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METHOD OF CLEANING FERROUS METAL STRANDS ELECTROLYTICALLY, INCLUDING MOVING SAID STRANDS IN A HORIZONTAL PLANE THROUGH AN ELECTROLYTE WHILE UNDER THE INFLUENCE OF ALTERNATING ELECTRICAL FIELDS

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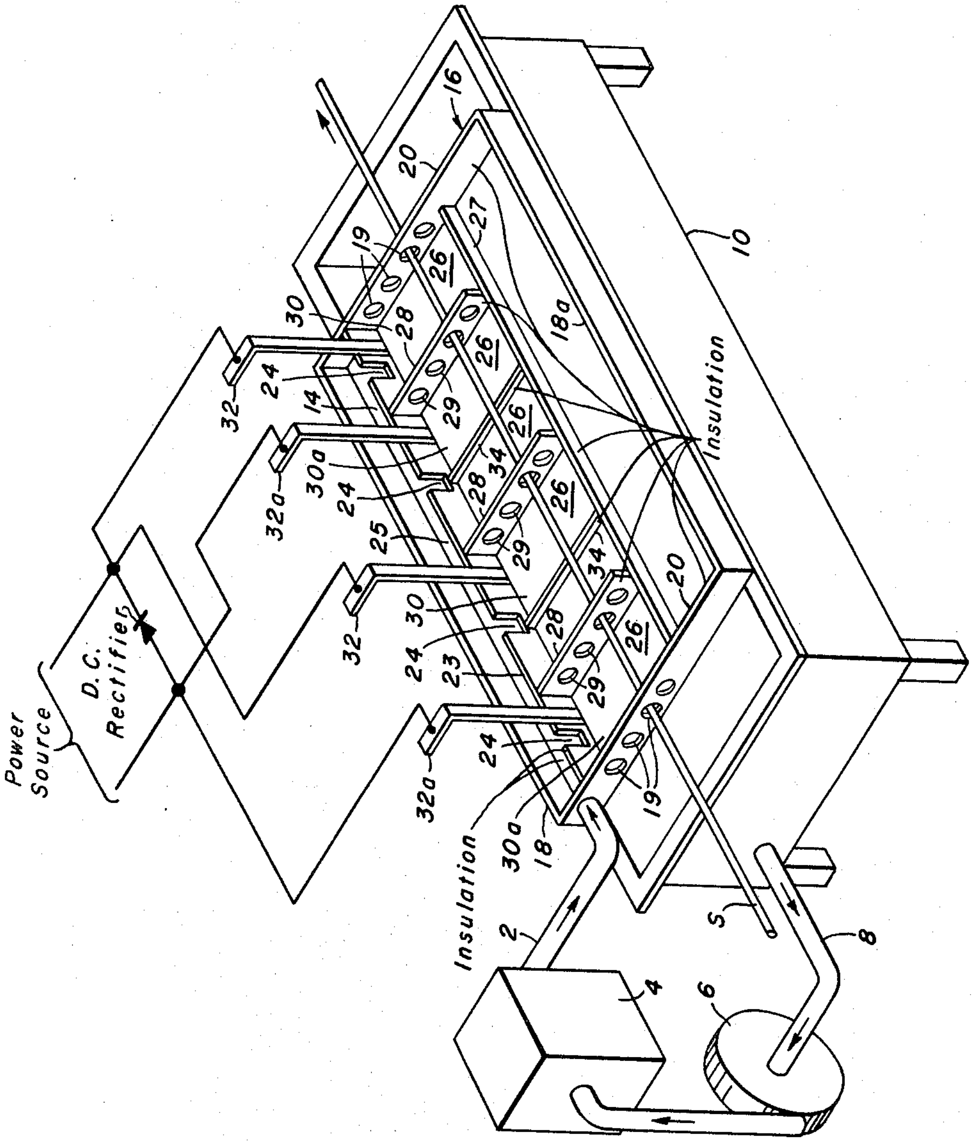

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METHOD OF CLEANING FERROUS METAL STRANDS ELECTROLYTICALLY, INCLUDING MOVING SAID STRANDS IN A HORIZONTAL PLANE THROUGH AN ELECTROLYTE WHILE UNDER THE INFLUENCE OF ALTERNATING ELECTRICAL FIELDS

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This application is a continuation-in-part of U.S. application S.N. 400,772, filed Oct. 1, 1964 now abandoned.

