a form of carbon steel, containing from 0.05 to 0.15 percent carbon as well as other alloying elements in limited proportions such as manganese, phosphorus, sulfur and silicon is generally preferred as the material of construction for bottle washing equipment because it is less expensive than either the alloy steels or stainless steels. This material of construction, however, has been found to be particularly susceptible to corrosive attack by the hydroxy carboxylic acid sequestering agents. Although this corrosion resulting from the use of these sugar acids is not significant insofar as the steel tanks are concerned, since these tanks may have a wall thickness of one-fourth to one-half inch, it is of particular significance in regard to the conveyor in view of the fact that the conveyor has parts which function under close dimensional tolerances. When these close dimensional parts such as the links in the conveyor system are corroded by the hydroxy carboxylic acids, this results in buckling, binding and improper operation of the conveyor system. This corrosion of the bottle washing equipment has been found to be most pronounced when a fresh solution of the sugar acid scale-inhibited alkaline composition is employed.

An object of this invention is, therefore, to provide a scale-inhibited alkaline bottle washing composition for use in continuous process bottle washing machinery wherein corrosion of the machinery parts contacted by the alkaline composition is prohibited or minimized.

A further object of this invention is to provide a process for washing bottles and similar glassware in continuous process bottle washing machinery with a scale-inhibited alkaline bottle washing composition wherein corrosion of the machinery parts contacted by the alkaline composition is prohibited or minimized.

I have now discovered that if either the sodium or potassium salt of lignin sulfonic acid is added to an alkaline bottle washing composition comprising an alkaline detergent and a hydroxy carboxylic acid scale-inhibiting agent a composition is obtained which, when employed in aqueous solution in continuous process bottle washing equipment, will surprisingly reduce the extent of the corrosive attack of the aforementioned type scale inhibitor on the bottle washing equipment.

In accordance with one of its aspects, this invention comprises new compositions of matter which may be employed in aqueous solutions for washing glassware and other similar articles of manufacture. These compositions contain from about 70 to 99 weight percent of an alkaline detergent, a hydroxy carboxylic acid sequestering agent in the amount of about 0.5 to 29 weight percent and a corrosion-inhibiting agent in the amount of about 0.5 to 20 weight percent.

The alkaline detergents which can be advantageously employed in the compositions of my invention include sodium hydroxide and potassium hydroxide as well as mixtures of these substances. Milder alkalis such as the sodium and potassium carbonates and sodium and potassium orthophosphates can be substituted to a limited extent for some of the principal alkaline material. Thus, 0 to 20 weight percent of the alkaline detergent can be

replaced with the orthophosphates or carbonates or mixtures of these materials.

The scale depressing additives useful in the compositions of my invention include, generally, hydroxy carboxylic acids, which are sometimes referred to as chelating agents, complexing agents, inhibitors, sequestering agents or stabilizing agents. Examples of these hydroxy carboxylic acids include, but are not limited to, the following: lactic, citric, tartaric, gluconic, arabonic, galactonic, 2-ketogluconic, saccharic, mucic and glucoheptonic acids. Mixtures of two or more of these acids as well as their sodium or potassium salts are equally suitable in the compositions of my invention. The sequestering agent to be effective in the compositions of my invention should be present to the extent of at least about 0.5 weight percent. The upper limit is, in general, dictated by economic considerations and usually does not exceed 29 or 30 weight percent of the total composition.

The corrosion-inhibiting agent which has been found to be highly effective as a retarder of the corrosive attack of the sugar acid sequestrants on the bottle washing machinery is a product, which is essentially a sodium lignosulfonate, having the following approximate composition on a moisture free basis:

	Weight percent
Sodium lignosulfonate.....	78.12
Non-reducing carbohydrates.....	11.55
Organic combined sodium not as sulfonate.....	3.11
30 $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$	1.28
$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	1.58
Na_2SO_4	4.26
Other.....	.10
55	100.00

The term "sodium lignosulfonate" is intended to designate the product formed by neutralizing a sulfonated pure or crude lignin (e.g. waste from a paper mill from which the cellulose has been removed) and as is well known to those skilled in the art such products frequently contain impurities. The above-identified sodium lignosulfonate is commercially available as a dark brown powder containing approximately 6% moisture and is sold by the Marathon Corporation of Rothchild, Wisconsin, under the trademark Marasperse N. The potassium salt of lignin sulfonic acid is equally suitable in the compositions of my invention. The sodium or potassium salt of lignin sulfonic acid to be effective as a corrosion inhibiting agent should be present in the compositions of my invention to the extent of at least about 0.5 weight percent. The upper limit as in the case of the sequestering agent is, in general, dictated by economic considerations but usually does not exceed about 20 weight percent of the total composition.

