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CONTINUOUS CLEANSING OF
RIGID MATERIALS

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5 Claims

ABSTRACT OF THE DISCLOSURE

An improvement in the continuous washing of rigid materials with a concentrated alkali washing bath which is periodically replenished comprising periodically replenishing said washing bath in order to maintain a level of from 0.02% to 0.4% of a stable liquid additive solution comprising from 1% to 40% by weight of a non-ionic detergent, from 5% to 30% by weight of an organic acid selected from the group of hydroxy and amino alkyl-1,1-diphosphonic acids, ethylenediaminetetra-(methylenephosphonic acid) and aminotri-(methylenephosphonic acid), an aliphatic alcohol and a mineral acid, if desired, with the balance water.

THE PRIOR ART

For the cleansing of rigid materials, such as work pieces consisting of metal or glass, and especially for the cleansing of bottles, the use of alkaline materials is known. These alkaline substances frequently contain, acid from caustic alkalies, soda, condensed phosphates such as pyro-, meta- and polyphosphates, wetting agents and, as required, foam depressants (antifoams) and disinfectants. In general, nonionic wetting agents or detergents are used which exhibit pronounced antifoaming action, and, for binding of hardness-formers present in water and for the prevention of scale or mineral formation, polyphosphates. These products usually are sold in commerce in form of powdered mixtures and are incorporated in the cleansing bath in batches, whereby the bath concentration of the cleaning agent usually lies between 0.2 and 2 percent, depending upon the intended use and degree of soilage.

In the past, liquid alkaline cleansing agent concentrates have also been employed. However, upon prolonged storage of these alkaline concentrates, losses of polymeric phosphates occur due to hydrolysis. Moreover, nonionic wetting agents or detergents and antifoams and also polyphosphates cannot be incorporated in these concentrates in sufficient quantities.

It now has been found that these drawbacks are averted by the instant invention. The process for continuous cleansing of rigid materials, especially glass bottles and metals, uses alkaline cleansers which are characterized by a complement of a liquid, acid, active concentrate containing a nonionic detergent and/or foam depressant, and also water-soluble organic acids which are capable of forming complexes with the hardness-causing ingredients of water or acid salts of these acids, furthermore or agent containing alkali, the latter in an excess.

Preferred nonionic wetting and antifoaming agents are those containing polyglycoether groups. These nonionic wetting agents or detergents are obtained by the addition of ethylene oxide on a hydrophobic component or by addition of propylene oxide on a hydrophilic component. Advantageously, addition products of ethylene oxide on polypropyleneglycol or on condensation products of propylene oxide and ethylene diamine are used. Other preferred nonionic wetting agents are addition products of

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propylene oxide on polyalcohols, especially carbohydrates and polyglycerols, and particularly those having 2 to 10 glycerol groups per molecule; or else, addition products of propylene oxide on short-chain alkanolamines, such as mono-, di- and triethanolamine, or on polyamines such as diethylenetriamines, triethylenetetramines and tetraethylenepentamines. The polyamines can be produced by the condensation of ethyleneimines and ammonia or ethylenediamines. Furthermore, as nonionic wetting agents or detergents addition products of ethylene oxide and propylene oxide on alkylphenols may be used, preferably alkylphenols having an alkyl radical of 8 to 12 carbon atoms; or addition products of ethylene oxide on fatty alcohols.

The foam depressants and wetting agents or detergents, respectively, are present in the active concentrates in quantities of 1 to 40 weight percent, preferably 10 to 35 weight percent.

Beside these wetting agents or detergents and/or foam depressants, the active concentrates contain water-soluble organic acids which are capable of forming complexes with the hardness-forming constituents present in water. In lieu of these acids, their acid salts may be used. This denotes such salts which react acidic in aqueous solution and preferably those which have a pH of less than 3.5 in a 1% aqueous solution.

