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PROCESS OF ELECTROLYTIC CLEANSING

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1 Claim. (Cl. 204—1)

The present invention relates to an electrolytic method for the cleansing of metals, particularly such as are in the form of wires, ribbons and the like, so as to prepare the same for subsequent coating or plating.

One of the objects of the invention is to continuously clean for an extended length of time annealed iron wire and also hard drawn steel or iron wire which has a firmly adherent oxide coating upon its surface by means of an electrolytic cleaning method in which the said iron or steel wire forms the anode.

It has heretofore been proposed in the patent literature to clean wire, preliminarily to applying a metal coating thereto, by running the wire continuously through a solution containing sulphuric acid and through which solution an electric current passes to the wire as an anode. In said patent literature, it has also been proposed to clean ferrous articles by passing current of a density higher than 20 amperes per square decimeter through a solution containing less than 250 grams per liter sulphuric acid to the article as an anode, but without specific reference therein to the length of the cleaning time and/or to the durability or longevity of the process when applied to the cleaning of wire running continuously through the bath, or to the necessary conditions therefor.

I am unaware that any process of anodically cleaning wire, ribbons, and the like, which are run continuously through the cleaning solution, and which are partially soluble in the cleaning solution, such as iron wire in the sulphuric acid solution, has ever been heretofore known or used which was satisfactory in respect to the durability or longevity of the process, to the uniformity and reliability of the cleaning action over extended periods of time; to the adherence of after-applied coatings (as, for instance, thick-zinc coatings produced either electrolytically or by dipping in molten zinc); to the requirements of a reasonable cost; or to the requirements of synchronous operation in line with the line of machinery in a modern continuous wire-processing plant. The limitations and insufficiencies of the processes of the prior art hereinabove set forth are obviated by the process of the present invention, as hereinafter more fully described.

According to the present invention, iron or steel wires, ribbons, or the like, are cleaned by running them in extended lengths, as anodes, continuously through an unheated electrolytic bath of dilute sulphuric acid having a determined or ascertained H_2SO_4 concentration at a determined or ascertained high current density, the H_2SO_4 concentration always being less than 250 g/l and the current density always being higher than 20 amperes per square decimeter, the determined or ascertained current-density and the determined or ascertained acid-concentration being mutually related (inversely) and also related to the time of exposure of any spot on the travelling wire to the sulphuric acid bath solution, and to the prevailing conditions of temperature. The determined high current density is such that enough oxygen is liberated over nearly the entire anode surface as to mechanically effect the loosening and detaching of the iron-oxide film from the iron or steel wire and clean the wire.

Unless the concentration of the sulphuric acid and the current density be properly determined with relation to one another, and to the time of exposure of the wire and the prevailing conditions of temperature, the cleaning process would nevertheless soon lose its cleaning effectiveness, or soon exhaust the available current supply, even though the sulphuric acid concentration of the bath be below 250 g/l and the current density be higher than 20 amps./sq.dcm.

The numerical figures for a determined concentration of sulphuric acid and for a determined current density in any concrete case are obtained by following the general rule of decreasing (sic) the H_2SO_4 concentration and increasing the current-density, the shorter the time the travelling wire is exposed to the bath, the H_2SO_4 concentration being in every case below 250 g/l and the current density, in every case, above 20 amps./sq.dcm. The speed of the wire determines the time of exposure for a given length of bath.

With a given length and size of bath and a given wire-speed, and taking into account the prevailing conditions of temperature, a suphuric acid concentration for the bath (below 250 g/l) and a current density (above 20 amps/sq.dcm.), is selected, being guided by the general rule above stated; the process is then put in operation, and the evolution of oxygen on the wire and the rise in temperature of the bath watched. If the current density is insufficient to maintain an oxygen cover on nearly the entire length of the wire in the bath or to give the required cleaning effect, the current density must be raised, and if the temperature of the bath continues to rise, then the concentration of the sulphuric acid in the bath must be lowered as often as required to arrive at a solution concentration which has a conductance (or resistance) required to limit the

flow of current to a current density which will give a copious evolution of oxygen over nearly the entire length of the wire and also produce the required cleaning effect, at a temperature at which the solution stabilizes when heated by the aforesaid required current.

If the wire or the like has thereon scale or grease, or other extraneous matter, especially if in considerable quantity, the wire or the like is preferably preliminarily treated in any of the well-known ways to remove such matter, or the greater part thereof, as by running it through pickling solutions, degreasing solutions, etc.

A critical study of the conditions within the solution while it is being operated for effecting cleaning, reveals that bubbles of oxygen do not appear on the wire (anode) immediately on the wire entering the electrolytic solution, and that there is a time interval (variable with the operating conditions) between the time the wire enters the solution and the time it becomes fully covered, while in the solution, with the oxygen bubbles. The length of the wire within the electrolytic cleaning solution may therefore be envisaged as comprising two portions,—one, a portion where it lacks an oxygen-gas cover, and another portion where it is covered with oxygen-gas. Now the length, within the solution, of the portion of the wire which lacks the oxygen cover depends not only on the interval between the time the wire enters the bath and the time when the wire becomes covered with oxygen gas, under a given set of conditions, but also on the speed of movement of the wire through the cleaning-bath. The speed of movement of the wire should preferably remain constant, and needs to where the cleaning is one stage or step in the train or series of operations for the continuous processing of wire. With the speed of the wire determined and the total length of the wire within the solution fixed by the size of the equipment it follows that the length of that portion of the wire which is subjected to the cleaning action of the gas, and which is covered with oxygen-gas, will depend on the time interval required for the oxygen-covering to form. The longer this time interval, the shorter the length of the wire undergoing cleaning action, and hence the less complete the cleaning. Iron or steel, however, is chemically dissolved from that portion of the wire within the bath which lacks the oxygen-cover.

