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3,218,260
CLEANER

Thaddeus Lewandowski, Burlington, Iowa, assignor, by mesne assignments, to Bonewitz Chemicals, Inc., Burlington, Iowa, a corporation of Iowa
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1 Claim. (Cl. 252-142)

This invention relates to an improved general cleaner. It is particularly useful for washing milk cans and containers of glass, plastics, and metals and for cleaning conventional equipment in the dairy, packing house and food processing industries. The invention is also useful in the treatment of water to provide a suitable rinse, for example, and in fact finds utility wherever hard water and soil conditions are present. The invention further finds utility in such industrial operations as water hardness control in enclosed systems.

We have found that an aqueous composition containing an organic acid or an inorganic acid or mixtures of the same, e.g., gluconic acid, glycolic acid, phosphoric acid and mixtures of the same with an anionic synthetic detergent as described in the patents of Parker-Bonewitz, Nos. 2,338,688, 2,338,689 and 2,424,049, are substantially improved for treating hard water and for enhancing their cleaning power when reinforced with certain nonionic synthetic detergents having the usual hydrophilic and hydrophobic components or bases.

These agents according to our discovery must contain at least about 10 moles of ethylene oxide per mole of the hydrophobic base, with the ethylene oxide constituting at least about 70% of the nonionic synthetic detergent. When synthetic detergents of this character are introduced into a composition of the acid and the anionic synthetic detergent, the solubility of the mixture in hard water is substantially improved. In this manner we are able to obtain and retain clarity in water of about 30 to 100 or more grains per gallon hardness at temperatures up to about 212° F. or boiling. It is interesting to observe that the improved results take place regardless of the acid or anionic synthetic detergents which are present in the mixture.

The results achieved by this invention were unexpected and are considered remarkable because when the nonionic synthetic detergents having characteristics below the critical properties above recited were added to a mixture of the acid and anionic synthetic detergent, the reduction of turbidity was not appreciable. However, we discovered by using the nonionic synthetic detergents having at least about 10 moles of ethylene oxide per mole of hydrophobic base and containing at least about 70% ethylene oxide (which are compounds outside of the popular conception and use of nonionic synthetic detergents) that the improved results are obtained in compositions containing the acid and the anionic synthetic detergents.

Of particular significance, it was observed that the presence of the higher molecular weight nonionic synthetic detergents improved the solubility of the well known acid and anionic synthetic detergent mixtures so that even in the case of extremely hard water of upwards of 100 grains or more per gallon, clarity was assured, showing conclusively that the invention resulted in maintaining hard water salts and other materials present in the water permanently in solution, and at extremely high temperatures up to and including boiling.

The practical value of our discovery can best be appreciated when it is realized that milk cans, and food containers, as well as dairy, food processing and similar equipment, must be maintained both physically and biologically clean. The present invention assures that at substantially all temperatures including high temperatures,

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soils and wastes will not only be removed from the equipment but will be permanently prevented from settling out or redepositing whereby scaling and objectionable accumulation of soils will be held to a minimum or is substantially eliminated. The unexpected achievement of this invention becomes more pronounced when it is appreciated that water hardness progressively increases with the increase of the soil load in the aqueous solution. It is to overcome the effect of such condition that this improvement is necessary in present day operations in the food processing and dairy industries and for cleaning in general.

The advantages of the present invention will be more completely understood upon reference to the following table which illustrates by comparison the percent of milk cans showing milkstone in a top quality conventional can washer during the use of at least one of the best cleaning compounds and the present invention.

TABLE 1

Month	Percent Cans Showing Milkstone		
	1957 Machine Washed	1958 Hand Washed*	1959 Hand Washed*
January.....	30.2	5.6	8.3
February.....	24.2	8.6	4.9
March.....	25.8	9.6	7.5
April.....	19.7	4.9	6.1
	Hand Washed*		
May.....	9.3	6.2	2.8 Periodically
			Present Invention
June.....	5.4	2.1	5.1
July.....	6.7	1.9	4.5
August.....	4.9	Periodically	3.3
September.....	8.1	3.4	3.3
October.....	8.7	5.9	3.2
November.....	4.7	5.8	5.5
December.....	5.5	8.6	2.6

*Hand washed periodically in addition to being machine washed.