Especially suitable are organic phosphonic acids which form complexes with the hardness-formers in water and have at least two phosphorus atoms in their molecules, such as hydroxy- and aminoalkyl-1,1-diphosphonic acids having an alkyl radical of 2 to 6 carbons and aminomethylenephosphonic acids, particularly aminotri-(methylenephosphonic acid) and ethylenediamino-tetra-(methylenephosphonic acid).

The active concentrates according to the invention contain the water-soluble organic acids or their salts, respectively, which are capable of forming complexes with the hardness formers found in water, in concentrations of 1 to 40 weight percent, and preferably 5 to 30 weight percent. It is feasible to use mixtures of the acids named in the concentrations as given.

The active concentrates additionally may contain solution promoters, especially lower aliphatic alcohols having 1 to 5 carbon atoms. The quantity of such promoters may be varied within a wide range and preferably is between 5 and 30 percent by weight. In most instances the addition of such a solution promoter is not required for the production of homogeneous solutions. The active concentrate, in addition, may contain mineral acids, e.g., phosphoric or sulfuric acid, in concentrations of 1-30 weight percent. The remainder of the active concentrates always is water.

The cleansing baths containing the active concentrate are completed by the addition of an agent containing an alkali which is present in an excess. The term "excess" in the context of this invention is to denote a quantity of alkali-containing agents sufficient to neutralize not only the active concentrate but to impart to the mixture of the two components a pH above 11, and preferably above 12. Opportunely the alkaline agent also is employed in the form of a concentrate of an aqueous component of preferably less than 70 percent. In many instances, it is advantageous to choose as the alkaline agent a concentrated alkali solution, e.g., sodium- or potassium hydroxide solution. This constitutes the preferred embodiment of the invention. However, as desired or required, other alkaline materials may be employed, such as alkali silicates, borates or carbonates.

Furthermore, a portion of the complex formers may be added to the alkaline agent. In general, however, it is preferred to incorporate the complex formers in the active concentrate because this enables, aside from other advantages, the use of two highly concentrated solutions.

The amounts of active concentrates to be put in the baths depend upon the water hardness and the material to be cleaned. Generally, the concentration of the active concentrates in the cleansing bath in 0.02 to 0.4 weight percent. When phosphonic acids having at least 2 phosphorus atoms in their molecules are present in the concentrate, it is added in such an amount that the quantity of these phosphonic acids in the entire bath is 100–300 mg./l.

The amount of alkaline agent simultaneously incorporated in the bath generally is 0.5 to 3.0 weight percent, preferably 1–2%, calculated on the total bath concentration.

The agents described are employed at the customary cleansing temperatures. In automatic bottle washing machines, these temperatures are approximately 60 to 80° C. When cleansing other rigid materials, such as metals, the temperatures generally also are above 50° C.

The washing process according to the invention has the advantage that the active concentrate and the alkaline agent can be metered into the bath continuously. The active concentrate is completely stable even upon prolonged storage and insures good cleaning without foam formation and reliable prevention of scale formation in the washing devices.

The invention now will be further explained by the following examples. However, it should be understood that these are given merely by way of illustration, and not by limitation, and that numerous changes may be made in the details without departing from the spirit of the invention.

All percentages not particularly specified are weight percent. All solutions are aqueous.

Example 1

Iron sheets were immersed for 2 minutes in a cleansing solution at 50° C., then rinsed for 2 minutes with water of 20° C. and dried for 2 minutes in a stream of hot air. This cycle was repeated 500 times, and the layers formed determined by weighing.

For the preparation of the solutions, water of hardness grades of 8°, 16° and 36°, respectively, was used. To the water 1% aqueous NaOH and increasing amounts of an active concentrate were added.

As active concentrates the following were employed:

(a)

	Weight parts
Hydroxyethanediphosphonic acid	20
Nonionic detergent (condensate of ethylene oxide with a reaction product of ethylene diamine and propylene oxide)	20
Water	60

(b)

Ethylenediaminetetra-(methylene phosphonic acid) ..	20
Nonionic detergent (same as in (a))	20
Water	60

The results obtained, i.e., the layers formed on the sheet metal, are compiled in Table 1.

