METHODS FOR CLEANING INDUSTRIAL EQUIPMENT WITH PRE-TREATMENT

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ABSTRACT
A method of cleaning equipment such as heat exchangers, evaporators, tanks and other industrial equipment using clean-in-place procedures and a pre-treatment solution prior to the conventional CIP cleaning process. The pre-treatment step improves the degree of softening of the soil, and thus facilitates its removal. The pre-treatment solution can be a strong acidic solution, a strong alkaline solution, or comprise a penetrant. A preferred strong acidic solution is an acid peroxide solution. In some embodiments, the pre-treatment may include no strong alkali or acid ingredient; rather, the penetrant provides acceptable levels of pre-treatment.
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CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 10/928,774 titled METHODS FOR CLEANING INDUSTRIAL EQUIPMENT WITH PRE-TREATMENT, filed on Aug. 27, 2004, the complete disclosure of which is incorporated herein by reference in its entirety.

FIELD

[0002] The invention relates to cleaning of industrial equipment such as evaporators, heat exchangers and other such equipment that is conventionally cleaned using a CIP (clean-in-place) process.

BACKGROUND

[0003] In many industrial applications, such as the manufacture of foods and beverages, hard surfaces commonly become contaminated with soils such as carbohydrate, proteinaceous, and hardness soils, food oil soils and other soils. Such soils can arise from the manufacture of both liquid and solid foodstuffs. Carbohydrate soils, such as cellulloses, monosaccharides, disaccharides, oligosaccharides and starches, gums and other complex materials, when dried, can form tough hard to remove soils, particularly when combined with other soil components such as proteins, fats, oils and others. The removal of such carbohydrate soils can be a significant problem. Similarly, other materials such as proteins, fats and oils can also form hard to remove soil and residues.

[0004] Food and beverage soils are particularly tenacious when they are heated during processing. Foods and beverages are heated for a variety of reasons during processing. For example, in dairy plants, dairy products are heated on a pasteurizer (e.g. HTST—high temperature short time pasteurizer or UHT—ultra high temperature pasteurizer) in order to pasteurize the dairy product. Also, many food and beverage products are concentrated or created as a result of evaporation.

[0005] Specific examples of food and beverage products that are concentrated using evaporators include dairy products such as whole and skimmed milk, condensed milk, whey and whey derivatives, buttermilk, proteins, lactose solutions, and lactic acid; protein solutions such as soya whey, nutrient yeast and fodder yeast, and whole egg; fruit juices such as orange and other citrus juices, apple juice and other pomegranate juices, red berry juice, coconut milk, and tropical fruit juices; vegetable juices such as tomato juice, beetroot juice, carrot juice, and grass juice; starch products such as glucose, dextrose, fructose, isomerose, maltose, starch syrup, and dextrine; sugars such as liquid sugar, white refined sugar, sweetwater, and inulin; extracts such as coffee and tea extracts, hop extract, malt extract, yeast extract, pectin, and meat and bone extracts; hydrolyzates such as whey hydrolyzate, soup seasonings, milk hydrolyzate, and protein hydrolyzate; beer such as de-alcoholized beer and wort; and baby food, egg whites, bean oils, and fermented liquors.

[0006] There are generally at least two sides to an evaporator. One side holds the steam or vapor heat source (typically 212°F (to 350°F)). The other side holds the process liquid to be concentrated. During the evaporation process, the liquid to be concentrated is introduced into the evaporator. The heat exchange across the tubes or plates evaporates water off the process stream concentrating the liquid solids. The liquid to be concentrated may be run through an evaporator several times until it is sufficiently concentrated.

[0007] There are many different types of evaporators including falling film evaporators, forced circulation evaporators, plate evaporators, circulation evaporators, fluidized bed evaporators, falling film short path evaporators, rising film evaporators, countercurrent-trickle evaporators, stirrer evaporators, and spiral tube evaporators. In addition to the evaporators, there are several other pieces of equipment in an evaporation plant including preheaters and heaters, separators, condensers, desalting/vacuum systems, pumps, cleaning systems, vapor scrubbers, vapor recompression systems, and condensate polishing systems. All of the evaporation plant equipment should be cleaned, however, the actual evaporator typically has the most difficult soil problems.

[0008] When a food or beverage product contacts any surface, soiling occurs where some part of the food or beverage product is left behind on that surface. When that surface is a heat exchange surface, the soil becomes thermally degraded rendering it even more difficult to remove. Over time, the layer of soil increases in thickness as more food or beverage product is passed over the heat exchange surface. The layer of soil acts as an insulator between the heat and the product being heated, thereby reducing the efficiency of the heat exchange surface and requiring more energy to create the same effect if the heat exchange surface were clean. When the heat exchange surface is an evaporator, the difference between a clean heat exchange surface and a soiled heat exchange surface can mean the difference in millions of dollars in energy costs for an evaporator plant. With the cost of energy increasing significantly, as well as an increased awareness of protecting the environment by preserving natural resources, there remains a need for cleaning programs that can clean heat exchange surfaces and create an efficient transfer of a heat.

[0009] Clean-in-place cleaning techniques are a specific cleaning regimen adapted for removing soils from the internal components of tanks, lines, pumps and other process equipment used for processing typically liquid product streams such as beverages, milk, juices, etc. Clean-in-place cleaning involves passing cleaning solutions through the system without dismantling any system components. The minimum clean-in-place technique involves passing the cleaning solution through the equipment and then resuming normal processing. Any product contaminated by cleaner residue can be discarded. Often clean-in-place methods involve a first rinse, the application of the cleaning solutions, a second rinse with potable water followed by resumed operations. The process can also include any other contacting step in which a rinse, acidic or basic functional fluid, solvent or other cleaning component such as hot water, cold water, etc. can be contacted with the equipment at any step during the process. Often the final potable water rinse is skipped in order to prevent contamination of the equipment with bacteria following the cleaning and/or sanitizing step.

[0010] Clean-in-place processing requires a complete or partial shutdown of the equipment being cleaned, which results in lost production time. Many times, the equipment is not thoroughly cleaned, due to the large downtime needed. What is needed is an improved method for cleaning this
equipment, using the clean-in-place process, which uses less
time to thoroughly remove the soils.

[0011] It is against this background that the present inven-
tion has been made.

