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## ELECTROLYTIC CLEANING PROCESS

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This invention relates to improvements in the art of cleaning metal surfaces electrolytically, particularly steel surfaces and the like, and to compositions for preparing electrolytic solutions suitable for such metal cleaning.

In the manufacture and fabrication of materials having metal surfaces, various soils are formed in or on the surface. These soils may be classified generally as comprising (1) substances not chemically associated with the basis metal, (2) substances derived from the basis metal, and (3) substances due to a physically altered basis metal layer. The soils commonly encountered in class 1 above consist of oils, greases, waxes, soaps, drawing compounds, buffing and polishing compounds and miscellaneous dirt acquired during manufacturing, fabrication, handling or shipping. The principal soil derived from the basis metal in class 2 above consists of oxides of the metal. Carbonates, sulfides, sulfates, chlorides, phosphates and nitrides of the basis metal may also be encountered. In addition, and particularly in the case of steel surfaces, finely divided grains of the metal itself may be encountered. In class 3 above the surface of the basis metal may be physically altered because of a surface film of stressed, distorted or broken basis metal resulting from grinding, polishing, rolling, drawing or other finishing process.

It has long been recognized in the art of metal finishing that thorough cleaning of metal surfaces is necessary if a satisfactory finished product is to be obtained. This is particularly true in the metal plating art where residues in any of the soil classes listed above remaining unremoved by the cleaning process are often the cause of unsatisfactory results in the final product. Various cleaning methods and compositions have been employed in the cleaning of metal surfaces and some of these, particularly the vapor degreasing processes employing a stabilized chlorinated hydrocarbon as shown in the patent to Clarence F. Dinley #2,096,735 have been very successful on a large variety of metals and for many finishing purposes. However, in the case of metal surfaces and the like which are to be subjected to a finishing operation requiring a plating step or the like, it has been found that the cleaning methods and compositions known to the art are not entirely satisfactory. While a general cleaning of such metal surfaces is attained by the use of such methods, some of the soils listed above effectively resist removal, particularly in the case of ferrous metal surfaces. One of the soils most difficult of removal is known in the art as "smut"

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and commonly remains on the surface after all other soils have been removed. This smut is of varying composition but generally consists of a combination of carbonized oils, carbon from the metal (if steel), iron oxide and metal particles. It will thus be seen that the metal cleaning art prior to the present invention has not had a cleaning process suitable for preparing smut-contaminated metal surfaces for a finishing operation requiring a very high degree of cleanliness. We have found that it is possible to obtain such cleaning by the use of an asymmetric reversing electric current in accordance with the teachings of this invention in combination with an electrolytic solution of the type or types hereinafter described. All the soils identified in the foregoing discussion, and their equivalents, are referred to in the appended claims as "smut-like materials."

The principal object of the present invention is to provide a process for thoroughly cleaning metal and particularly ferrous metal surfaces.

A further object is to provide an electrolytic process for thoroughly removing soils, and particularly smut, from metal surfaces without corroding or pitting and without depositing foreign materials on the metal surface.

A still further object is to provide compositions for carrying out the electrolytic cleaning process of the present invention.

The foregoing and other objects are attained according to our invention by passing an asymmetric, reversing current between an electrode and the metallic article to be cleaned in aqueous solutions of salts whose principal components form soluble ions in the presence of metal dissolved from the metal article and whose negative ions and their derivatives will not readily discharge at the metal article or at the electrode and whose occasional discharge does not produce harmful effects at the surface of the article.

In describing our invention, several descriptive terms will be used whose definitions vary in industry. Therefore, these terms are defined below as they are used in this specification and the claims.

The term "direct current" is used to describe a current which flows only in one direction for the period under discussion. The polarity may be either positive or negative. Unless otherwise specified, the current potential is considered to be nominally constant.

The term "reversing current" is used to describe a current whose direction of flow is continually reversed.

The term "pulse current" is used to describe a current which is reduced at intervals to zero or some relatively small value.

The term "reversing pulse current" is used to describe a current which after being made a direct current in one direction for an interval, is reduced to substantially zero value for an interval and then made a direct current in the other direction for an interval.