TABLE 1.—LAYER FORMED (g./m.²)

Test No.	Additive (In addition to 1% NaOH)	Water hardness ¹		
		8°	16°	36°
1.....	Blank test.....	10	25	55
2.....	0.03% concentrate (a).....	0.2	1.0	7
3.....	0.06% concentrate (a).....	0.2	1.25	6
4.....	0.09% concentrate (a).....	0	0	3
5.....	0.12% concentrate (a).....		0.2	4
6.....	0.15% concentrate (a).....	0.3	0.8	6
7.....	0.03% concentrate (b).....			30
8.....	0.06% concentrate (b).....			6
9.....	0.09% concentrate (b).....			9
10.....	0.12% concentrate (b).....			9
11.....	0.15% concentrate (b).....			13

¹ The hardness degrees used in all examples are "°d.H.," i.e., German standard hardness degrees, wherein 1°d.H.=10 mg. CaO/l.

Example 2

Beer bottles were cleaned in a commercial bottle washing machine having 2 solution zones and an hourly throughput of 16,000 bottles. As cleansing solution a 1% aqueous NaOH solution was used in each zone which had been produced by dilution of 50% NaOH. To this solution, 0.075 weight percent of an active concentrate were added consisting of 25% hydroxyethanediphosphonic acid, 35% nonionic detergent (condensation product of ethylene oxide with polypropyleneglycol), 10% ethanol, and the remainder water. The water used for cleansing had a temporary hardness of approximately 36°. The cleansing solution was applied at a temperature of 70° C. and was kept at the original strength by means of addition of 50% NaOH and active concentrate, as required.

The bottles were entirely clean, and the labels had come off. No foam formation occurred during the 6-day use of the wash.

Example 3

Mineral water bottles were cleaned in a commercial bottle washing machine of an hourly throughput of 10,000 bottles. The cleansing solution consisted of a 1.5 weight percent alkaline solution containing 95 parts NaOH and 5 parts Na₂SiO₃, 0.25 percent of an active concentrate of 10 weight parts monosodiumhydroxyethanediphosphonate, 10 weight parts of a nonionic detergent (condensation product of ethylene oxide with propyleneglycol), 1% of an addition product of 9 mols ethylene oxide and 10 mols propylene oxide on nonylphenol, and the balance water. This solution was replenished as required with active concentrate and NaOH.

The water available had a temporary hardness of 25°. The temperature of the cleansing solution was 70–75° C. The mineral water bottles emerged from the process well cleaned, and undisturbed refilling of the bottles was observed.

Example 4

Milk bottles were cleaned in a commercial bottle washing machine having two solution zones and a throughput of 12,000 units per hour. The cleansing solution for each zone was a 1.2 weight percent potassium hydroxide solution. To this solution, 0.15 weight percent of an active concentrate were added having the following composition:

	Percent weight
Monopotassiumhydroxyethanediphosphonate	10
Nonionic detergent, as in Example 1 (a)	10
Water	80

The cleansing solution was made up to its original strength, as required, by addition of KOH and active concentrate. The water used had a temporary hardness of 8°, the temperature of the cleansing solution was 65° C.

The bottles were entirely clean after washing, scale formation was successfully prevented, and no foaming occurred in the cleansing bath.

Like results were obtained by using as nonionic detergents addition products of ethylene oxide on polypropylene; addition products of propylene oxide on carbohydrates or on polyglycerols having 2 to 10 glycerol groups per molecule; addition products of propylene oxide on short-chain alkanolamines, e.g., mono-, di- and triethanolamine; addition products of propylene oxide on polyamines produced by condensation of ethyleneimine with ammonia or ethylenediamine; addition products of ethylene oxide on fatty alcohols, preferably C₁₂ to C₁₈ alcohols; or addition products of ethylene oxide and propylene oxide on alkylphenols having an alkyl of 8–12 carbon atoms.