SUMMARY OF THE DISCLOSURE

[0012] Surprisingly, it has been discovered that food and
beverage soils, and especially baked-on food and beverage
soils can be removed from surfaces using a two-step method
where the soil is contacted with a pre-treatment composition
in a pre-treatment step, followed by a conventional clean-in-
place process. The invention relates to methods of cleaning
equipment such as heat exchangers, evaporators, tanks and
other industrial equipment using clean-in-place procedures.
The method is suitable for organic soil removal or, more
particularly, for food or beverage soil removal. Further, the
method relates to cleaning processes for removing carbohy-
drate and proteinaceous soils from food and beverage manu-
factoring locations using a clean-in-place method.

[0013] In one aspect, the invention is directed to a method
that includes pre-treating the soiled surfaces with a strong
acidic solution. A conventional clean-in-place process fol-
ows this pre-treatment step. A preferred acidic solution is an
acid peroxide solution. It has been found that a conventional
clean-in-place process using an alkaline detergent after the
acidic pre-treatment step provides particularly effective
results. The concentration of the active ingredients in an
acidic pre-treatment solution for some applications is at least
0.1% and usually at least 0.6%.

[0014] In another aspect, the invention is directed to a
method that includes pre-treating the soiled surfaces with a
strong alkaline solution. A conventional clean-in-place pro-
cess follows this pre-treatment step. It has been found that a
conventional clean-in-place process using an acidic detergent
after the strong alkaline pre-treatment step provides particu-
larly effective results.

[0015] Either of the pre-treatments, either acidic or alka-
line, may include a penetrant. The addition of a penetrant
improves the degree of softening of the soil, and thus facili-
tates the removal of the soil. The concentration of penetrant in
a pre-treatment solution is at least 0.01% and usually at least
0.15%. A concentration of about 1% is acceptable.

[0016] In another aspect, the invention is directed to a
method that includes pre-treating the soiled surfaces with a
penetrant, without the presence of appreciable amounts of
acid or alkaline. A conventional clean-in-place process fol-
ows this penetrant pre-treatment step. Here, the concen-
tration of penetrant in the pre-treatment solution (without acid
or alkalinity) is at least 0.01% and usually is at least 0.15%. In
one particular embodiment, the penetrant pre-treatment solu-
tion comprises approximately 0.9% of solvents; other levels
of solvents as penetrants are suitable.

[0017] In one particular embodiment, the invention is a
method of cleaning soils from industrial equipment using a
CIP process. The method includes applying a pre-treatment
solution to the soil, the solution comprising at least 0.25 wt-%
active ingredients, with the active ingredients including any
of an alkaline source, an acidic source, a penetrant, an oxi-
dizer, and a builder. The method also includes recirculating
a first CIP solution through the equipment after the pre-treat-
ment solution, the CIP solution comprising a dilute detergent
and then rinsing the equipment. The pre-treatment solution
can have 0.25 to 1.5 wt-% acid and/or 0.01 to 1 wt-% oxidant,
such as a peroxide. A penetrant, such as glycol ether, may be
present at 0.4 to 10 wt-%.

[0018] In another particular embodiment, the method
includes pre-treating the soil with a pre-treatment solution
comprising at least 0.5 wt-% active ingredients, the active
ingredients including any of an alkaline source, an acidic
source, a penetrant, an oxidizer, a surfactant, and a builder,
removing at least a portion of the penetrated soil with a dilute
detergent solution, and rinsing the equipment. In some
embodiments, the pre-treatment solution includes an alkaline
source and the dilute detergent includes an acid.
In other
embodiments, the pre-treatment solution includes an acid
source and the dilute detergent is alkaline.

[0019] The present invention includes using two different
CIP solutions.

[0020] These and other embodiments will be apparent to
these of skill in the art and others in view of the following
detailed description. It should be understood, however, that
this summary and the detailed description illustrate only
some examples, and are not intended to be limiting to the
invention as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 is a schematic diagram of an industrial pro-
cess that includes equipment to be cleaned, CIP process
equipment, and pre-treatment equipment.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The present invention is directed to cleaning of
industrial equipment using a pre-treatment step in combina-
tion with clean-in-place procedures. Use of a pre-treatment
step, in combination with conventional clean-in-place solu-
tions and processes, provides increased soil removal than the
conventional process alone. Additionally, use of a pre-treat-
ment step, followed by a water rinse, provided unexpected
amounts of soil removal. Use of a pre-treatment step allows
the use of traditionally incompatible chemicals and at higher
concentrations then applied in conventional cleaning pro-
grams.

[0023] As used herein, “weight percent”, “wt-%”, “percent
by weight”, “% by weight”, and variations thereof refer to the
concentration of a substance as the weight of that substance
divided by the total weight of the composition and multiplied
by 100. It is understood that, as used here, “percent”, “%”,
and the like are intended to be synonymous with “weight
percent”, “wt-%”, etc.

[0024] As used herein, the term “about” refers to variation
in the numerical quantity that can occur, for example, through
typical measuring and liquid handling procedures used for
making concentrates or use solutions in the real world;
through inadvertent error in these procedures; through differ-
ences in the manufacture, source, or purity of the ingredients
used to make the compositions or carry out the methods; and
the like. The term “about” also encompasses amounts that
differ due to different equilibrium conditions for a composi-
tion resulting from a particular initial mixture. Whether or not
modified by the term “about”, the claims include equivalents
to the quantities.

[0025] It should be noted that, as used in this specification
and the appended claims, the singular forms “a,” “an” and
“the” include plural referents unless the context clearly dic-
tates otherwise. Thus, for example, reference to a composi-
tion containing “a compound” includes having two or more compounds. It should also be noted that the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

[0026] The method of the present invention applies to equipment generally cleaned using clean-in-place (i.e., CIP) cleaning procedures. Examples of such equipment include evaporators, heat exchangers (including tube-in-tube exchangers, direct steam injection, and plate-in-frame exchangers), heating coils (including steam, flame or heat transfer fluid heated) re-crystallizers, pan crystallizers, spray dryers, drum dryers, and tanks. This method can be used in generally any application where caked on soil or burned on soil, such as proteins or carbohydrates, needs to be removed; applications include the food and beverage industry (especially dairy), brewing, oil processing, industrial agriculture and ethanol processing.