The term "asymmetric current" as used in this specification refers to current wave forms other than unvarying direct current or a sine wave, in which the asymmetry relates to relative time of current flow in a single cycle.

The term "asymmetric reversing current" designates current having a cycle in which the current flows in one direction for a given period of time and subsequently flows in the other direction for a different period of time, or a cycle in which the current flows in one direction at a given rate for a given time and subsequently flows in the other direction at a different rate for a different time.

In preparing aqueous electrolytic solutions suitable for use with our invention we have found that the polyphosphates and citrates produce ions which have the desired properties even in dilute solutions. We have also found that in more concentrated solutions the phosphates other than polyphosphates, acetic acid-acetate mixtures, bicarbonates and dichromates likewise provide satisfactory electrolytic solutions, suitable for use in carrying out our novel process.

The polyphosphates employed in the practice of our invention are broadly the phosphates having more than one phosphorus atom per molecule. Among the more common polyphosphates which are suitable may be listed the pyrophosphates $(P_2O_7)^{-4}$, and particularly acid sodium pyrophosphate and tetrasodium pyrophosphate, the tripolyphosphates $(P_3O_{10})^{-5}$, the hexametaphosphates $(P_6O_{10})^{-6}$ and equivalent polyphosphates and mixtures thereof. While polyphosphates having a wide variety of anions are soluble in water and are suitable in practicing the processes of this invention, the alkali metal polyphosphates are preferred since they are readily available and relatively inexpensive. The term "polyphosphate" as used throughout the present specification and claims does not include the ordinary orthophosphates, such as trisodium phosphate ($Na_3PO_4$), monosodium orthophosphate

($NaH_2PO_4$)

or the other orthophosphates or sodium metaphosphate ($NaPO_3$), but is specifically restricted to the phosphates having a plurality of phosphorus atoms per molecule and the polyphosphoric acids analogous thereto. The aforementioned and other phosphates having less than two phosphorus atoms per molecule are referred to herein simply as mono-phosphates.

The aqueous polyphosphate solutions are effective in the practice of this invention over a wide range of concentrations. These solutions may contain as little as 0.01% polyphosphate ion by weight or may be totally saturated solutions. We have discovered, however, that particularly rapid and thorough cleaning is attained by maintaining the polyphosphate in concentrations between .05 and 5 gram equivalents of polyphosphate ion per liter of solution.

Excellent cleaning is also attained by means of our reverse-current process in combination with a dilute electrolyte containing citrate ions.



These citrate electrolytes are effective over a concentration range from 0.01% by weight and below to a saturated citrate solution. For optimum cleaning we have found that the preferred concentration ranges vary depending upon the alkalinity or acidity of the solution. However, we have found that in acid solution preferred cleaning is attained with an electrolyte containing from 0.15 to 5 gram moles of citrate ions per liter and in alkaline solution preferred cleaning is attained with an electrolyte containing from 0.4 to 5 gram moles of citrate ions per liter. An acid solution of citrate ions is preferably produced by mixing a soluble citrate with citric acid and water.

The citric acid-citrate mixtures of our invention preferably vary in pH from 4 to 10 and contain citric acid and a soluble citrate in proportions adapted to attain a pH falling within this range. Preferred proportions, however, range from 1 to 4 moles of alkali metal citrate per mole of citric acid.

Excellent metal cleaning is further attained according to our invention by providing an electrolyte which on discharge does not yield any oxidizing gas except oxygen itself, provided the electrolytic solution is sufficiently concentrated to retard excessive local formation of hydrogen ions at the anode due to local hydrolysis of the decomposed electrolyte ions. Examples of such suitable compositions are the mono-phosphates, acetates, bicarbonates, and chromates. These ions when present in dilute solutions deposit undesirable films on the anode during the reverse current process but surprisingly yield excellent cleaning at ionic concentrations of about 10 gram equivalents per liter and above.

The term "mono-phosphates" includes the phosphates other than polyphosphates. Common examples of mono-phosphates are, among others, the orthophosphate $(PO_4)^{-3}$, the metaphosphate $(PO_3)^{-1}$, and the acid phosphates of these radicals.