Aqueous solutions of the compositions of my invention can be made up by intimately blending the ingredients in the dry state in any suitable mixing apparatus and subsequently dissolving the intimately blended mixture in an aqueous medium or by adding the ingredients separately to an aqueous medium. The composition of the present invention is a mixture of solids and consists generally of from about 70 to 99 weight percent of an alkaline detergent, from about 0.5 to 29 weight percent of a hydroxy carboxylic acid sequestrant and from about 0.5 to 20 weight percent of a corrosion inhibiting agent. An alkaline detergent product having the proportions indicated is added to water to form a detergent solution containing from about 1 to 10 weight percent of the alkaline detergent ingredient. Preferred concentrations, however, are in the range of about 1 to 7 weight percent of the alkaline detergent ingredient. This latter range is preferred because the attack on the glassware is not as significant as when higher concentrations of the alkaline detergent are employed.

In general, the compositions of my invention are useful

over a wide temperature range. Alkaline detergent compositions containing a hydroxy carboxylic acid sequestrant and a corrosion inhibiting agent of my invention are preferably employed at elevated temperatures in order to clean the glassware, and good results are obtained at temperatures varying from 120° to 180° F. Preferred temperatures, however, are in the range of 140 to 160° F. The intermediate temperature range is preferred because it reduces the number of cooling steps necessary to bring the glassware down to room temperature, and also because the alkali attack on the glassware is not as pronounced as it would be at higher temperatures. The glassware to be washed is, in general, subjected to an aqueous solution of the alkaline detergent product for a time period of about 1 to 10 minutes. The exact time of washing is, however, dependent upon the type of bottle washing machinery being employed.

Wetting agents can also be advantageously incorporated into the compositions of my invention. When wetting agents or surfactants are used in soaker type washers, there is a reduction in the amount of the residual alkali retained on the glassware, a reduction in the alkali carry-over from the soaker tanks to the rinse tanks and a reduction in the average bacterial count on the glassware. These advantages accrue because the wetting agent promotes a more thorough rinsing and draining of the bottles and because the surfactant increases the penetrating properties of the alkaline detergent. The anionics and low foaming nonionics have been found to be the most suitable types of wetting agents. Examples of wetting agents which can be advantageously employed in the compositions of this invention include, but are not limited to, the following: sodium sulfate derivative of 2-ethyl hexanol-1 marketed by Carbide & Carbon Chemicals Company under the trade designation Tergitol 08, sodium alkyl aryl sulfonate marketed by the E. I. du Pont de Nemours & Company under the trade designation Alkanol WXN, alkyl aryl polyether alcohol marketed by Rohm & Haas Company under the trade designation Triton X-100 and a polyoxypropylene-polyoxyethylene condensate marketed by Wyandotte Chemicals Corporation under the trademark Pluronic grade designation L61. Wetting agents can be most advantageously employed in the range .05 to 2.0 weight percent.

In accordance with a second aspect of this invention, there is a process for washing glassware and the like which comprises contacting the glassware for a time period of about 1 to 10 minutes at a temperature in the range of 120 to 180° F. with an aqueous solution of an alkaline detergent product having the composition as described above wherein the concentration of the alkaline detergent ingredient is about 1 to 5 weight percent in the aqueous medium.

The following example next to be referred to is merely for the purpose of illustration of a way in which the invention may be practiced.