The following examples illustrate the manner in which the compositions are produced, all amounts being recited by weight of active materials.

Example 1

9% of gluconic acid, 5.1% of alkyl aryl sulfonate ("Ultrawet DS" of Atlantic Refining Co.), 4% nonionic synthetic detergent ("Igepal CO 880," Antara Chemical Co.) and water to make 100% are suitably mixed at room temperature. The composition is then ready to be employed as a cleaner upon suitable dilution in water. Some of the composition water is supplied by the gluconic acid which is preferably introduced as a 50% solution but may be introduced in solution of any amount notably 25 to 75% concentration. The composition has a pH on the acid side below pH 2.

Example 2

This example is like Example 1, except that instead of gluconic acid, 13½% of phosphoric acid is used.

Example 3

This example is like Example 1, except that it contains 9% gluconic acid and 13½% phosphoric acid.

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Example 4

This example is like Example 1, except that it contains 9% gluconic acid and 12.6% glycolic acid.

Example 5

This example is like Example 1, except that 13½% phosphoric acid and 12.6% glycolic acid were used.

Example 6

This example is like Example 1, except that 12.6% glycolic acid alone was used.

With respect to the amounts by weight of the organic and inorganic acids which are employed, preferably not less than about 9% by weight is used. The upper limits for the respective acids content do not present any particular criticality. For instance, the phosphoric acid of Example 2 is useful in amount up to about 65% and compositions containing as much as 50% of gluconic acid have been found feasible.

The concentrated or stock solutions of which the foregoing examples are representative as stated will have a pH on the acid side, i.e., below 2. In some cases the pH may be below 1.0.

The lower limit of active anionic detergent is about 1.0% and the upper limit is not particularly critical. Up to 10% has been found satisfactory but greater amounts are not precluded and have also been found useful.

While the lower limit for the nonionic detergent is about 0.4% and the upper limit likewise is not critical, up to 10% having been found useful and larger amounts also having been successfully employed, all amounts being by weight of active ingredient. The amounts used of the respective synthetic detergents is dependent on the character of the water, the soil conditions encountered and other properties connected with the cleaning operation, the lower limits recited being somewhat critical in amount to assure a successful result but the upper limits not being critical as recited since an excess will not preclude a successful result.

In using the concentrates they are diluted with water and usually by employing 1 oz. of the concentrate per gallon of water. This dilution of course will be carried out by the operator and varied in accordance with the character of the water used, the soil conditions, and the general nature of the metal, glass or plastic surface to be cleaned and of course the method of application. The diluted solution is useful with cleaning systems which employ circulation, spraying, soaking, brushing by hand and in fact in all of the usual ways as practiced by the particular industry. In some cases, of course, the dilution is also varied in accordance with the particular type of equipment being cleaned and by the cleaning procedures in use at a particular plant. In this connection, the product may also be used as a final rinse. As a practical matter, as little as about ¼ ounce of the concentrate per gallon of water or less has been found useful and under certain conditions it may be found imperative to use the concentrate at full strength.

The acids which are useful in this invention in accordance with the foregoing examples are phosphoric, glycolic and gluconic and mixtures of the same, namely, glycolic and gluconic, phosphoric and gluconic and phosphoric plus glycolic. The relative proportions in which the mixtures are made up is not critical. Thus, in Example 3, the amount of gluconic acid could be greater than the amount of phosphoric acid and in Example 4 the gluconic acid can be in greater amount than the glycolic, while in Example 5 the amount of phosphoric can be greater than the amount of glycolic. The total amount of the acids present should be within the ranges set forth above. The foregoing are preferable but other acids which may be used in the same manner are citric, lactic, levulinic, tartaric, oxalic, fumaric and aconitic. Inorganic acids which may be used alone or mixed with each other or with the organic acids are sulfamic, hydrochloric, sul-

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phuric, mixed acids, alkali metal acid phosphates including sodium acid pyrophosphate, monosodium phosphate, sodium bisulfate, and the sodium and potassium acid phosphates in general.