The chromates referred to herein consist of the ordinary chromate ion $(CrO_4)^{-2}$ in alkaline solution and the dichromate ion $(Cr_2O_7)^{-2}$ in acid solution and equivalent ions containing chromium in combination with oxygen.

The bicarbonates described herein are the soluble acid salts of carbonic acid generally, preferably the alkali metal bicarbonates such as $NaHCO_3$ and the like.

In referring to acetates, we include compositions which are dissolved in water to produce acetate ions, which are often represented by the formula $(CH_3COO)^{-1}$. Alkali metal acetates such as $CH_3COONa$ are preferred because of their solubility and low cost. Acetate ions are also introduced to form an acid solution by dissolving acetic acid in water.

Within the group comprising the polyphosphates, monophosphates, acetates, citrates, dichromates and bicarbonates, optimum cleaning results are obtained by using mixtures which provide solutions having a pH below 8. While the tendency of the solution to corrode the containing tank decreases above pH 8, the rapidity of cleaning also decreases with pH increase substantially above 8. The rate of cleaning increases as the pH is reduced but further reduction of pH may at times result in a decreased net cleaning effect since deposits of foreign materials are found on the metal after prolonged treatment at relatively low pH values. Therefore, while we may practice our invention at pH values from

3.5 to 10, we find that the effectiveness of cleaning reaches a peak at pH values between 6 and 8.

The temperature of the electrolyte may be varied within wide limits (for example, 40° F. to boiling) but a temperature ranging from about 140° F. to about 160° F. has been found to provide particularly thorough and rapid cleaning with a minimum rate of decomposition of cleaning solution.

Economical operation of polyphosphate solutions requires recognition of the fact that polyphosphates are subject to hydrolysis, forming orthophosphates as the end product. Because of hydrolysis, it is desirable, as mentioned above, to maintain electrolyte solution temperatures below 180° F. In general, the hydrolysis rate will increase also with decreasing pH. We find too, that using our solutions in stainless steel tanks or in tanks lined with lead, provides an extension in the effective life of the solution. Hydrolysis does not appear to present any problem in the use of citrates, which do not hydrolyze to any appreciable extent under the conditions of operation.

It is sometimes found with particular solutions that ordinary mild steel tanks are adequate containers for the electrolyte, provided that inhibitors are added to minimize reaction between the tank and the electrolyte. For instance, in an electrolyte having a pH of 7 or above, the addition of a small amount of an alkali metal ferricyanide inhibits accelerated hydrolysis in a mild steel container. As an example, 0.2% of potassium ferricyanide in a 12% solution of tetrasodium pyrophosphate has been found to retard the deterioration of the cleaning solution appreciably. Ferricyanide should not be used in acid solutions since it plates out on the electrodes.

In addition to the essential ingredients of the electrolytes of this invention, borax or nitrates or combinations of the two may be incorporated in solution in various quantities. While these substances have only a minor effect upon the electrolytic cleaning properties of the solutions, if not used in excessive quantities, they provide a means of introducing additional ions into solution, thereby increasing the conductivity of the electrolyte, at a lower cost than would obtain if additional quantities of polyphosphates, acetates, citrates or phosphates were added above the amounts required for proper cleaning. The amount of nitrate and/or borax that may be added with beneficial effect varies with the particular metal to be cleaned but is usually less than 25% of the weight of the polyphosphate, phosphate, acetates, chromates, bicarbonates, or citrates present.

As a further preferred embodiment of our invention, we have found that where particularly rapid cleaning is desired, it is preferred to incorporate in our solutions a small quantity of wetting agent. The particular wetting agent used may vary according to the composition and particularly with the pH of the solution. In addition, it is desirable that the wetting agent be stable with regard to electrical currents so that it is not decomposed at the electrodes. Within these restrictions many suitable wetting agents may be chosen from the innumerable wetting agents available. We have found that an anionic wetting agent the molecules of which consist of a long non-polar chain, with a polar group attached to the chain at a point near its middle is suitable. Another suitable wetting agent is a wetting agent of the detergent type, consisting



of a long-chain organic compound with a polar group at one end of the chain. We have also found that a compound of the non-ionic type having a long non-polar chain and a short polar chain at one end is suitable. The wetting agents are preferably incorporated in amounts of 0.1% to 5% of the total weight of polyphosphate, mono-phosphate, acetates, dichromates, bicarbonates, or citrates present.

