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METHOD FOR CLEANING METAL ARTICLES

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The present invention relates, as indicated, to a method for cleaning metal articles, especially ferrous metal articles. In a more particular sense, it relates to a novel, acidic aqueous solution adapted for the cleaning of metal articles prior to a surface-treatment thereof.

In the metal finishing industry, it is known that a metal article must be thoroughly cleaned prior to subjecting said article to surface-treatment operations such as phosphating, anodizing, bluing, staining, etc. If the metal article has not been cleaned adequately, satisfactory results are not secured in subsequent surface-treatment operations. Thus, it becomes important to provide a method for cleaning a metal article in a manner so as to insure the success of later surface-treatment operations.

Nearly all unfinished metal articles such as plate steel, steel strip stock, rough core castings, etc., bear surface contaminants or "soils" such as drawing compounds, slushing oils, cutting oils, core compounds, and the like. It is common practice in the industry to clean such unfinished metal articles by subjecting them to the action of hot aqueous solutions containing one or more alkaline materials such as sodium hydroxide, potassium hydroxide, trisodium phosphate, sodium carbonate, sodium silicates, sodium polyphosphates, etc. In many instances, however, the contaminants on the surface of the metal article are not satisfactorily removed by these known alkaline solutions. Then additional costly and time consuming cleaning operations such as vapor-degreasing, pickling, sandblasting, or polishing must be employed to prepare the article for surface-treatment.

Commercially available acidic cleaning solutions (principally dilute aqueous solutions of orthophosphoric acid containing minor amounts of water-soluble mono- or poly-hydric alcohols) have been shown to be useful in some instances where alkaline cleaning solutions have been unsatisfactory. They have not, however, proved effective for removing many frequently-encountered soils. Moreover, such available acidic cleaning solutions are highly corrosive to iron and steel and, consequently, all associated apparatus such as tanks, piping, and spray-nozzles must be made corrosion-proof by the use of special alloys, rubber or plastic linings, etc. As a result, dilute acidic cleaning solutions (to be distinguished from the concentrated pickling acids employed to remove mill scale) have not gained wide acceptance in the metal finishing industry.

In accordance with the present invention, certain novel, acidic aqueous solutions characterized principally by the presence therein of the anions of a plurality of certain lower aliphatic dicarboxylic acids and of certain cations have been found to be effective against a wide variety of soils and to be substantially non-corrosive to ferrous metals.

It is, therefore, an object of this invention to provide a novel, substantially non-corrosive, acidic aqueous solution adapted for the cleaning of metal articles.

Another object is to provide a method for cleaning a metal article, the surface of which bears difficultly-removable soil.

A further object is to provide an improved method for cleaning and phosphating a soiled metal article.

These and other objects of the invention are realized by means of an acidic aqueous solution adapted for the cleaning of metal articles which contains as essential ingredients a major proportion of water and minor proportions each of tartaric acid anion; oxalic acid anion; citric acid anion; a cation selected from the group consisting of ammonium, substituted ammonium, and metal cations; and at least one surface-active agent which is stable at a pH less than 7.

In most instances, the anion-cation balance of the solution will be controlled by the addition of a sufficient amount of a base containing ammonium, substituted ammonium, or metal cations so that the pH of the solution lies within the range from about 3.0 to about 6.5, preferably from about 5.0 to about 6.0. These cations are most conveniently introduced into the solution by the addition thereto of nitrogen bases such as ammonia, ammonium hydroxide, and substituted ammonias such as dimethyl amine, trimethyl amine, ethyl amine, diethyl amine, aniline, etc., or of basic metal compounds such as sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, lithium hydroxide, barium hydroxide, strontium hydroxide, and other basic alkali or alkaline earth metal compounds. In the above-indicated pH ranges, the solution exhibits the maximum cleansing power consistent with a desirably low corrosive action on the ferrous metal apparatus normally used to contain and convey the solution.