[0027] CIP processing is generally well-known. The process includes applying a dilute solution (typically about 0.5-3%) onto the surface to be cleaned. The solution flows across the surface (3 t 6 feet/second), slowly removing the soil. Either new solution is re-applied to the surface, or the same solution is recirculated and re-applied to the surface.

[0028] A typical CIP process to remove a soil (including organic, inorganic or a mixture of the two components) includes at least three steps: an alkaline solution wash, an acid solution wash, and then a fresh water rinse. The alkaline solution softens the soils and removes the organic alkaline soluble soils. The subsequent acid solution removes mineral soils left behind by the alkaline cleaning step. The strength of the alkaline and acid solutions and the duration of the cleaning steps are typically dependent on the durability of the soil. The water rinse removes any residual solution and soils, and cleans the surface prior to the equipment being returned online. The present invention provides a pre-treatment step, prior to the CIP process, which penetrates into the soil. The penetrating materials soften the soil, act as a catalyst, or otherwise enhance the activity of the conventional CIP solution when it contacts the soil. Thus, the pre-treatment facilitates the soil removal.

[0029] Referring now to FIG. 1, a schematic diagram of process equipment is illustrated at reference numeral 10. Process 10 includes a tank 20, which is the equipment to be cleaned. A feed line 25 supplies the various cleaning solutions to tank 20, and a drain line 27 removes solution from tank 20. Operably connected via appropriate pipes, valves, pumps, etc. is equipment for a CIP process, designated as reference numeral 30. CIP process 30 includes a tank 35 for retaining the dilute CIP chemistry. Drain line 27 from tank 20 is used to recirculate solution from tank 20 back to CIP process 30 and tank 35. Process 10 also includes equipment for the pre-treatment process, designated as reference numeral 40. Pre-treatment equipment 40 includes a first tank 42 and a second tank 44. When two tanks are used, generally one tank, e.g., tank 42, will contain an alkaline pre-treatment and the other tank, e.g., tank 44, will contain an acidic pre-treatment. The appropriate pipes, valves, pumps, etc. are in place for operably connecting tanks 42, 44 with feed line 25 into tank 20. This set-up of process 10 allows a pre-treatment to be applied to tank 20 without the use of large amounts of additional equipment, such as piping. Additional details regarding the method of cleaning tank 20 is described below.

[0030] The Pre-Treatment Solution

[0031] As described above, the pre-treatment solution or pre-treatment step is applied to the soil prior to the application of conventional CIP chemistries. The chemistry of the pre-treatment solution is selected to facilitate removal of the soils on the surfaces to be cleaned. The pre-treatment solution pre-coats and penetrates into the soil, softening the soil. The specific chemistry used can be selected based on the soil to be removed. The chemistry used can be compatible with the CIP chemistry. In some embodiments, it is desired to have a pre-treatment that is incompatible with the CIP chemistry; in such instances, the pre-treatment reacts with the CIP chemistry. It has been found that using incompatible chemistries further increases the soil-removal effectiveness.

[0032] The pre-treatment solution comprises 0.25% of active ingredients, in some cases at least 0.5%, preferably at least 2% and more preferably at least 3%. By use of the term “active ingredients” what is intended is the non-inert ingredients that facilitate the softening, dissolving and removal of soil. These active ingredients include any alkaline/base, acid, penetrant (including surfactant), builder, oxidizer, catalyst and chelating agent. In most embodiments, water is the remainder of the solution. Typically, the solution has no more than about 15% active ingredients, preferably no more than about 10%. For most applications, a concentration of about 1-10% is preferred; a concentration of about 1-5% is suitable for most applications.

[0033] Alkaline or Acidic Ingredients

[0034] The pre-treatment solution optionally and preferably includes alkaline or acidic ingredients. Examples of suitable alkaline sources include base salts, amines, alkanol amines, carbonates and silicates. Particularly preferred alkaline sources include NaOH (sodium hydroxide), KOH (potassium hydroxide), TEA (triethanol amine), DEA (diethanol amine), MEA (monoethanolamine), sodium carbonate, and morpholine, sodium metasilicate and potassium silicate.

[0035] Examples of suitable acidic sources include mineral acids (such as phosphoric acid, nitric acid, sulfuric acid), and organic acids (such as lactic acid, acetic acid, hydroxyacetic acid, citric acid, glutamic acid, glutaric acid, and gluconic acid).

[0036] The amount of alkaline or acid in the pre-treatment solution in some cases is at least 0.25 wt-% and no greater than 10 wt-%. Suitable levels of alkaline or acid include 2 to 5 wt-% and 0.5 to 1.5 wt-%.

[0037] Penetrants

[0038] A penetrant may be present in the pre-treatment solution. The penetrant may be combined with an alkaline or acid source in the solution, or the penetrant may be used without an alkaline or acid source. Preferably, the penetrant is water miscible.

[0039] Examples of suitable penetrants include alcohols, short chain ethoxylated alcohols and phenol (having 1-6 ethoxylate groups). Organic solvents are also suitable penetrants. Examples of suitable organic solvents, for use as a penetrant, include esters, ethers, ketones, amines, and nitrated and chlorinated hydrocarbons.

[0040] Another preferred class of penetrants is ethoxylated alcohols. Examples of ethoxylated alcohols include alkyl, aryl, and alkylaryl alkoxylates. These alkoxylates can be further modified by capping with chlorine-, bromine-, benzyl-, methyl-, ethyl-, propyl-, butyl- and allyl-groups. A preferred level of ethoxylated alcohols in the solution is 1 to 20 wt-%.
Another class of penetrants is fatty acids. Some non-limiting examples of fatty acids are C_{10} to C_{18} straight or branched fatty acids. Preferred fatty acids are liquid at room temperature.

Another class of preferred solvents for use as penetrants is glycol ethers, which are water soluble. Examples of glycol ethers include diisopropylene glycol methyl ether (available under the trade designation Dowanol DPM from Dow Chemical Co.), diethyleneglycol methyl ether (available under the trade designation Dowanol DM from Dow Chemical Co.), propylene glycol methyl ether (available under the trade designation Dowanol PM from Dow Chemical Co.), and ethylene glycol monobutyl ether (available under the trade designation Dowanol EB from Dow Chemical Co.). A preferred level of glycol ether in the solution is 0.5 to 20 wt-%.