The asymmetric reversing current employed in the practice of the present invention may be generated in a wide variety of ways. We have found that it is desirable to pass a greater total quantity of electricity while the metal which is to be cleaned acts as anode than the quantity passed while the metal being cleaned acts as a cathode. This is conveniently accomplished by making the metal act as an anode for a longer period of time than it acts as a cathode. According to this method, the bath and the soiled metal are impressed with an anodic current, by which we mean a current flowing from a source through a work piece of metal as anode and through the electrolytic bath to a cathode which may be the container or a separate electrode immersed in the electrolyte. Following the anodic flow, the current is reversed and the electrolyte and the soiled metal are impressed with a cathodic current, by which we mean a current that flows from a source through an anode which may be the container or a separate electrode immersed in the electrolyte, through the electrolytic bath and then through the work piece of metal as a cathode. In the foregoing manner, the current is periodically reversed throughout the cleaning process. A particular preferred method of reversing current is accomplished by making the metal which is to be cleaned the anode for a short period of time, say 4 seconds, then reversing the direction of current flow for about 1 second such that the aforesaid metal is then the cathode and repeating this cycle until satisfactory cleaning is accomplished.

There is a broadly optimum ratio of time of application of the anodic current to time of application of cathodic current which varies with the frequency of current reversal and in usual operation lies in the range of 2:1 to 8:1. For anode to cathode time ratios in this range, we have operated successfully over a current reversal frequency range from less than 2 cycles per minute to several hundred cycles per minute. However, for this particular ratio range optimum results are obtained in the range from about 12 cycles per minute to about 24 cycles per minute. For other ratios, the optimum frequency range may increase indefinitely being limited only to the point where the necessary reactions no longer have time to take place between current reversals.

The reversing current process of this invention may be modified by providing a time interval during which no current flow takes place, this interval being interposed between periods of cathodic and anodic flow. We refer to this modification as a reversing pulsed current. The flow may be interrupted after application of anodic flow or cathodic flow or at both times during the cycle. Other methods and times of interrupting the current are effective for particular purposes.

We find in practicing all the aforementioned reversing current techniques that variations in voltage and amperage values have an effect on the length of time required to obtain optimum results, according to the particular metal and

soil characteristics. Satisfactory cleaning results are obtainable in the time range from 8 minutes down to 15 seconds and under by employing voltages in the range from 3 volts and greater at current densities of 30 amperes or more per square foot of metal surface being cleaned.

In practicing the novel current-reversal process of the present invention at a 4 to 1 ratio of anodic current time to cathodic current time as heretofore described. it might be expected that the effectiveness of cleaning would vary in a linear relationship with the frequency of current reversal, if it should vary at all. However, we have found that the latter is not the case, since cleaning is moderately effective at reversal frequencies below 12 cycles per minute, becomes unusually effective within the range of 12-24 cycles per minute, and then lapses back into a less effective stage at frequencies above 24 cycles per minute. The particular ratio of 4 to 1 has been used for descriptive purposes in this specification, since with the proper reversal frequency, voltage and cleaning electrolyte, this ratio is one which produces excellent results and is more easily and economically accomplished with standard electrical generating equipment available at this time. It is not intended that the scope of this invention should be limited to an anode to cathode time ratio of 4 to 1. For instance, in a case where still more rapid cleaning is desired and the cost of generating equipment is of less importance, a cycle of lower anode to cathode time ratio and higher frequency may advantageously be employed. Also, for certain soils a modified cycle may be used such that relatively high voltages of about 20 volts or above are applied during the anodic and cathodic portions of the cycle and these portions of the cycle are separated by periods of time in which there is no flow of current.

The combined action of the polyphosphate, citrate, acetate, mono-phosphate, bicarbonate, dichromate or combination thereof and the asymmetric reversing electric current upon the metal removes soils from the metal surface with surprising speed and thoroughness and provides cleaning results superior to those heretofore known. The coaction of the two essential elements of an electrolyte having characteristics as hereinafter described and an asymmetric electric current as disclosed herein results in superior cleaning with a rapidity that is surprisingly in excess of the additive effects of the separate elements. The electrolytes themselves do not attack the work chemically to any significant extent; the loss of metal from the work is substantially the result of electrochemical action.