Optionally present in the solution of this invention is a minor proportion, generally from about 0.02 to about 0.5 and more often from about 0.05 to about 0.2 weight percent, of an alkali metal salt, ordinarily a sodium or potassium salt, of an aromatic carboxylic acid, which component appears to inhibit further any corrosive action of the solution on ferrous metals. Alkali metal salts useful for the purpose include the alkali metal salts, principally the sodium or potassium salts, of aromatic carboxylic acids such as benzoic, anthranilic, para-tertiary butylbenzoic, para-phenylbenzoic, para-methoxybenzoic, salicylic, isopropyl salicylic, phthalic, terephthalic, naphthoic, para-amino benzoic, ortho-chlorobenzoic, ortho-nithrobenzoic, etc., acids. In most instances the alkali metal salt will be a sodium salt of an aryl monocarboxylic acid such as benzoic, phenylbenzoic, or naphthoic acid. By reason of its availability, low cost, and excellence as a corrosion inhibitor in the solutions of this invention, sodium benzoate is particularly preferred.

Also optionally present in the hereindescribed solution is a minor proportion, generally from about 0.5 to about 5 weight percent, of a water-soluble alcohol such as ethanol, isopropanol, beta-butoxyethoxy-ethanol, beta-butoxy-ethanol, etc. The alcohol appears to aid the surface-active agent in reducing the surface tension between the solution and the soil on the metal article being cleaned.

Either or both of the above-described optional components may be omitted from the solution of this invention. Best results are obtained, however, when at least one and preferably both of these components are present.

The tartaric acid, citric acid, and oxalic acid anions which characterize the solution of this invention are ordinarily supplied by dissolving minor proportions, generally from about 0.05 to about 3 and more often from about 0.5 to about 1.5 weight percent, of each of the corresponding acids in water. The resulting solution will then contain the corresponding weight percentages of the several acid anions. In some instances, however, it may be desirable to use a mixture of acids and salts such as, for example, a mixture of oxalic acid, citric acid, and sodium

potassium tartrate (Rochelle salt) or a mixture of sodium citrate, tartaric acid, and oxalic acid. In any event, either acid mixtures or acid-salt mixtures may be used just so long as the solution thereof in water is acidic, i.e., exhibits a pH less than 7. As indicated eariler, the pH of the solution is adjusted, if necessary, to come within the preferred pH range by the introduction of a base containing ammonium, substituted ammonium, or metal cations. It is generally preferred to control the anion-cation balance and pH of the solution by the introduction of a base containing ammonium or sodium cations. If the pH of the solution has risen above 6.5, it can be restored conveniently to the desired pH range by the addition of one or more of the above characterizing acids. In some instances, it is also desirable to buffer the pH of the solution by means of boric acid.

The surface-active agent employed in the solution of this invention must be one which is stable at a pH less than 7, i.e., does not lose its surface-active properties by reason of chemical transformation or decomposition at the indicated pH. Conventional soaps such as sodium or potassium stearates and oleates are not suitable for the purposes of this invention since they tend to precipitate the parent fatty acid in acidic solutions. Surface-active agents which are stable at a pH less than 7 include principally the commercially available wetting agents and detergents such as alkali metal aliphatic sulfonates, alkali metal alkaryl sulfonates, alkali metal aliphatic sulfates, alkylcarboxypolyalkoxyalkanols, polyalkoxyalkanols, and alkaryloxypolyalkoxyalkanols. This list is, of course, not complete. Continuing research in the field of detergents and wetting agents will undoubtedly result in new materials which are stable in solution at a pH less than 7 and which, therefore, will serve the purposes of this invention. The surface-active agent is present in a minor proportion, generally from about 0.02 to about 0.5 wt. percent, in the solution of this invention. Although a single surface-active agent is serviceable, best results are obtained when two or more chemically different surface agents, e.g., a sodium alkaryl sulfonate and an alkylphenoxypolyalkoxyalkanol, are employed. The alkaryloxypolyalkoxyalkanols, of which the just-cited alkylphenoxypolyalkoxyalkanol is a sub-genus, form an important class of commercial wetting agents. They possess the following structure:

$$R_x—Q—O—(R'O)_yR'OH$$

Wherein—

Q=mono- or poly-aryl nucleus
R=alkyl or alkenyl radical containing from 5 to 40 carbon atoms
R'=lower alkylene radical containing 2–5 carbon atoms
x=1–5 inclusive
y=1–50, inclusive