The effect of the dissolved iron ($FeSO_4$) is to change the resistance of the solution. If the concentration of sulphuric acid in the bath is above 250 g/l the ferrous sulphate resulting from the chemical action of the sulphuric acid solution on the iron or steel wire always causes a net decrease of the resistance, with the result that the current density will increase inversely, proportionally. Proportionally with the increase in current density there will also be a larger amount of electrical energy dissipated in the bath, the net result of which will be a rise in the temperature of the bath. This, in turn, lowers the resistance still further. The chemical dissolving action of the solution also increases with the temperature, thus accelerating the spiral decrease of the resistance and the spiral increase in current density, and thus causing the limit of the electric generator capacity to be rapidly reached. Moreover, by reason of the changes taking place in the solution, the whole process is made variable, irregular and uncertain. Even below a sulphuric acid concentration of 250 g/l the effect of iron going into solution may be likewise unless checked by a corresponding increase in resistance through the selection of a concentration to suit the current density.

The effect of increased temperature of the solution on the effectiveness of the process can be demonstrated with a laboratory experiment. For instance, with a solution containing 80 g/l H_2SO_4 and a bath temperature of about 20° C., the evolution of oxygen will set in after 2 or 3 seconds after the circuit is completed. At 30° C. and with the same current density, it will take 10 seconds before the oxygen evolution begins. At 40° C., it will be more than 60 seconds before oxygen is liberated.

The importance of the time element in continuous cleaning operation under actual industrial conditions is quite obvious when one considers that 80 f. p. m. is not regarded as a very high speed in a wire galvanizing plant and that the length of the cleaning bath for economical reasons is usually held at approximately 20 ft. This allows only 15 seconds for the cleaning operation. It follows that the time it takes for the oxygen to appear should be only a small fraction of the 15 seconds if the cleaning efficiency is to be high. If, however, after say 24 hours operation, the temperature of the bath has increased so that, as in the above example, it would take 10 seconds for the oxygen to appear (whereas it took only 2 seconds at the start), it is evident that conditions which are set to produce effective cleaning at one bath temperature will not be effective when such an increase of bath temperature occurs as is contrasted in the examples given above.

By employing above 20 amps./sq.dm. current densities which will produce copious amounts of oxygen over nearly the entire submerged surface to be cleaned, so that the chemical dissolving action of the solution is retarded and a powerful mechanical cleaning action is obtained, and by diluting the solution having a concentration lower than 250 g/l sulphuric acid, to such an extent that the temperature of the bath will stabilize under the employed conditions of current density and temperature, the cleaning effectiveness of the bath will be greatly prolonged and the useful life of the solution extended for a long period of continuous use.

Cooling of the bath in any well known manner, as by running cold-water through coils immersed in the bath, may be practiced, to thereby stabilize the temperature of the bath at a low level against the heat generated by the current flow, to diminish the chemical action of the solution on the wire, and to counteract the rise in conductance due to the temperature factor.

The high current density is essential to operation with a dilute and cold solution thereby insuring an ample evolution of oxygen to effect a thorough cleaning and to greatly retard the dissolving action of the acid solution on the wire (anode). As the speed of the wire is increased, the current density must be increased while the concentration of the sulphuric acid should be decreased.

Water and sulphuric acid are supplied to replenish the portions of the solution lost by gas-formation and escape and dragout, in such manner as to not increase the conductivity of the solution. In practice the maintenance of the solution at a constant hydrometer reading will suffice.

It is to be understood that in the use of the process a cathode should be chosen which is not affected by, or soluble in, sulphuric acid.

The action of the oxygen in this invention is to protect a large portion of the surface to be cleaned from the chemical action of the solution, and also to mechanically roughen the surface so that subsequently applied metal coatings, especially of zinc, will adhere securely to the surface. The high current densities needed to accomplish this can, by observing the conditions of my invention herein disclosed, be applied without affecting either the stability of the process or the cleaning effectiveness to any harmful extent.

The essential feature or features of this invention reside in so selecting and correlating the conditions of wire-speed, length of wire exposed in the solution, temperature, concentration, and current density for an acid solution in an electrolytic cleaning process in which an object chemically soluble in the solution, as iron or steel, is run continuously through the solution while current passes thereto as an anode, that the dissolving of the metal will be retarded and a rapid liberation of oxygen be effected, and that the working condition of the electrolyte will remain substantially unchanged for a long period of constant use.

A reference is made herein to my abandoned application Serial No. 445,225, April 17, 1930.

What is claimed is:

In a process for cleaning iron or steel wire, ribbons and the like in which initially unheated sulphuric acid of concentrations below 250 grams per liter are used, in which the wire travels continuously at a substantial speed through the bath and in which the wire is directly connected as an anode to a current source, the anode current density being high enough to liberate oxygen over nearly the entire submerged anode surface, that improvement for prolonging the useful life of the bath with respect to its uniformity and reliability of cleaning action over extended periods of continuous operation which comprises correlating and controlling the current density, wire speed, temperature, and concentration of the acid bath in a manner that the concentration of acid is always maintained less than 250 grams per liter and the current density is always higher than 20 amperes per square decimeter, the temperature is stabilized at a moderate increase over the initial temperature and the wire speed is not less than that of a continual wire processing operation, and compensating for increase of temperature due to heating effects of the current in the bath which tend to render the cleaning operation variable, irregular and uncertain by decreasing the concentration of acid in the bath and for increase in wire speed or both speed and temperature increase by decreasing concentration of acid in the bath while increasing the current density.

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