Surfactants also are a suitable penetrant for use in the pre-treatment solution. Examples of suitable surfactants include nonionic, cationic, and anionic surfactants. Nonionic surfactants are preferred. Nonionic surfactants improve soil removal and can reduce the contact angle of the solution on the surface being treated. Examples of suitable nonionic surfactants include alkyl-aryl-, arylalkyl-, and alkylglycosides and their derivatives, amines and their derivatives, and amides and their derivatives. Additional useful nonionic surfactants include those having a polyalkylene oxide polymer as a portion of the surfactant molecule. Such nonionic surfactants include, for example, C_{12}-C_{18} alkylphenol ethoxylates having 1 to about 100 ethylene oxide groups; C_{12}-C_{18} alkenylphenol ethoxylates having 1 to about 100 ethylene oxide groups; C_{12}-C_{18} monoalkylpolyglycosides having 1 to about 20 glycoside groups, C_{12}-C_{18} fatty acid ester ethoxylates, propoxyxylethers, or propylene glycerides, and C_{12}-C_{18} mono- or dialkylamidomonomers.

If a surfactant is used as a penetrant, the amount of surfactant in the pre-treatment solution is typically at least 0.25%.

Overall, when an alkaline or acid source is present, the amount of penetrant in the pre-treatment solution is at least 0.2 wt-% and no greater than 2.5 wt-%. Acceptable levels of penetrant, when an alkaline or acid source is present, include 0.4-2 wt-%; 1.2-2 wt-% is preferred. The amount of penetrant, in relation to any alkaline or acid source when present, is generally 1:1 to 1:5.

For pre-treatment solutions without an alkaline or acid source, the amount of penetrant in the solution is at least 0.05 wt-% and no greater than 50%. Generally, the level is 0.1 to 25 wt-%. Acceptable levels of penetrant include 0.5 to 10 wt-%, and 1 to 5 wt-%.

Oxidizers

Pre-treatment solutions may include an oxidizing agent or an oxidizer, such as a peroxide or peroxyacid. The resulting solution is very effective against protein and starch soils. Further, reaction of these oxygen compounds with the soil, especially when combined with an alkaline source, creates vigorous mechanical action on and within the soil, which enhances removal of the soil beyond that caused by the chemical and bleaching action.

Suitable ingredients are oxidants such as chlorites, bromine, bromates, bromine monochloride, iodide, iodine monochloride, iodates, permanganates, nitrates, nitric acid, borates, perborates, and gaseous oxidants such as ozone, oxygen, chlorite dioxide, chlorite, sulfur dioxide and derivatives thereof. Peroxygen compounds, which include peroxides and various percarboxylic acids, including percarbonates, are suitable.

Peroxycarboxylic (or percarboxylic) acids generally have the formula R(CO_2)H, where, for example, R is an alkyl, aryalkyl, cycloalkyl, aromatic, or heterocyclic group, and n is one, two, or three, and named by prefixing the parent acid with peroxy. The R group can be saturated or unsaturated as well as substituted or unsubstituted. Medium chain peroxycarboxylic (or percarboxylic) acids can have the formula R(CO_2)H_2, where R is a C_{3}-C_{11} alkyl group, a C_{3}-C_{11} cycloalkyl, a C_{3}-C_{11} arylalkyl group, or a C_{3}-C_{11} heterocyclic group, and n is one, two, or three. Short chain fatty acids can have the formula R(CO_2)H_3, where R is C_{3}-C_{6} and n is one, two, or three.

Some peroxyacetic acids include peroxyxypentanoic, peroxyhexanoic, peroxyheptanoic, peroxyoctanoic, peroxynonanoic, peroxyisononanoic, peroxydecanoic, peroxyundecanoic, peroxydodecanoic, peroxyacetic, peroxyacidic, peroxyacidic, peroxyacetic, and peroxyacetic acid, mixtures thereof, or the like.

Branched chain peroxyacetic acid includes peroxyxypentanoic, peroxyhexanoic, peroxyheptanoic, peroxysococtanoic, peroxyisononanoic, peroxydodecanoic, peroxyxypentanoic, peroxyhexanoic, peroxyheptanoic, peroxyoctanoic, peroxydecanoic, peroxyundecanoic, peroxyxypentanoic, peroxyhexanoic, peroxyheptanoic, peroxyoctanoic, peroxydecanoic, peroxyundecanoic, mixtures thereof, or the like.

Typical peroxygen compounds include hydrogen peroxide (H_2O_2), peracetic acid, peroxyacetic acid, a persulphate, a perborate, or a percarbonate.

The amount of oxidant in the pre-treatment solution is at least 0.01 wt-% and no greater than 1 wt-%. Acceptable levels of oxidant are 0.01 to 0.50 wt-%; 0.3 wt-% is a particularly suitable level. Suitable levels of oxidant, in relation to any acid source, are generally 1:1 to 1:10, 1:3 to 1:7, or 1:20 to 1:50. Solutions of 0.25 wt-% to 10 wt-% phosphoric acid with 50-5000 ppm (0.005 wt-% to 0.5 wt-%) hydrogen peroxide are particularly suitable. An example pre-treatment solution includes 0.75 wt-% phosphoric acid and 500 ppm (0.05 wt-%) hydrogen peroxide, which is a 1:15 ratio of oxidant:acid.

Builders

The pre-treatment solution preferably includes a builder. Builders include chelating agents (chelators), sequestering agents (sequestrants), detergent builders, and the like. The builder often stabilizes the composition or solution. Examples of builders include phosphonic acids and phosphonates, phosphates, aminocarboxylates and their derivatives,
pyrophosphates, polyphosphates, ethylenediamine and ethylenetriamine derivatives, hydroxyacids, and mono-, di-, and tri-carboxylates and their corresponding acids. Other builders include aluminofluorides, nitriloacacetates and their derivatives, and mixtures thereof. Still other builders include amionic carboxylates, including salts of ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetetraacetic acid (HEDTA), and diethylenetriaminopentacetic acid. Preferred builders are water soluble.

Particularly preferred builders include EDTA (including tetr sodium EDTA), TKPP (tripotassium polyphosphate), PAA (polyacrylic acid) and its salts, phosphonobutane carboxylic acid, and sodium gluconate.

The amount of builder in the pre-treatment solution, if present, is typically at least 0.25 wt-% and no greater than 5 wt-%. Acceptable levels of builder include 0.5 to 1.0 wt-% and 1 wt-% to 2.5 wt-%.