The sodium alkaryl sulfonates, likewise an important and well-known class of commercial wetting agents and detergents, possess the following structure:

$$R_a—Q—(SO_3Na)_b$$

Wherein—

Q=mono- or poly-aryl nucleus
R=alkyl or alkenyl radical containing from 5 to 20 carbon atoms
a=1–3, inclusive
b=1–2, inclusive

When two or more different surface-active agents are employed, the concentration of each agent will normally lie in the range from about 0.01 to about 0.25 weight percent of the solution. Specific examples of surface-active agents useful for the purposes of this invention include, e.g., sodium octylsulfonate, lithium dodecylsulfonate, potassium tridecylsulfonate, sodium lauryl sulfate, potassium tridecyl sulfate, sodium mono-dodecylbenzene sulfonate, sodium monotridecylbenzene sulfonate, lithium cetylbenzene sulfonate, potassium dihexylbenzene sulfonate, octylphenoxyheptaethoxyethanol, isononylphenoxyoctadecaethoxyethanol, etc.

The metal article to be cleaned is contacted with the hereindescribed acidic aqueous solution, usually at an elevated temperature in the range from about 100° F. to about 212° F. and preferably in the range from about 120° F. to about 190° F. If desired, temperatures above 212° F., such as 250° F., 300° F., or higher can be employed by contacting the metal article with the solution at super-atmospheric pressures. The contacting of the metal article with the solution may be accomplished by any of the ordinary techniques employed in the metal finishing industry such as dipping, spraying, tumbling, brushing, etc. Spraying appears to be the most effective and, therefore, preferred method. Depending on the character and quantity of the soil present on the metal article and the technique of applying the solution, the time of cleaning will vary from as little as one or two seconds to ten minutes or more. In most cases, one or two minutes is sufficient to clean the article thoroughly.

After the article has been cleaned, it is optionally rinsed with water and/or a water-soluble alcohol. Subsequent surface treatments such as phosphating, anodizing, bluing, etc., are preferably carried out on the cleaned metal article without delay, since the cleaned article, particularly if it is made from a ferrous metal, is very susceptible to oxidation or rusting.

Metal articles cleaned by the hereindescribed method have been found to be very receptive to phosphate coatings. Such coatings, which are widely used in the metal finishing industry to inhibit oxidation or rusting and to form an adherent substrate for the subsequent application of organic coating compositions such as paint, varnish, enamel, lacquer, synthetic resins, etc., are generally formed on a metal surface by means of aqueous solutions which contain the phosphate ion and, optionally, certain auxiliary ions including metallic ions such as sodium, manganese, zinc, cadmium, iron, copper, lead, nickel, cobalt, and antimony ions, and non-metallic ions such as ammonium, chloride, bromide, nitrate, and chlorate ions. These auxiliary ions modify the character of the phosphate coating and adapt it for a wide variety of applications. The preparation and use of aqueous phosphating solutions is well-known in the metal finishing industry as shown by U.S. Patents 1,206,075; 1,247,668; 1,305,331; 1,485,025; 1,610,362; 1,980,518; 2,001,754; and 2,859,145.

Aqueous phosphating solutions are generally prepared by dissolving in water minor amounts of phosphoric acid and, optionally, a metal salt such as a nitrate, phosphate, nitrite, sulfate, chloride, or bromide of manganese, sodium, zinc, cadmium, iron, nickel, copper, lead, or antimony. Ordinarily an oxidizing agent such as sodium chlorate, potassium perborate, sodium nitrate, ammonium nitrate, sodium chlorite, potassium perchlorate, or hydrogen peroxide is included in the phosphating solution to depolarize the metal surface being treated and thereby increase the rate at which the phosphate coating is formed on the metal surface. Other auxiliary agents such as antisludging agents, coloring agents, and metal cleaning agents may also be incorporated in the phosphating solution. One common type of commercial phosphating bath which contains zinc ion, phosphate ion, and a depolarizing agent is made by dissolving small amounts of zinc dihydrogen phosphate, sodium nitrate, and phosphoric acid in water.