While a complete scientific explanation of the complex and changing interactions responsible for the surprising cleaning results provided by the practice of the present invention has not been developed, and while it is not intended that this invention should be restricted by virtue of any theory expressed in the present specification, the following is believed to be a partial explanation of the cleaning results obtained. In the solution current is carried by the movement of the ions of the electrolyte. In the conductors outside the electrolytic cell the current is carried by the moving electrons in the conductor. At the boundary between the conductors (electrodes) and the electrolyte (solution) the current is carried by electrochemical reactions taking place at the electrode. When the electrical circuit is completed, a potential is applied at the electrodes and cations are drawn to the cathode, anions to the anode. For an extremely short period of time, current at the anode is carried by metal going into solution because sufficient anions are not present at the anode, ready for discharge, to carry all the current, and until sufficient anions have been drawn over, current is carried by metal going into solution. This provides a cleaning action of very short duration. As soon as anions discharge, in most cases oxygen is evolved, either from decomposition of the anion or from reaction of the anion with water, and immediately an oxide may be formed or a layer of oxygen gas covers the anode so that in the first case the decomposition potential of the anode is effectively increased or in the second case the anode is no longer a metal anode but an oxygen anode. The result of this is that metal ceases to dissolve from the anode very soon after the start of current flow and consequently there is little, if any, further cleaning.

Now by reversing the current and making the work cathode for a short period, anions are pushed away from the work and cations (hydrogen ions in most cases) are discharged. (These hydrogen ions have been accumulating at the anode during the previous cycle because the discharging anions, having reacted with water and liberated oxygen have formed the acid of the particular anion, which in dilute solutions, dissociates, liberating hydrogen ions). If now, the current is reversed again and the work is again made anodic, the process starts over again and more metal is dissolved and more cleaning takes place provided that the conditions of electrolyte and current are such as to avoid other reactions harmful to cleaning.

Beneficial cleaning is attained by combining a suitable asymmetric reversing current cycle with an electrolyte which enters into desirable reactions at the surface of the work. Many electrolytes decompose to produce an oxidizing gaseous product other than oxygen (such as a halogen) which corrodes the surface of the work. Many electrolytes are ineffective in penetrating the passive metal film or oxide film which forms at the surface of the work during the period of anodic flow. Moreover, some electrolytes decompose during the period of cathodic flow, producing ionizable acidic compounds with resultant undesirable increase of hydrogen ion concentration and corrosion of the work. We have found that excellent cleaning results are attained by passing an asymmetric reversing current through the work as an electrode and through an electrolytic solution which does not decompose at the work to produce an oxidizing gas other than oxygen, which penetrates a passive metal film or metal oxide film at the work, and does not decompose to produce excessive amounts of acidic substances at the work during the cycle. While the components of our electrolytes form soluble ions in the presence of metal dissolved from the metal surface, it is to be noted that relatively involved interaction takes place in many instances. This appears to be illustrated by the action of sodium pyrophosphate, since iron pyrophosphate is not soluble in water or in a dilute solution of sodium pyrophosphate.

The following specific examples are given to illustrate the present invention, but it is not intended that the scope of the invention be limited thereby since these examples are merely illustrative of specific cleaning operations:

*Example 1*

Light gauge sheet steel having oil and smut soils was immersed in an aqueous solution of acid sodium pyrophosphate in a stainless steel container. The pyrophosphate solution was made up by adding 10 grams of technical acid sodium pyrophosphate to ½ liter of water (pH 4.2). The solution was heated to 160° F. and held at this temperature throughout the cleaning operation. Electrical connections were then made from a generator to the sheet steel and to the stainless steel container. The current generated was of the reversing-current type and asymmetric, the anodic portion of the cycle being 4 seconds and the cathodic portion of the cycle being 1 second. The voltage was 9.2 and the current 100 amperes per square foot of sheet steel surface. Cleaning time was 15 seconds and the results excellent, the metal showing no trace of soil when wiped with a white cloth.