Methods of Pre-Treating

The method of the present invention is directed to applying the pre-treatment solution to the surface to be cleaned, prior to a conventional CIP process. The resulting CIP process requires less steps and/or less time for each step. For example, a conventional CIP process includes five steps after an initial water rinse: a conventional alkaline (NaOH) wash to remove soil, an interim rinse, a conventional acid wash to remove minerals and scale, a water rinse, and a conventional sanitizing step. This process can be replaced with a three-step process after the initial water rinse: a pre-treatment step, a conventional wash, and a water rinse.

By using either of the two pre-treatment processes described immediately above, the amount of water used in the overall cleaning process with pre-treatment is reduced by about 30% or more compared to the conventional five-step process. The amount of time for the overall process with pre-treatment is reduced by about 30% or more compared to the conventional five-step process. The specific number of steps, the water usage, or the processing time reduced will depend on the concentration and chemistry of the pre-treatment solution.

Referring again to FIG. 1, the pre-treatment solution is stored at the equipment designated as 40. In this process, tank 42 holds an alkaline pre-treatment solution and tank 44 holds an acidic pre-treatment solution that includes peroxide.

To clean 20, tank 20 and its connection lines are drained of any product that may be present. A water rinse may be included to remove any residual product. In one embodiment, an alkaline pre-treatment solution from tank 42 is pumped via piping and feed line 25 into tank 20. Conventional CIP application equipment, such as a spray head, applies the pre-treatment solution onto the interior surface of tank 20. The pre-treatment solution cascades or otherwise flows down the surface of tank 20, softening the soil. A second application of pre-treatment solution may be applied, although this is not generally needed.

After application and draining of the pre-treatment solution, a conventional CIP process, using the detergent from process 30 and tank 35, is performed. The CIP detergent may be acidic or alkaline. Detergent from tank 35 is recirculated through tank 20 via feed line 25, return line 27, and other appropriate piping.

In another embodiment, a pre-treatment solution containing hydrogen peroxide from tank 44 is pumped via piping and feed line 25 into tank 20. After application and draining of the peroxide pre-treatment solution, a conventional CIP process, using an alkaline detergent such as sodium hydroxide, from process 30 and tank 35, is performed. The sodium hydroxide activates any residual peroxide on the walls of tank 20.

When introducing the pre-treatment solution into the CIP process, it may be beneficial to add the pre-treatment solution at specific places depending on the piece of equipment. For example, when treating an HTST pasteurizer, it is preferable to introduce the pre-treatment solution at the feed balance tank. Alternatively, the pre-treatment solution can be introduced on the suction side of the booster pump or at the T or valve location just prior to plate assembly. When treating a UHT pasteurizer, it is preferable to introduce the pre-treatment solution at the water balance tank. Alternatively, the pre-treatment solution can be introduced at the product balance or feed tank, or the suction side of the booster pump. When treating an evaporator, it is preferable to introduce the pre-treatment solution on the suction side of the effect recirculation pump. Alternatively, the pre-treatment solution can be introduced at the CIP balance tank. Finally, when treating a beer distillation re-boiler, it is preferable to introduce the pre-treatment solution on the suction side of the boiler recirculation pump. Alternatively, the pre-treatment solution can be introduced in the valves between recirculation pump and the distillation column, or the CIP balance tank. The pre-treatment solution is preferably injected closer to the surface to be cleaned. This allows for higher chemical concentrations by avoiding dilution of the pre-treatment chemistry by the entire volume of the CIP supply tank and distribution lines.

Various generic examples of suitable pre-treatment steps are provided below.

In one particular example, an alkaline pre-treatment solution of 10 wt-% NaOH is sprayed onto the interior surfaces of a holding tank and allowed to drain. After about 20 minutes, the CIP process, having a 1% acidic solution, is initiated.

In a second particular example, an acidic pre-treatment solution of 1 wt-% phosphoric acid is circulated onto the interior surfaces of a plate-in-frame heat exchanger. The solution includes 0.1 wt-% H₂O₂. The peroxide is also catalytically activated by a subsequent conventional alkaline CIP solution which causes further effervescence, formation of high oxidation potential species, and soil removal.

In a third particular example, an acidic pre-treatment solution, having about 1.0 wt-% mineral acids and 1.0 wt-% solvent penetrant, is circulated onto the heat exchanging surfaces of an evaporator and drained from the surface. After about 20 minutes, the CIP process is initiated. A conventional alkaline wash, approx. 0.5 wt-% active NaOH, is fed into the evaporator. The alkaline reacts with any acidic residue, generating heat and mechanical action furthering the removal of the soil.

While the present invention has been discussed primarily in the context of cleaning surfaces having food and beverage soils, it is understood that the invention may be used in applications needing cleaning in general including membranes such as spiral-bound membranes, flat sheet ceramic membranes used for water filtration or desalination and heat exchanges surfaces in the chemical and pharmaceutical industries.
For a more complete understanding of the invention, the following examples are given to illustrate some embodiments. These examples and experiments are to be understood as illustrative and not limiting. All parts are by weight, except where it is contrarily indicated.

**EXAMPLES**

Example 1

**Test Procedure**

Solid milk pellets were prepared by mixing 3 grams of dry milk powder and 3 grams of soil. The resulting mix was pressed in a die for 30 seconds at 10,000 lb, and then more pressure was added to again apply 10,000 lb for 30 additional seconds. The pellets were placed in screens and immersed in the pre-treatment solutions, described below, for 5 minutes, removed, and then drained for 5 minutes. The screen and dried pellets were placed in a beaker of 0.5 wt-% NaOH at 120°F. (The test designated as “None” had no pre-treatment step; the test designated as “None *” had no pre-treatment step and used a 3.0% NaOH cleaning at 120°F., rather than the 0.5% NaOH). The beakers were placed on a hot plate set to 49°C (approx. 120°F.) with large stir bars rotating at 350 rpm. After 30 minutes, the screen and pellets were removed from the cleaning solution and gently immersed in and removed from deionized water five times, and then dried overnight at a 50°C oven. The results of the testing are below.