The nonionic synthetic detergents which are useful, may be stated generically to be nonyl and t-octyl, phenols or polyoxypropylene having an average ethylene oxide content of at least about 70% and an average number of moles of ethylene oxide per mole of hydrophobic base of at least about 10. The useful nonyl phenols are the "Igepals" made by Antara Chemical Co. and sold under the trade names of Igepal CO-710, Igepal CO-730, Igepal CO-850 and Igepal CO-880. Thus, t-octyl phenols made by Rohm and Haas and sold under the trade names of Triton X-102, Triton X-165, Triton X-205, and Triton X-305. A suitable and preferable polyoxypropylene is made and sold by Wyandotte Chemical Co. under the trade name of Pluronic F-68.

There are many other types of nonionic synthetic detergents or wetting agents which are suitable and the foregoing are indicated as representative in that they have the pronounced effect when added to an acid and an anionic synthetic detergent in accordance with the foregoing examples of affording enhanced cleaning action on the one hand and imparting the permanent clarity to the cleaning solution notwithstanding that the condition of the water be as high and even greater than 100 grams per gallon of hardness and the temperatures range from room temperature to and through boiling 212° F., on the other hand.

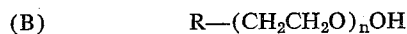
With respect to the anionic synthetic detergents employed, with this invention, and illustrated in the foregoing examples, a great many may be utilized and they are generally of the class consisting of alkyl aryl sodium sulfonates in which the alkyl may be decyl or dodecyl and the aryl may be benzene or naphthalene. Thus suitable examples are "Ultrawet DS" made by Atlantic Refining Co. and containing at least 85% decyl benzene sodium sulfonate, "Nacconol Z" made by National Aniline Co. and containing at least 85% dodecyl benzene sodium sulfonate, and "Petro AA" made by Petro Chemical Co. and containing at least 98% alkyl naphthalene sodium sulfonate.

In a mixture of gluconic and glycolic acids which proved quite successful we used 6% of the "Ultrawet DS," with 4% of the Igepal CO-710 or Igepal CO-730; as described in the foregoing examples. Also we used 6% of the Nacconol Z with 4% of the Igepal CO-730 or Igepal CO-850 in the mixture of gluconic acid and glycolic acids in accordance with the foregoing examples. We further successfully used 5.2% Petro AA in connection with 6% of the mixture of gluconic and glycolic acids, with Igepal CO-730 as in the foregoing examples.

In the appended claims wherein I have called for a cleaning composition comprising an acid selected from the group consisting of organic and inorganic acids and an anionic synthetic detergent, the improvement is recited as comprising in such a composition a nonionic synthetic detergent having at least about 70% ethylene oxide and about 10 mols of ethylene oxide per mol of the hydrophobic base of said nonionic detergent, and water. Also, the claims bring out that the pH is on the acid side, i.e., is less than about pH 2 and may be less than about pH 1. The organic and inorganic acids are well known cleaning agents as are the anionic detergents, but in reciting the nonionic synthetic detergents, I have for purposes of definiteness stated them to have the formulae:



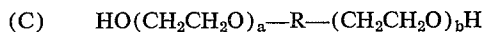
in which R is nonyl phenyl, and n is at least about 10 and equivalent to at least about 70% of the finished product.



in which R is t-octyl phenol and n is at least about 10

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and equivalent to at least about 70% of the finished product.



in which R is polyoxypropylene and a plus b representing 5
mols of ethylene oxide is equivalent to at least about 70% of the molecule.

I claim:

An acid cleaning composition consisting essentially of
at least about 9% gluconic acid, at least about 1% of a 10
higher alkyl aryl sulfonate, at least about 0.4% of a non-ionic synthetic detergent selected from a group consisting of ethylene oxide condensates of nonyl phenols, t-octyl phenols and polyoxypropylene, said detergent having at least about 10 mols of ethylene oxide per mol of the 15
hydrophobic base of said non-ionic detergent and water to make 100%, said cleaning composition having a pH below about 2, said composition increasing the solubility

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of the detergents in hard water and obtaining and retaining clarity in water as much as 30 to 100 grains per gallon hardness up to boiling temperature.

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JULIUS GREENWALD, *Primary Examiner.*