*Example 2*

In a tank such as described above, 6 grams of tetrasodium pyrophosphate, 13 grams of acid sodium pyrophosphate, 6 grams of borax and ¼ gram of wetting agent were added to ½ liter of water and brought to a temperature of 140° F. (pH 6.5). Using the generator, cycle and metal described above, 6 volts were applied in the manner described, giving a current density of 100 amperes per square foot. The cleaning time was 20 seconds and the results excellent.

*Example 3*

The process described in Example 2 was carried out at 4 volts and 50 amperes per square foot for an applied current time of 30 seconds. As in Example 2, the cleaning results were excellent.

*Example 4*

The solution described in Example 2 is heated to 160° F. in a stainless steel container and electrical connections are made from a direct current generator through a reversing switch having an open switch position to the sheet steel to be cleaned and to the stainless steel container. The current is then applied as in Example 1 except that ½ second intervals of no current are interposed between the anodic and cathodic portions of the cycle. The metal is cleaned rapidly, leaving no smut deposit visible upon wiping with a white cloth.

*Example 5*

A charge of 5 grams of acid sodium pyrophosphate and 6 grams of tetrasodium pyrophosphate was dissolved in 330 cc. of water and the solution, containing .075 moles of each phosphate per liter, was heated to a temperature of 150° F. A piece of cold rolled steel covered with smut was immersed in the solution and connected electrically in a circuit including a reversing generator whereby the current generated by the generator passed through the steel piece and the phosphate solution. The generator supplied a current which held the cold rolled steel electrically positive for 4 seconds and then changed direction to hold the cold rolled steel piece electrically negative for one second. After repeating this cycle for a period of 45 seconds the piece of cold rolled steel was removed from the electrolyte and an excellent cleaning effect was observed.



*Example 6*

Following the procedure outlined in Example 5, with a solution containing 1.2 mole of sodium citrate per liter as electrolyte, good cleaning was attained after passing current through the metal and electrolyte for one minute. Excellent cleaning was observed after 3 minutes of treatment.

*Example 7*

The procedure as outlined in Example 5 was was followed, using a solution containing 0.6 mole per liter of sodium citrate and 0.2 mole citric acid. The pH of the electrolyte was approximately 6. Cleaning in one minute was excellent.

*Example 8*

A solution containing 1.6 mole of sodium citrate and 0.8 mole of citric acid per liter was prepared. The pH of the solution was approximately 5. The procedure of Example 5 was followed using this solution as electrolyte. In ten seconds' time excellent cleaning was attained.

*Example 9*

The procedure of Example 5 was followed. The electrolyte comprised a solution containing 2.4 moles of citric acid per liter and 1.2 moles of sodium citrate per liter. The pH of the solution was approximately 3.5. Excellent cleaning was attained in 40 seconds.

*Example 10*

The procedure of Example 5 was practiced, in which the electrolyte consisted of 1.4 mole of tetra sodium pyrophosphate per liter and the pH of the solution was 8.5–9.0. Fair cleaning was attained after one minute, and excellent cleaning resulted after three minutes.

*Example 11*

A saturated solution of monosodium orthophosphate having a pH of approximately 4 was heated to a temperature of 150° F. and placed in an electrolytic container. A piece of cold rolled steel covered with smut was connected and current was passed through the solution as described in Example 5. After three minutes of treatment the surface of the steel was clean and bright.

*Example 12*

A solution containing 14.5 moles of sodium acetate per liter was prepared. Acetic acid was added to the solution until the resulting pH was approximately 6. The procedure of Example 5 was then followed. Very good cleaning was attained after passage of current for one minute and excellent cleaning was attained after three minutes.