EXAMPLE I

Three alkaline detergent compositions were formulated and, as will be noted from Table I, were designated as compositions A, B and C. Each of these compositions contained a hydroxy carboxylic acid sequestrant marketed by the Pfanstiehl Laboratories, Inc., 104 Lake View Avenue, Waukegan, Illinois under the trade designation Seqlene 250. Seqlene 250 sequestrant is a mixture of the alpha and beta isomers of sodium hexahydroxyheptonate and is supplied as a water solution in concentrations of 25% solids. The water was evaporated in order to prepare the anhydrous material. Composition A consisted of 70 parts by weight of sodium hydroxide and 30 parts by weight of anhydrous Seqlene 250 sequestrant. Composition B consisted of 70 parts by weight of sodium hydroxide, 25.5 parts by weight of anhydrous Seqlene 250 sequestrant, 3.0 parts by weight of sodium lignosulfonate and 1.5 parts by weight of the sodium sulfate derivative

of 2-ethyl hexanol-1 marketed by Carbide & Carbon Chemicals Company under the trade designation Tergitol 08. Composition C consisted of 71.5 parts by weight of sodium hydroxide, 25.5 parts by weight of Seqlene 250 sequestrant and 3.0 parts by weight of sodium lignosulfonate. Each of these compositions was added to 18 grain hard water so as to prepare an alkaline detergent solution wherein the sodium hydroxide was present to the extent of 3 weight percent in the aqueous medium.

The aqueous solutions of compositions A, B and C which had been prepared in 18 grain hard water were added consecutively to an experimental bottle washing machine which was constructed out of mild steel in order to compare the effectiveness of the sodium lignosulfonate in controlling the corrosive attack of the hydroxy carboxylic acid sequestrant on the conveyor chain. Five continuous runs at 19.8 hours per run were carried out at solution temperatures of 170° F. The conveyor chain was weighed at the beginning and end of each run to determine the extent of the weight change during that run. The weight changes, as shown in Table I, are cumulative. The hardness of the water was checked daily and corrected, when necessary, to make up solutions having 18 grain hardness.

Table I

Composition (parts by wt.)	A	B	C
Sodium hydroxide.....	70.0	70.0	71.5
Sodium hexahydroxyheptonate.....	30.0	25.5	25.5
Sodium lignosulfonate.....		3.0	3.0
Sodium sulfate derivative of 2-ethyl hexanol-1.....		1.5	
	100.0	100.0	100.0
Aqueous solutions (wt. percent):			
Sodium hydroxide.....	3.00	3.00	3.00
Additives.....	1.29	1.29	1.20
Water.....	95.71	95.71	95.80
	100.00	100.00	100.00
	Cumulative wt. loss and gain, milligrams		
Run No. (19.8 hrs. per run):			
1.....	-45	-58	-37
2.....	-35	-54	-91
3.....	-144	-58	-71
4.....	-194	-31	-28
5.....	-204	+49	+45
6.....	-152	+171	
7.....	-178		
8.....	+38		
9.....	+144		

Thus, as will be noted from Table I, the presence of the sodium lignosulfonate in the alkaline detergent composition significantly reduces the extent to which the hydroxy carboxylic acid sequestrant corrodes the mild steel conveyor chain.

A typical cycle of operations, when employing bottle washing equipment of the soaker type, consists of the following:

- Prerinse with warm water
- Soak at 140° F. in alkaline solution of 3.0-3.5 weight percent caustic soda content
- Soak at 155° F. in alkaline solution of about 3.0 weight percent caustic soda content
- Water rinse at lower temperature, about 125° F.
- Water rinse at lower temperature, about 95° F.
- Internal and external brushing
- One or more internal and external cool water rinses
- Internal chlorination rinse

Prior to the time the bottles enter the second stage or soaking step of the bottle washing operation, they are usually passed through a prerinse tank containing a small amount of caustic alkali for the purpose of softening and flushing out sediment and tenacious residues. The second stage, or soaking step, is the most critical in the bottle washing operation because it is in this step that the bottles come in contact with the alkaline detergent compositions

containing the sugar acid sequestrants. Thus, it is in this stage of the bottle cleaning process that the most extensive corrosion of the conveyor chain takes place. I have now found that this corrosion of the conveyor chain can be significantly reduced, yet still maintaining the advantageous properties of the sugar acid sequestrant, by employing an alkaline detergent composition comprising an alkaline detergent, a hydroxy carboxylic acid sequestrant and sodium or potassium lignosulfonate in the alkaline wash step of the bottle washing operation.