In order to provide commercially satisfactory coating weights and coating speeds, an aqueous phosphating solution should generally have a total acidity within the range from about 5 to about 100 points, preferably from about 5 to about 50 points. It is possible, however, by certain special techniques to employ phosphating solutions having a total acidity substantially higher than 100 points, e.g., 125, 200, 250, or 300 points or more. The term "points total acidity" as employed in the phosphating art represents the number of milliliters of 0.1 normal sodium

hydroxide solution required to neutralize a 10 milliliter sample of a phosphating solution in the presence of phenolphthalein as an indicator.

A particularly desirable and effective class of aqueous phosphating solutions or baths is set forth in co-pending application Ser. No. 373,449, filed August 10, 1953. It is intended that the disclosure of the said application be considered as forming a part of the present specification. The phosphating solutions described therein have a total acidity within the range from about 5 to about 100 points and contain as essential ingredients zinc ion, phosphate ion, nitrate ion, and an ion selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium ions. Of the several metallic ions enumerated, the calcium ion is preferred. Such phosphating solutions provide a dense, adherent, microcrystalline or amorphous phosphate coating which shows substantially no visible crystal structure at a magnification of 100 diameters and which is preferred for the purposes of the present invention. A particularly useful sub-group of aqueous phosphating solutions for the purposes of this invention have a total acidity within the range from about 5 to about 100 points and contain as essential ingredients from about 0.1 to about 1.0 percent of zinc ion, from about 0.25 to about 2.0 percent of phosphate ion, from about 0.25 to about 8.0 percent of nitrate ion, and from about 0.1 to about 4.0 percent of calcium ion.

In view of the extensive commercial development of the phosphating art and the many journal publications and patents describing the application of phosphating solutions, it is believed unnecessary to lengthen this specification unduly by a detailed recitation of the many ways in which the phosphating step may be accomplished. Suffice it to say that any of the commonly used phosphating techniques such as spraying, brushing, dipping, roller-coating, or flow-coating may be employed, and that the temperature of the aqueous phosphating solutions may vary within wide limits, e.g., from room temperature to about 212° F. In general, best results are obtained when the phosphating solution is used at a temperature within the range from about 150° F. to about 210° F. If desired, however, the aqueous phosphating bath may be used at higher temperatures, e.g., 225° F., 250° F., or even 300° F., by employing superatmospheric pressures.

The phosphating operation is usually carried out until the weight of the phosphate coating formed on the cleaned metallic surface is at least about 25 mg. per square foot of surface area and is preferably within the range from about 50 to about 1000 mg. per square foot of surface area. The time required to form the phosphate coating will vary according to the temperature, the type of phosphating solution employed, the particular technique of applying the phosphating solution, and the coating weight desired. In most instances, however, the time required to produce a phosphate coating of the weight preferred for the purposes of the present invention will be within the range from about 5 seconds to about 15 or 20 minutes.

Upon completion of the phosphating operation, the phosphated metal article is rinsed, optionally, with water and/or a hot, dilute aqueous solution of chromic acid containing from about 0.01 to about 0.2 percent of CrO_3. The chromic acid rinse appears to "seal" the phosphate coating and improve its utility as a base for the later application of paint, lacquer, varnish, and other organic coating compositions. In lieu of the dilute aqueous chromic acid, dilute aqueous solutions of metal chromates, metal dichromates, chromic acid-phosphoric acid mixtures, and chromic acid-metal dichromate mixtures may be used.