While the present invention has been described in detail in the above examples, it will be understood that various mixtures of polyphosphates, phosphates, citrates, acetates, bicarbonates, dichromates, and the corresponding acids of these radicals provide excellent electrolytes for the practice of our invention. Various other changes may also be made particularly with regard to the voltage and the current employed. While optimum results are obtained within the ranges set forth in the specification, considerable latitude may be exercised within and beyond such ranges to meet the requirements of any particular cleaning problem. It will be noted that optimum cleaning using the processes of the present invention is obtained only through the coaction of

a plurality of conditions. So far as we are aware, we are the first to achieve satisfactory electrolytic cleaning by combining these conditions which include passing an asymmetric reversing electric current through metallic articles suspended in an aqueous solution of a polyphosphate salt or salts of similar characteristics. In keeping with the theory proposed herein, we believe that this cleaning is derived in part from the fact that we employ aqueous solutions of salts whose principal components form soluble ions in the presence of metal dissolved from the articles being cleaned and whose negative ions and their derivatives will not readily discharge at the articles or at other electrodes and whose occasional discharge does not produce harmful effects at the surface of the metal being cleaned.

While we have illustrated our invention by reference to certain specific examples it will be understood that a wide variety of equivalent electrolytes may be employed and that considerable variation is possible with regard to the electric current employed all within the scope of the appended claims.

Having thus described our invention, we claim:

1. In a process for the electrolytic cleaning of smut-like materials from metal articles in which the article serves as one of the electrodes, the steps which comprise immersing the surface to be cleaned in an aqueous solution of a cleaning compound selected from the group consisting of the polyphosphates, citrates, mono phosphates, acetic acid-acetate mixtures, bicarbonates and dichromates, said solution having a pH of approximately 3.5 to approximately 10, and passing an asymmetric reversing electric current through said metal and through said solution, the relative current values being such that the total quantity of positive electricity passed is greater than the total quantity of negative electricity passed, the ratio of time of application of positive current to time of application of negative current being in the range of 2:1 to 8:1.

2. The process of claim 1 in which the asymmetric reversing electric current is a reversing pulsed current.

3. The process of claim 1 in which the solution consists of a mixture of acid sodium pyrophosphate and tetrasodium pyrophosphate.

4. In a process for the electrolytic cleaning of smut-like materials from metal articles in which the article serves as one of the electrodes, the steps which comprise contacting the surface of said metal with an aqueous polyphosphate cleaning solution having a pH of approximately 3.5 to approximately 10, and passing an asymmetric reversing electric current through said metal and through said solution, the relative current values being such that the total quantity of positive electricity passed is greater than the total quantity of negative electricity passed, the ratio of time of application of positive current to time of application of negative current being in the range of 2:1 to 8:1.

5. In a process for the electrolytic cleaning of smut-like materials from metal articles in which the article serves as one of the electrodes, the steps which comprise contacting the surface of said metal with an aqueous cleaning solution containing citrate ions, said solution having a pH of approximately 4 to approximately 10, and passing an asymmetric reversing electric current through said metal and through said solution, the relative current values being such that the total quantity of positive electricity passed is greater than the total quantity of negative electricity passed, the ratio of time of application of positive current to time of application of negative current being in the range of 2:1 to 8:1.

6. In a process for cleaning smut-like materials from a metal surface, the steps which comprise contacting said metal surface with an aqueous cleaning solution containing .05–5 gram equivalents of a polyphosphate ion per liter, said solution having a pH of about 3.5–10, and passing through said solution and said metal a series of alternately anodic and cathodic electrical currents in which the ratio of time of application of anodic current to cathodic current is from about 2:1 to about 8:1, the anodic current-time product being greater than the cathodic current-time product.

7. In a process for removing smut-like materials from a metal surface, the steps which comprise contacting said metal surface with an aqueous cleaning solution containing .05–5 gram equivalents per liter of a polyphosphate, said solution having a pH of approximately 3.5 to approximately 10, and passing through said solution and said metal a series of alternately anodic and cathodic currents in which the ratio of time of application of anodic current to cathodic current is about 2:1 to 8:1 and the number of current reversals per minute lies in the range from about 12 to about 24, the anodic current-time product being greater than the cathodic current-time product.

8. In a process for cleaning smut-like materials from a metal surface, the steps which comprise contacting said metal surface with an aqueous polyphosphate cleaning solution containing tetrasodium pyrophosphate, acid sodium pyrophosphate, and borax, said solution having a pH of approximately 3.5 to approximately 10, and passing an asymmetric reversing electric current through said metal and through said solution, the relative current values being such that the total quantity of positive electricity passed is greater than the total quantity of negative electricity passed, the ratio of time of application of positive current to time of application of negative current being in the range of 2:1 to 8:1.