What is claimed is:

1. A composition for washing glassware consisting essentially of a mixture of about 70 to 99 weight percent of an alkaline detergent selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof, about 0.5 to 29 weight percent of a hydroxy carboxylic acid sequestrant and about 0.5 to 20 weight percent of a corrosion-inhibiting agent, said corrosion-inhibiting agent being a member selected from the group consisting of sodium lignosulfonate, potassium lignosulfonate and mixtures thereof.

2. A composition in accordance with claim 1 wherein said hydroxy carboxylic acid sequestrant is a member selected from the group consisting of lactic, citric, tartaric, gluconic, arabonic, galactonic, 2-ketogluconic, saccharic, mucic and hexahydroxyheptonic acids and mixtures thereof.

3. A composition for washing glassware consisting essentially of about 70 to 99 weight percent of sodium hydroxide, about 0.5 to 29 weight percent of sodium hexahydroxyheptonate and about 0.5 to 20 weight percent of sodium lignosulfonate.

4. A composition for washing glassware consisting essentially of a mixture of about 70 to 99 weight percent of an alkaline detergent, about 0.5 to 29 weight percent of a hydroxy carboxylic acid sequestrant and about 0.5 to 20 weight percent of a corrosion-inhibiting agent, said corrosion-inhibiting agent being a member selected from the group consisting of sodium lignosulfonate, potassium lignosulfonate and mixtures thereof, wherein up to 20 weight percent of said alkaline detergent is a member selected from the group consisting of sodium orthophosphate, sodium carbonate, sodium salts of molecularly dehydrated phosphates and mixtures thereof and the remainder of said alkaline detergent is a member selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof.

5. In a process for washing glassware wherein conveyor equipment employed to transport said glassware into contact with a bottle washing composition is fabricated from ferrous metal and alloys thereof, the improvement which comprises contacting said glassware with an aqueous solution of an alkaline detergent composition, said alkaline detergent composition consisting essentially of a mixture of about 70 to 99 weight percent of an alkaline detergent, said alkaline detergent being a member selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof, about 0.5 to 29 weight percent of a hydroxy carboxylic acid sequestrant and about 0.5 to 20 weight percent of a corrosion-inhibiting agent, said corrosion-inhibiting agent being a member selected from the group consisting of sodium lignosulfonate, potassium lignosulfonate and mixtures thereof whereby corrosion of said conveyor equipment is minimized.

6. A process in accordance with claim 5 wherein said hydroxy carboxylic acid sequestrant is a member selected from the group consisting of lactic, citric, tartaric, gluconic, arabonic, galactonic, 2-ketogluconic, saccharic, mucic and hexahydroxyheptonic acids and mixtures thereof.

7. A process in accordance with claim 5 wherein a sufficient quantity of said alkaline detergent composition is present in said aqueous solution so as to provide an aqueous solution having an alkaline detergent concentration of 1 to 5 weight percent.

8. In a process for washing glassware wherein conveyor equipment employed to transport said glassware into contact with a bottle washing composition is fabricated from ferrous metal and alloys thereof, the improvement which comprises contacting said glassware with an aqueous solution of an alkaline detergent composition, said alkaline detergent composition consisting essentially of a mixture of about 70 to 99 weight percent of sodium hydroxide, about 0.5 to 29 weight percent of sodium hexahydroxyheptonate and about 0.5 to 20 weight percent of sodium lignosulfonate, said alkaline detergent composition being present in said aqueous solution in sufficient quantity so as to provide an aqueous solution having an alkaline detergent concentration of about 1 to 5 weight percent whereby corrosion of said conveyor equipment is minimized.

9. A process for washing glassware in automatic bottle washing machinery which comprises placing said glassware on a metal conveyor, passing said conveyor and said glassware deposited thereon into contact with an aqueous solution of an alkaline detergent composition, said alkaline detergent composition consisting essentially of a mixture of about 70 to 99 weight percent of an alkaline detergent, said alkaline detergent being a member selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof, about 0.5 to 29 weight percent of a hydroxy carboxylic acid sequestrant and about 0.5 to 20 weight percent of a corrosion-inhibiting agent, said corrosion-inhibiting agent being a member selected from the group consisting of sodium lignosulfonate, potassium lignosulfonate and mixtures thereof, said alkaline detergent composition being present in said aqueous solution so as to provide an alkaline detergent concentration of about 1 to 5 weight percent whereby corrosion of said metal conveyor is minimized.

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