The following examples are presented to illustrate specific modes of practicing the present invention. They are submitted for purposes of illustration only and are not to be construed as limiting the scope of the present invention, except as the latter is defined by the appended claims. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

An acidic aqueous solution is prepared by dissolving 26.7 grams (0.66 percent) of tartaric acid, 26.7 grams (0.66 percent) of oxalic acid, 26.7 grams (0.66 percent) of citric acid, 1.5 grams (0.038 percent) of a sodium alkaryl sulfonate available commercially under the trade designation "Santomerse S," and 0.5 gram (0.0125 percent) of an isooctylphenoxypolyethoxyethanol available commercially under the trade designation "Triton X–100" in sufficient water to yield 4 liters of solution. The resulting solution shows a pH of 1.6.

EXAMPLE 2

80.3 grams of 75% aqueous ammonium hydroxide is added to the solution of Example 1, whereupon the pH rises to 5.5.

EXAMPLE 3

An acidic aqueous solution is prepared by dissolving 50 grams (1.25 percent) of sodium potassium tartrate, 40 grams (1.0 percent) of oxalic acid, 30 grams (0.75 percent) of citric acid, and 4 grams (0.1 percent) of sodium lauryl sulfate in sufficient water to yield 4 liters of solution. While the solution is stirred, 25% aqueous sodium carbonate is added slowly until the pH rises to 6.0.

EXAMPLE 4

An acidic aqueous solution is prepared by dissolving 40 grams (1.0 percent) of tartaric acid, 80 grams of oxalic acid (2.0 percent), 20 grams (0.5 percent) of sodium citrate, and 10 grams (0.25 percent) of sodium dodecylbenezene sulfonate in sufficient water to yield 4 liters of solution. While the solution is stirred, trimethyl amine is added slowly until the pH rises to 3.5.

EXAMPLE 5

An acidic aqueous solution is prepared by dissolving 258 grams (0.91 percent) each of tartaric acid, oxalic acid, and citric acid, 19.2 grams (0.067 percent) of Triton X–100, 57.5 grams (0.2 percent) of Santomerse S, 28.7 grams (0.1 percent) of sodium benzoate, and 767 grams (2.7 percent) of beta-butoxyethanol in sufficient water to yield 7.5 gallons of solution. While the solution is stirred, 75% aqueous ammonium hydroxide is added until the pH rises to 5.5.

EXAMPLE 6

An acidic aqueous solution is prepared in the manner set forth in Example 5, except that in lieu of the indicated quantities of Triton X–100 and Santomerse S there is employed 38.3 grams (0.135 percent) each of Triton QS–15 (an oxyethylated sodium phenolate) and Triton CF–10 (an alkaryl polyether).

EXAMPLE 7

An acidic aqueous solution is prepared in the manner set forth in Example 5 with the following exceptions: 86.2 grams (0.3 percent) of sodium mono-tridecylbenzene sulfonate is used in lieu of the indicated quantities of Santomerse S and Triton X–100, and 1,136 grams (4 percent) of beta-butoxyethoxyethanol is used in lieu of the indicated quantity of beta-butoxyethanol.

A number of solutions of the invention were compared with known solutions in tests designed to evaluate their corrosive action upon ferrous metals and their effectiveness as cleaners in sequential cleaning and phosphating operations.

A large number of 4-inch x 8-inch panels of 20-gauge SAE 1012 cold-rolled steel were brush-coated with several different commercially available drawing compounds and then placed in an oven for 3 minutes at 400° F. to fix the drawing compounds on the panels. For convenient identification, the coated panels are labeled as shown in Table I.

Table I

Panels, Group	Type of Drawing Compound on Surface Thereof
1	Sulfochlorinated fatty ester base; contains 1.4 percent chlorine, 2.7 percent sulfur, and shows a pH of 3.4.
2	Chlorinated fatty ester base; contains 36 percent chlorine, 0.6 percent sulfur, and shows a pH of 6.95.
3	Chlorinated paraffin wax base; contains 29.7 percent chlorine, 0.3 percent sulfur, and shows a pH of 5.75.
4	Chlorinated paraffin wax—sodium sulfonate base; contains 18 percent chlorine, 0.5 percent sulfur, and shows a pH of 7.85.

Thereafter, the panels were cleaned and phosphated in a continuous conveyor-line apparatus according to the schedule set forth in Table II.