9. The process of claim 8 in which the cleaning solution contains tetrasodium pyrophosphate, acid sodium pyrophosphate, borax, a compatible nitrate, a compatible wetting agent, and a ferricyanide, said solution having a pH of approximately 7 to approximately 10.

10. In a process for cleaning smut-like materials from a metal surface, the steps which comprise contacting said metal surface with an aqueous cleaning solution containing citric acid and citrate ions, said solution having a pH of approximately 4 to approximately 10, and passing an asymmetric reversing electric current through said metal and through said solution, the relative current values being such that the total quantity of positive electricity passed is greater than the total quantity of negative electricity passed, the ratio of time of application of positive current to time of application of negative current being in the range of 2:1 to 8:1.

11. The process of claim 10 in which the aqueous cleaning solution contains from 1 to 4 moles citrate per mole citric acid.

12. The process of claim 10 in which the asymmetric reversing electric current is a reversing pulsed current.

13. In a process for cleaning smut-like materials from metal surfaces, the steps which com-

prise contacting said metal with an aqueous cleaning solution containing 0.15–5 gram equivalents of the citrate ion content of a citric acid-citrate mixture per liter said solution having a pH of approximately 4 to approximately 10, and passing through said solution and said metal a series of alternately anodic and cathodic electrical currents in which the ratio of time of application of anodic current to cathodic current is from about 2:1 to about 8:1, the anodic current-time product being greater than the cathodic current-time product.

14. In a process for removing smut-like materials from a metal surface, the steps which comprise contacting said metal with an aqueous citric acid-citrate cleaning solution containing .15–5 gram equivalents per liter total citrate ion present in the citric acid-citrate mixture, said solution having a pH of approximately 4 to approximately 10, and passing through said solution and said metal a series of alternately anodic and cathodic currents in which the ratio of time of application of anodic current to cathodic current is about 2:1 to 8:1 and the number of current reversals per minute lies in the range from about 12 to about 24, the anodic current-time product being greater than the cathodic current-time product.

15. The process of claim 14, in which the cleaning solution contains citric acid, an alkali metal citrate, borax, a compatible nitrate, a compatible wetting agent, and a ferricyanide, said solution having a pH of approximately 7 to approximately 10.

16. In a process for cleaning smut-like materials from a metal surface, the steps which comprise contacting said metal surface with an aqueous cleaning solution containing citric acid, an alkali metal citrate, and borax, said solution having a pH of approximately 4 to approximately 10, and passing an asymmetric reversing electric current through said metal and through said solution, the relative current values being such that the total quantity of positive electricity passed is greater than the total quantity of negative electricity passed, the ratio of time of application of positive current to time of application of negative current being in the range of 2:1 to 8:1.

17. In a process for cleaning smut-like materials from a metal surface, the steps which comprise contacting said metal surface with an aqueous cleaning solution of an ion selected from the class which consists of the polyphosphates, citrates, mono phosphates, acetic acid-acetate mixtures, bicarbonates and dichromates at a concentration of at least 10 gram equivalents per liter, said solution having a pH of approximately 6 to approximately 8, and passing an asymmetric reversing electric current through said metal and through said solution, the relative current values being such that the total quantity of positive electricity passed is greater than the total quantity of negative electricity passed, the ratio of time of application of positive current to time of application of negative current being in the range of 2:1 to 8:1.

18. The process of claim 17 in which the asymmetric reversing electric current is a reversing pulsed current.

19. In an electrolytic process for cleaning smut-like materials from metal wherein the metal serves as one of the electrodes, the steps comprising immersing the metal in an aqueous cleaning solution selected from the group consisting of the polyphosphates, citrates, mono phosphates, acetic acid-acetate mixtures, bicarbonates and dichromates, said solution having a pH of approximately 3.5 to approximately 10 maintaining the solution at a temperature of approximately 140° F. to approximately 160° F., and passing through said metal and solution a cyclic reversing current wherein the metal is alternately anodic and cathodic, the time of application of anodic current exceeding the time of application of cathodic current in each cycle and the total anodic current-time product exceeding the total cathodic current-time product.

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