<table>
<thead>
<tr>
<th>Pre-Treatment</th>
<th>Screen wt (g)</th>
<th>Screen wt - pellet wt, before clean (g)</th>
<th>Screen wt - pellet wt, after clean (g)</th>
<th>Pellet wt - before clean (g)</th>
<th>Pellet wt - after clean (g)</th>
<th>% wt loss of pellet</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.30</td>
<td>17.01</td>
<td>6.28</td>
<td>6.28</td>
<td>6.28</td>
<td>28.14%</td>
</tr>
<tr>
<td>2</td>
<td>23.68</td>
<td>17.15</td>
<td>6.53</td>
<td>6.53</td>
<td>6.53</td>
<td>24.12%</td>
</tr>
<tr>
<td>3</td>
<td>23.93</td>
<td>17.22</td>
<td>6.71</td>
<td>6.71</td>
<td>6.71</td>
<td>23.68%</td>
</tr>
<tr>
<td>4</td>
<td>23.69</td>
<td>17.22</td>
<td>6.47</td>
<td>6.47</td>
<td>6.47</td>
<td>24.12%</td>
</tr>
<tr>
<td>None</td>
<td>23.81</td>
<td>17.22</td>
<td>6.59</td>
<td>6.59</td>
<td>6.59</td>
<td>28.14%</td>
</tr>
<tr>
<td>None*</td>
<td>23.81</td>
<td>17.22</td>
<td>6.59</td>
<td>6.59</td>
<td>6.59</td>
<td>24.12%</td>
</tr>
<tr>
<td>None*</td>
<td>23.81</td>
<td>17.22</td>
<td>6.59</td>
<td>6.59</td>
<td>6.59</td>
<td>29.11%</td>
</tr>
</tbody>
</table>

The results show both consistency within the cleaning processes and differences when comparing the methods. The results indicate that lower levels of NaOH are better than higher levels, and that pre-treatment solutions 3 and 4 are superior to pre-treatment solutions 1 and 2. This difference, however, may be due to the test procedure used. Tests 1 and 2 were done on one hot plate whereas tests 3 and 4 were done on a second hot plate. It is possible that these two hot plates were not equal at maintaining the 120°F temperature.

A 10 wt-% solution of active NaOH was prepared and used as a pre-treatment. The pre-treatment had 100,000 ppm sodium hydroxide (an alkaline cleaner).

Pre-Treatment 2

A pre-treatment solution was prepared having 1360 ppm tetra sodium EDTA (a builder and/or chelant), 3000 ppm sodium gluconate (a builder and/or chelant), 2400 ppm potassium silicate (an alkaline cleaner), 7000 ppm alkyl polyglycoside (a surfactant), and 4200 ppm potassium hydroxide (an alkaline cleaner). This Pre-Treatment 2 had 3.66% alkaline, 0.43% builder/chelant, and 0.7% surfactant, providing 4.79% active ingredients.

The results show both consistency within the cleaning processes and differences when comparing the methods. The results indicate that lower levels of NaOH are better than higher levels, and that pre-treatment solutions 3 and 4 are superior to pre-treatment solutions 1 and 2. This difference, however, may be due to the test procedure used. Tests 1 and 2 were done on one hot plate whereas tests 3 and 4 were done on a second hot plate. It is possible that these two hot plates were not equal at maintaining the 120°F temperature.

A drastic difference was seen between the duplicate tests (i.e., 61% and 39% for solution 4); it is possible that one of the pellets had a crack in it, providing a weak location for the pellet to break. The high exposed surface area would result in an increase rate if disintegration.

The tests were rerun on the same hotplate in an attempt to determine if there was any inconsistency between temperature control of the hotplates. The results are provided in the table below, under the column designated “% wt loss of pellet with pre-treat”.

As an alternative, and comparative method, 1 gram of the Pre-treatment solution were added to 315 grams of the 0.5% NaOH cleaning solution. Thus, rather than applying the pre-treatment chemistry as a separate step, the pre-treatment chemistry was added to the cleaning solution. The results are provided in the table below, under the column designated “% wt loss of pellet without pre-treat”.

Pre-Treatment 3

A pre-treatment solution was prepared having 41150 ppm polycarboxylated alcohol ethoxylate (a surfactant), 9540 ppm octyl amine oxide (a surfactant), 25500 ppm alkyl polyglycoside (a surfactant), and 4510 ppm 2-ethylhexanol ethoxylate (a penetrant). This Pre-Treatment 3 had 0.4% penetrant and 7.6% surfactant, providing 8% active ingredients.

Pre-Treatment 4

A pre-treatment solution was prepared having 1600 ppm potassium hydroxide (an alkaline cleaner), 9465 ppm sodium hydroxide (an alkaline cleaner), 18500 ppm polyacrylic acid (a builder and/or chelant), and 4625 ppm phosphonobutane tricarboxylic acid (a builder and/or chelant). This Pre-Treatment 4 had 1.10% alkaline and 2.3% builder/chelant, providing 2.9% active ingredients.
The results indicate that eliminating the separate pre-treatment step and adding the chemicals directly to the cleaning solution increased the performance of the two less effective solutions (1-10% NaOH; 2-10% KX-3108) and decreased the performance of the two more effective solutions (3-10% Quadexx 400; 4-10% Quadexx 500). All of these results were better than if no pre-treatment was present (which provided pellet loss of about 29%).

Example 2

Test Procedure

Soiled stainless steel test panels, having soil on one side, were prepared by drying a mixture of mashed corn solids onto one side of the panel in an oven at 120 °C for 4 hours. The soiled panels were then cleaned as described below.

Pre-treatment 5

A pre-treatment solution was prepared having 400 ppm tetra sodium EDTA (a builder and/or chelant), 4500 ppm tri potassium polyphosphate (a builder and/or chelant), 3852 ppm potassium hydroxide (an alkaline cleaner), 3000 ppm polyethylene phenol ether phosphate (a surfactant), 1000 ppm sodium metasilicate (an alkaline cleaner), 9000 ppm ethylene glycol monobutyl ether (a penetrant), and 2400 ppm sodium xylene sulfonate (a surfactant). This Pre-Treatment 5 had 0.5% alkaline, 0.5% builder/chelant, 0.5% surfactant, and 0.9% penetrant, providing 2.4% active ingredients.

Table 1 shows the percent soil removal of various pre-treatment and main wash chemistries.