Example 5

Soft drink bottles were cleaned in a commercial bottle washing machine equipped with 3 dip-washing zones. For the several zones, a 2% aqueous NaOH was used. To

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this solution, 0.1 weight percent of an active concentrate were added consisting of 20% by weight aminoethanediphosphonic acid, 30% nonionic detergent (a condensation product of ethylene oxide with polypropyleneglycol), 15% ethanol and the balance water. The original strength of the baths was kept up by the addition of NaOH and active concentrate, as required. The water employed had a temporary hardness of 16°, and the cleansing solution was at a temperature of 80° C. The bottles were well cleaned after passing the machine, no foam was observed and no scale formation in the warm water zone, even after prolonged activity.

Example 6

Milk bottles were cleaned in a commercial bottle washing machine having two solution zones and an hourly throughput of 10,000 units. The solutions for zones 1 and 2 were 2.5% aqueous NaOH solutions, to which 0.12 weight percent of an active concentrate were added having the following composition:

	Percent weight
Hydroxypropanediphosphonic acid	25
Nonionic detergent (addition product of 6.6 mols propylene oxide per OH group on polyglycerol of an OH value of 1,080)	30
Water	45

The baths, as required, were replenished by addition of NaOH and active concentrate. The bath temperature was approximately 70° C., and the wash water had a temporary hardness of approximately 17°. The cleansing action was excellent, and even after prolonged use of the solution, no foaming nor scale formation could be observed.

Example 7

Wine bottles were cleaned in a small automatic washer having an hourly throughput of 4,000 bottles at a temperature of 70° C. The cleansing solution was a 1.5% NaOH to which 0.15 percent of an active concentrate had been added consisting of the following:

	Percent weight
Hydroxypentanediphosphonic acid	20
Nonionic detergent (addition product of 27.5 mols propylene oxide on triethanolamine)	20
Water	60

The water employed had a temporary hardness of 12°. The solution was brought up to strength, as required, by addition of 50% NaOH and active concentrate.

The cleansing effect was excellent even in instances of strong soilage by residual red wine. No scale formation occurred in the warm water zone, and no foaming took place in the solution zone, during the duration of the test which lasted several days.

Example 8

Dirty motor parts were cleaned in a dual chamber spray washing device with a 1.5% aqueous NaOH solution at 70° C. To the solution, 0.1 percent of an active concentrate were added having the following composition:

	Percent weight
Aminobutanediphosphonic acid	30
Nonionic detergent as in Example 1 (a)	25
Addition product of 9 mols ethylene oxide and 10 mols propylene on nonylphenol	1
Water	44

The water used had a temporary hardness of 20°. The motor parts could be sprayed clean with this solution.

Example 9

Beer bottles were cleaned in a commercial bottle washing machine having two solution zones. In both these zones a cleansing solution was employed containing 1% NaOH and 0.1% of an active concentrate composed as follows:

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	Percent weight
Aminotri-(methylenephosphonic acid)	25
Nonionic detergent (condensation product of ethylene oxide with propylene glycol)	25
Water	50

The water used had a temporary hardness of 15°. The cleansing solutions were employed at temperatures of 60–65° C., and brought back to the original strength by addition of NaOH and concentrate, as required. Cleansing and removal of the labels were excellent. No scale formation occurred, and no foam developed throughout the use of the solution.

Practically the same results were obtained when 0.15% of an active concentrate replaced the one named above which had the following composition:

	Percent weight
Monotriethanolamine salt of aminotri-(methylenephosphonic acid)	20
Nonionic detergent as in Example 1	20
Addition product of 9 mols ethylene oxide and 10 mols propylene oxide on nonylphenol	1
Isopropanol	10
Water	49

Example 10

Soft drink bottles were cleaned in a commercial bottle washing machine having three dip zones. For the several dipping baths, a 1.2% aqueous NaOH was used to which 0.15% of an active concentrate were added having the following composition:

	Percent weight
Ethylenediaminetetra-(methylenephosphonic acid)	20
Nonionic detergent (condensation product of ethylene oxide with propyleneglycol)	20
Ethanol	15
Water	45

The solution was used at a temperature of 70–80° C. and replenished by addition of active concentrate and NaOH when required. The water had a temporary hardness of 6°. Cleansing action was very good, no foam developed, and so scale formation took place even upon prolonged use.