Table II

SEQUENCE OF CLEANING AND PHOSPHATING OPERATIONS

Operation No.	Description
1	Spray the panel with the selected cleaning solution for one minute at 140°–160° F.
2	Spray-rinse the panel with water for one to two minutes at 140°–150° F.
3	Spray the panel with an aqueous phosphating solution for two minutes at 160° F. The aqueous phosphating solution employed contains 0.17% zinc ion, 0.58% phosphate ion, 1.34% nitrate ion, 0.37% calcium ion, and 0.07% sodium ion. It is prepared by dissolving 2.1 grams of ZnO, 8.0 grams of 75% H_3PO_4, 3.0 grams of 42° Baumé HNO_3, 1.2 grams of NaOH, and 20 grams of Ca $(NO_3)_2 \cdot 3H_2O$ in 200 ml. of water and then diluting the whole to make one liter of solution.
4	Spray-rinse the panel with water for one minute at 120° F.
5	Spray-rinse the panel with dilute aqueous chromic acid (0.125 gram CrO_3 per liter) for one minute at room temperature.

The results observed in above-described cleaning and phosphating operations are set forth in Table III. It will be noted that the acidic aqueous solutions of this invention are superior to a widely-used, commercial, alkali-base aqueous cleaner and a commercial, aqueous acid cleaner for the purpose of cleaning a soiled metal panel prior to phosphating.

Table III

CLEANING AND PHOSPHATING OF STEEL PANELS

Panels, Group	Cleaning Solution Used in Operation No. 1	Appearance of Phosphate Coating, Inspector's Remarks
1	Commercial alkali-base cleaner (used at recommended concentration of 1 oz./gal.).	Borderline acceptable phosphate coating; yellow stain near edges due to incomplete removal of soil.
1	Cleaning solution of this invention, Example 5.	Good phosphate coating; a few light streaks are visible.
1	Cleaning solution of this invention, Example 6.	Do.
2	Commercial alkali-base cleaner (used at recommended concentration of 1 oz./gal.).	Very poor, spotty phosphate coating—unacceptable.
2	Cleaning solution of this invention, Example 5.	Fair, acceptable phosphate coating.
2	Cleaning solution of this invention, Example 6.	Very similar to the above result, but panel has somewhat darker appearance.
3	Commercial alkali-base cleaner (used at recommended concentration of 1 oz./gal.).	Poor, heavily stained, unacceptable phosphate coating.
3	Cleaning solution of thi invention, Example 5.	Fair, acceptable phosphate coating; a slight stain is visible.
3	Cleaning solution of this invention, Example 6.	Very similar to the above result, but panel is slightly darker.
4	Commercial alkali-base cleaner (used at recommended concentration of 1 oz./gal.).	Very poor and largely incomplete phosphate coating due to incomplete removal of yellowish-appearing soil.
4	Commercial aqueous acid cleaner (contains orthophosphoric acid, betabutoxyethanol and surface-active agents).	Poor, incomplete phosphate coating; areas of unremoved soil are clearly visible.
4	Cleaning solution of this invention, Example 5.	Fair, acceptable phosphate coating; a few dark spots and stains are evident.
4	Cleaning solution of this invention, Example 6.	Good phosphate coating; a few dark spots are evident.

A laboratory corrosion test was employed to determine the relative corrosiveness toward steel of a widely-used commercial aqueous acid cleaner and the acidic aqueous solutions of this invention. In this test a 1-inch x 3-inch strip of 20-gauge SAE 1020 cold-rolled steel is immersed to a depth of 1.5 inches in the solution being tested and the whole is maintained at 140°±5° F. for 9 days. Every third day, the pH of the solution is measured and, if it has changed, it is restored to the original pH by the addition of more of the fresh acidic aqueous solution (in the case of a higher measured pH) or of ammonium hydroxide (in the case of a lower measured pH). The steel strip is removed at the end of the ninth day, dried by heating on a hot plate for a few minutes under a current of dry air, and weighed. The results obtained in this corrosion test are set forth in Table IV.