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Chemistry</th>
<th>Tradename</th>
<th>15 Min Pre-treatment % Soil Removal</th>
<th>15 Min CIP Main Wash % Soil Removal</th>
<th>% Soil Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH</td>
<td>3.00</td>
<td>100.0%</td>
<td>100.0%</td>
<td>75.70</td>
</tr>
<tr>
<td>2</td>
<td>Na2CO3</td>
<td>2.00</td>
<td>100.0%</td>
<td>100.0%</td>
<td>65.00</td>
</tr>
<tr>
<td>3</td>
<td>MEA (99%)</td>
<td>4.00 NaOH</td>
<td>3.00</td>
<td>3.00</td>
<td>75.00</td>
</tr>
<tr>
<td>4</td>
<td>DEA</td>
<td>4.00 NaOH</td>
<td>3.00</td>
<td>3.00</td>
<td>82.40</td>
</tr>
<tr>
<td>5</td>
<td>TEA</td>
<td>4.00 NaOH</td>
<td>3.00</td>
<td>3.00</td>
<td>79.50</td>
</tr>
<tr>
<td>6</td>
<td>Morpholine</td>
<td>4.00 NaOH</td>
<td>3.00</td>
<td>3.00</td>
<td>82.60</td>
</tr>
<tr>
<td>7</td>
<td>Cyclohexylamine</td>
<td>4.00 NaOH</td>
<td>3.00</td>
<td>3.00</td>
<td>84.50</td>
</tr>
<tr>
<td>8</td>
<td>n-Methyl Pyrrolidine</td>
<td>4.00 NaOH</td>
<td>3.00</td>
<td>3.00</td>
<td>84.90</td>
</tr>
<tr>
<td>9</td>
<td>Monoisopropanol amine</td>
<td>4.00 NaOH</td>
<td>3.00</td>
<td>3.00</td>
<td>94.60</td>
</tr>
<tr>
<td>Exp #</td>
<td>Chemistry</td>
<td>Tradename</td>
<td>15 Min CIP Main Wash</td>
<td>% Soil Removal</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td>------------</td>
<td>---------------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>95.00</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>97.40</td>
<td></td>
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<tr>
<td>12</td>
<td>DEA</td>
<td>NaOH</td>
<td>3.00</td>
<td>90.00</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>TEA</td>
<td>NaOH</td>
<td>3.00</td>
<td>89.80</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Merphosphate</td>
<td>NaOH</td>
<td>3.00</td>
<td>94.80</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Cyclohexylamine</td>
<td>NaOH</td>
<td>3.00</td>
<td>82.10</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>n-Methyl Pyrrolidine</td>
<td>NaOH</td>
<td>3.00</td>
<td>92.70</td>
<td></td>
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<td>17</td>
<td>Monopropylammonium</td>
<td>NaOH</td>
<td>3.00</td>
<td>94.90</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Dowanol EB</td>
<td>NaOH</td>
<td>3.00</td>
<td>96.40</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Dowanol DM</td>
<td>NaOH</td>
<td>3.00</td>
<td>84.60</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Dowanol PaB</td>
<td>NaOH</td>
<td>3.00</td>
<td>97.00</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Dowanol EpH</td>
<td>NaOH</td>
<td>3.00</td>
<td>80.20</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Dowanol DmpP</td>
<td>NaOH</td>
<td>3.00</td>
<td>87.60</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Dowanol PnP</td>
<td>NaOH</td>
<td>3.00</td>
<td>86.20</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Dowanol PPh</td>
<td>NaOH</td>
<td>3.00</td>
<td>84.80</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Propylene Carbonate</td>
<td>NaOH</td>
<td>3.00</td>
<td>71.90</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>92.00</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>96.50</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>97.00</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>92.00</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>99.00</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>99.80</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>99.20</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>88.4</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Dequest 2000</td>
<td>NaOH</td>
<td>3.00</td>
<td>89.30</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>Dequest 2010</td>
<td>NaOH</td>
<td>3.00</td>
<td>86.20</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>EDTA</td>
<td>NaOH</td>
<td>3.00</td>
<td>89.20</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>STPP</td>
<td>NaOH</td>
<td>3.00</td>
<td>79.70</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>TKPP</td>
<td>NaOH</td>
<td>3.00</td>
<td>89.10</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Sodium Gluconate</td>
<td>NaOH</td>
<td>3.00</td>
<td>89.50</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Dequest 2000</td>
<td>NaOH</td>
<td>3.00</td>
<td>93.00</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>94.10</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>95.00</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>95.00</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>97.00</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>H₂O₂</td>
<td>NaOH</td>
<td>3.00</td>
<td>93.00</td>
<td></td>
</tr>
</tbody>
</table>
Example 4

[0092] Example 4 compared the ability of various oxidizers to remove corn beer thin stillage syrup. For this example, the screens were soaked with corn beer thin stillage syrup and cleaned as described in Example 3. Table 2 shows the impact of various oxidizers on soil removal.

<table>
<thead>
<tr>
<th>Exp # Chemistry</th>
<th>% Soil Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>94.90</td>
</tr>
<tr>
<td>Sodium Peroxide</td>
<td>96.40</td>
</tr>
<tr>
<td>Sodium Persulfate</td>
<td>82.80</td>
</tr>
<tr>
<td>Potassium Permanganate</td>
<td>72.30</td>
</tr>
</tbody>
</table>

Example 5

[0093] Example 5 compared the amount of time it took to clean the screens using the pre-treatment solutions of the present invention compared to using only sodium hydroxide. This example tested the time to clean corn beer thin stillage syrup and whole milk soil. The corn beer thin stillage syrup soil was prepared and cleaned as described in Example 3.