Like results were obtained when as the active concentrate 0.25% of the following mixture were employed, in lieu of the one given above:

	Percent weight
Monosodium salt of ethylenediaminetetra-(methylenephosphonic acid)	10
Nonionic detergent as in Example 1	10
Water	80

Example 11

Beer bottles were cleaned in a commercial bottle washing machine having two cleansing zones. In both these zones, a cleansing solution was employed which contained 1% NaOH and to which had been added 0.1% of an active concentrate of the following composition:

	Percent weight
Hydroxyethanediphosphonic acid	20
Nonionic detergent (addition product of 5 mols propylene oxide per N-atom on tetraethylenepentamine)	20
Water	60

The water used had a temporary hardness of 15°. The cleansing solutions were applied at a temperature of 60–65° C. and replenished as required by addition of NaOH and active concentrate. Cleansing action and removal of the labels were faultless. Calcification in the warm water zone could not be observed, and no foam developed during the time of application.

Example 12

Milk bottles were cleansed in a commercial bottle washing machine having two wash zones and an hourly capacity of 10,000 units. The solutions for both zones had 2.5% NaOH and 0.12% of an active concentrate of the following composition:

	Percent weight
Aminotri-(methylphosphonic acid) -----	20
Nonionic detergent (additive of 9 mols ethylene oxide and 10 mols propylene oxide on nonylphenol) ----	20
Isopropanol -----	15
Phosphoric acid (75%) -----	20
Water -----	25

The cleansing baths were made up to strength with NaOH and concentrate, as required. The bath temperature was 70° C., and the water had a temporary hardness of substantially 17°. Cleansing action was excellent, and even after prolonged use no calcium deposit nor foaming was observed.

The same results were obtained when the active concentrate used had the following composition:

	Percent weight
Aminotri-(methylenephosphonic acid) -----	20
Nonionic detergent (additive of 2 ethylene oxide) groups on oleyl alcohol) -----	20
Isopropanol -----	25
Sulfuric acid (96%) -----	15
Water -----	20

I claim as my invention:

1. In the continuous process for cleaning rigid materials which comprises continuously passing said rigid materials through a periodically replenished washing bath having a pH of about 11 and a temperature above 50° C., and a rinsing bath, said washing bath being composed essentially of from 0.5% to 3% by weight of an alkali selected from the group consisting of sodium hydroxide and potassium hydroxide and from 0.02% to 0.4% of a liquid additive containing a non-ionic detergent, the balance being water and periodically replenishing said alkali and said liquid additive as the same is consumed, the improvement which consists of utilizing as said liquid additive being periodically replenished, a stable aqueous acid active concentrate solution composed of from 1% to 40% by weight of a non-ionic detergent and from 5% to 30% by weight of an organic water-soluble acid selected from

the group consisting of hydroxy and amino alkyl-1,1-di-phosphonic acids having an alkyl of from 2 to 6 carbon atoms, ethylenediaminotetra(methylenephosphonic acid) and aminotri-(methylenephosphonic acid), said active concentrate having a pH of below 3.5 in a 1% aqueous solution.

2. The process of claim 1 wherein said washing bath being periodically replenished is maintained at a concentration of said organic water-soluble acid of from 100 mg./l. to 300 mg./l.

3. The process of claim 1 wherein said active concentrate also contains 5 to 30 weight percent of an aliphatic alcohol having 1 to 5 carbon atoms and a proportionately lower water content.

4. The process of claim 1 wherein said active concentrate, in addition to the ingredients named, contains 1 to 30 weight percent of a mineral acid.

5. The process of claim 4 wherein said mineral acid is selected from the group consisting of sulfuric and phosphoric acid.

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