Table IV

CORROSION OF SAE 1020 STEEL, NINE-DAY TEST

Acidic Solution under Test	Weight Change of Steel Strip, Milligrams
Commercial aqueous acid cleaner (contains orthophosphoric acid, beta-butoxy-ethanol, surface-active agents, and a commercial corrosion inhibitor)	−824
Acidic aqueous solution of the invention, Example 2	[1] +20
Acidic aqueous solution of the invention, Example 5	[1] +110

[1] Light yellow film on the steel strip; no corrosion evident beneath this film.

It will be noted that whereas the commercial aqueous acid cleaner severely corroded the steel, the solutions of this invention actually prevented corrosion (believed to be due at least in part to the thin protective film formed on the metal surface).

Although the acidic aqueous solutions of the present invention find their principal utility in the cleaning of ferrous metals, they are also useful for the cleaning of non-ferrous metals and alloys thereof such as aluminum, magnesium, copper, brass, bronze, white metal, etc. They are also useful for the cleaning of galvanized ferrous surfaces or plated ferrous surfaces such as, e.g., copper-plated, nickel-plated, and cadmium-plated ferrous surfaces.

What is claimed is:

1. An acidic aqueous solution adapted for the cleaning of metal articles which consists essentially of water; from about 0.05 to about 3 percent each of tartaric acid anion, oxalic acid anion, and citric acid anion; a cation selected from the group consisting of ammonium, substituted ammonium, and metal cations in an amount sufficient to adjust the pH of said acidic aqueous solution to a value within the range from about 3.0 to about 6.5; and at least one surface-active agent which is stable at a pH less than 7 and which is selected from the group consisting of alkali metal aliphatic sulfonates, alkali metal alkaryl sulfonates, alkali metal aliphatic sulfates, and alkaryloxypolyalkoxyalkanols.

2. An acidic aqueous solution in accordance wtih claim 1 further characterized in that it additionally contains a minor proportion of an alkali metal salt of an aromatic carboxylic acid.

3. An acidic aqueous solution adapted for the cleaning of metal articles which has a pH within the range from about 3.0 to about 6.5 and which contains as essential ingredients from about 0.05 to about 3 percent each of tartaric acid anion, oxalic acid anion, and citric acid anion; an amount of sodium ion effective to produce an anion-cation balance within the aforesaid pH range; from about 0.01 to about 0.5 percent of a sodium alkaryl sulfonate; and from about 0.02 to about 0.5 percent of a sodium salt of an aryl monocarboxylic acid.

4. An acidic aqueous solution adapted for the cleaning

of metal articles which has a pH within the range from about 5.0 to about 6.0 and which contains as essential ingredients from about 0.5 to about 1.5 percent each of tartaric acid anion, oxalic acid anion, and citric acid anion; an amount of sodium ion effective to produce an anion-cation balance within the aforesaid range; from about 0.01 to about 0.25 percent each of a sodium alkylphenyl sulfonate and an octylphenoxypolyethoxyethanol; and from about 0.05 to about 0.2 percent of sodium benzoate.

5. A method for cleaning a metal article which comprises contacting said article with the acidic aqueous solution of claim 1, said solution being maintained at a temperature within the range from about 100° F. to about 212° F.

6. A method for cleaning a metal article which comprises spraying said article with the acidic aqueous solution of claim 3 at a temperature within the range from about 120° F. to about 190° F.

References Cited in the file of this patent

UNITED STATES PATENTS

1,334,092	Harneling	Mar. 16, 1920
1,911,537	Tanner	May 30, 1933
2,067,215	Tanner et al.	Jan. 12, 1937
2,164,042	Romig	June 27, 1939
2,178,831	Bruson	Nov. 7, 1939
2,250,508	Thompson et al.	July 29, 1949
2,469,493	Barker	May 10, 1949
2,493,327	Vance	Jan. 3, 1950
2,552,874	Snyder et al.	May 15, 1951
2,860,106	Little et al.	Nov. 11, 1958
3,011,907	Davis et al.	Dec. 5, 1961
3,070,464	Levy	Dec. 25, 1962