[0094] For the whole milk soil, the soil was prepared by weighing stainless steel discs to be soaked and affixing the disc to the bottom of a 1.5 foot, 3 inch diameter stainless steel tube. A water bath was heated to 205°F to 210°F and the tubes with the discs were placed in the water bath. A ½ gallon of whole milk was added to each tube used and allowed to sit for 4 hours. After 4 hours, the tubes were removed and allowed to dry for at least 48 hours. When cleaning the whole milk soil, the disc was affixed to an overhead stirrer. The desired cleaning solution was heated to 180°F using a hot plate. The disc was inserted into a 1 L beaker of cleaning solution for 10 minutes and the overhead stirrer was set to 50 rpm. After 10 minutes, the disc was removed from the cleaning solution and placed in a beaker of deionized water. The overhead stirrer was set at 200 rpm for 30 seconds. The disc was removed and allowed to dry at least 48 hours before weighing. The percent soil removal was calculated using the following formula:

\[
\frac{\text{Soiled wt} - \text{After wt}}{\text{Soiled wt} - \text{virgin wt}} \times 100 = \% \text{ Soil Removal}
\]

Tables 3 and 4 show the time it took to remove 100% of the soil on the screen or disc when using sodium hydroxide alone, Stabicip Oxi pre-treatment followed by a sodium hydroxide wash, and Formula A (74% hydrogen peroxide (35%), 9.75% sodium cumene sulfonate (40%), 5.25% sodium octane sulfonate, 3.50% hydroxyethylidene diphasphonic acid (60%), 3% methane sulfonic acid, 1% n-butyl capped alcohol ethoxylate (5EO), and 3.5% pelargonic acid) followed by a sodium hydroxide wash. Stabicip Oxi is a hydrogen peroxide based composition commercially available from Ecolab Inc. (St. Paul, Minn.).

<table>
<thead>
<tr>
<th>Time to Clean Corn Beer Thin Stillage Syrup Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp # Chemistry</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>1 NaOH</td>
</tr>
<tr>
<td>2 Stabicip Oxi</td>
</tr>
<tr>
<td>3 Stabicip Oxi</td>
</tr>
</tbody>
</table>
Table 3 shows that including a hydrogen peroxide based pre-treatment composition together with a sodium hydroxide wash cuts the time to clean corn beer thin stillage syrup in half when compared to a sodium hydroxide wash alone.

Table 4 shows that including a hydrogen peroxide based pre-treatment composition together with a sodium hydroxide wash cuts the time to clean whole milk soil in half when compared to a sodium hydroxide wash alone. Using Formula A together with a sodium hydroxide wash cuts the time to clean whole milk soil by more than half when compared to sodium hydroxide wash alone.

Example 6

Example 6 tested the effectiveness of various different pre-treatment and main wash chemistries on the removal of whole milk soil. For this test, the whole milk soil was prepared and cleaned as described in Example 5. Table 5 shows the percent removal of the various combinations.

Table 5

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Pre-treatment Chemistry</th>
<th>Main Wash Chemistry</th>
<th>Time (Min) to 100% Soil Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH</td>
<td>2.00</td>
<td>&gt;60 min</td>
</tr>
<tr>
<td>2</td>
<td>Stabicip Oxi</td>
<td>NaOH 2.00</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>Formula A</td>
<td>NaOH 2.00</td>
<td>27</td>
</tr>
</tbody>
</table>

The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

1. - 12. (canceled)
13. A method for cleaning soil from industrial equipment using a CIP process, the method comprising:
(a) applying a pre-treatment solution to the soil, the solution comprising at least 0.25 wt% active ingredients, the active ingredients comprising:

- a builder selected from the group consisting of sodium gluconate; a polyphosphate; a phosphonic acid; phosphono-1,2,4-tricarboxylic acid and mixtures thereof; and

- an oxidizer selected from the group consisting of hydrogen peroxide, peroxycarboxylic acids, and mixtures thereof; and

(b) circulating a second solution through the equipment, the second solution comprising a dilute alkaline detergent, wherein there is no rinse step between the application of the pre-treatment solution and the second solution; and

(c) rinsing the equipment.
14. The method of claim 13, wherein the builder is present in an amount of at least about 0.25 wt %.
15. The method of claim 14, wherein the builder is sodium gluconate.
16. The method of claim 13, wherein the oxidizer is present in an amount of about 0.01 wt%- to about 1 wt%.
17. The method of claim 16, wherein the oxidizer is hydrogen peroxide.
18. The method of claim 13, wherein the pre-treatment solution further comprises about 0.25 wt%- to about 10 wt% of an organic acid.
19. The method of claim 18, wherein the organic acid is selected from the group consisting of pelargonic acid, methanesulfonic acid, hydroxyethylidene diphosphonic acid, gluconic acid and mixtures thereof.
20. The method of claim 19, wherein the pre-treatment solution further comprises about 0.4 wt-% to about 8.0 wt-% of a penetrant.

21. The method of claim 20, wherein the penetrant comprises an alkyl capped polyoxyethylene glycol ether.

22. The method of claim 21, wherein the pre-treatment solution comprises:
   (a) sodium gluconate;
   (b) hydrogen peroxide;
   (c) hydroxyethylidene diphosphonic acid;
   (d) pelargonic acid; and
   (e) n-butyl capped alcohol ethoxylate (5EO).

23. The method of claim 22, wherein the pre-treatment solution further comprises methanesulfonic acid.

24. The method of claim 22, wherein the pre-treatment solution further comprises a mineral acid.

25. The method of claim 24, wherein the mineral acid is phosphoric acid.

26. A method for cleaning soil from industrial equipment using a CIP process, the method comprising:
   (a) applying a pre-treatment solution to the soil, the solution comprising at least 0.25 wt % active ingredients, the active ingredients comprising:
      an oxidizer selected from the group consisting of hydrogen peroxide, peroxyacetic acids, and mixtures thereof; and
      an acid selected from the group consisting of mineral acids, organic acids, and mixtures thereof;
   (b) circulating a second solution through the equipment, the second solution comprising a dilute alkaline detergent, wherein there is no rinse step between the application of the pre-treatment solution and the second solution; and
   (c) rinsing the equipment.

27. The method of claim 26, wherein the organic acid is selected from the group consisting of gluconic acid, pelargonic acid, methanesulfonic acid, hydroxyethylidene diphosphonic acid, and mixtures thereof.

28. The method of claim 27, wherein the organic acid is gluconic acid.

29. The method of claim 27, wherein the pre-treatment solution further comprises a builder selected from the group consisting of sodium gluconate; a polyphosphate; a phosphonic acid; phosphono-1,2,4-tricarboxylic acid and mixtures thereof.

30. The method of claim 29, wherein the builder is sodium gluconate.

31. The method of claim 26, wherein the mineral acid is phosphoric acid.

32. The method of claim 26, wherein the pretreatment solution further comprises an alkaline source.

33. The method of claim 32, wherein the alkaline source is sodium carbonate.

34. The method of claim 32, wherein the alkaline source is selected from the group consisting of potassium hydroxide, sodium hydroxide, and mixtures thereof.

35. The method of claim 34, wherein the pre-treatment solution further comprises a polyphosphate.

* * * * *