This invention relates to method and apparatus for cleaning strands of electrically conductive metal. More particularly, the invention relates to the continuous electrolytic treatment of steel strands. The term "strand" as used herein refers to wire, strip, sheet, etc., without regard to length or cross section.

When steel is exposed to elevated temperatures as in hot rolling, heat treating, etc., scale and/or oxides form on the surface. It is then necessary to clean the steel to facilitate subsequent processing and to provide a product with good surface qualities. Scale may be mechanically broken and removed from the surface of the steel, but it is generally impossible to remove all the scale in this manner. Acid cleaning and electrolytic cleaning have also been used to improve the surface finish. Conventional electrolytic cleaning is probably the most effective for removal of scale and oxide films; however, difficulties with conventional electrolytic cleaning render this approach far from perfect. Among the problems encountered in conventional cleaning are the adaptability of the system to in-line processing and the possibility of hydrogen embrittlement resulting from the accumulation of hydrogen, by deposition, on the metal strand.

Many continuous cleaning systems in the past have involved looping or bending strands into a cleaning solution or electrolyte. By precluding straight line travel of the work, such systems severely limit line speeds and cannot be used effectively in high-speed, continuous processing lines. With current emphasis on continuous and high-speed operations, cleaning must be accomplished rapidly and the cleaning procedure must lend itself to utilization in high-speed production systems.

The present invention provides method and apparatus which not only accomplish rapid and effective removal of scale and oxide but are also capable of treating metal strands at high line speeds. Moreover, hydrogen embrittlement is minimized by reducing the exposure time of the strand to gaseous hydrogen. Hydrogen embrittlement results from the absorption of hydrogen which is a function of exposure time and hydrogen concentration. High current densities are used in accordance with the present method, with a sulfuric acid electrolyte, to reduce cleaning time and minimize hydrogen contact with the strand. In addition, electrolytic cleaning is also more efficient at high current densities. It has been found that when current densities of 40 to 50 amps/in.^{2} are used, excellent cleaning may be obtained with minimum hydrogen embrittlement.

The cleaning technique of the invention is particularly efficacious when applied to a strand on which scale has previously been mechanically broken; however, thin oxide films may be removed without prior mechanical treatment. Where the strand contains scale formed at hot rolling conditions, mechanical breaking of the scale prior to electrolytic cleaning is essential. Scale breaking is also essential for "open air patenting" ("OP" Patenting) wherein the strands are heated in an oxidizing or reducing

atmosphere furnished by products of combustion. The patenting process is a heat treating operation for annealing the strands.

Mechanical treatment of scale can be accomplished in any conventional manner, such as by bending the work around rolls or abrading the surface. One preferred method, however, involves bending the strands about sheaves positioned in perpendicular planes; the first sheave in a vertical plane and the second in a horizontal plane. This method is equally effective if the strand is reversed and wrapped 180° around the vertical sheave. To accommodate straight-line processing, the strand centerline of the incoming strand is lowered a distance approximately the thickness of a strand more than the root diameter of the sheaves after passing around both sheaves. In such a system, the sheave diameter is dependent upon the size of the strand being descaled, and the ratio of the sheave diameter to strand diameter is desirably maintained between 14 to 1 and 24 to 1 with an optimum of 18 to 1. The scale-breaking sheaves are mounted as close together as possible to prevent twisting of the strand and permit the strand to be cracked in perpendicular planes. Multistrand operations can be provided with this type of reverse-bend mechanical scale-breaking unit.

In accordance with the invention, metal strands are electrolytically cleaned by passing the strand in a horizontal plane through electrolyte in a processing zone divided into a plurality of electrolytic chambers. In one preferred embodiment, electrolyte for the processing zone flows transverse to the direction of strand travel, thereby sweeping hydrogen off the strand. Electrodes are located in each chamber and adjacent electrodes are connected to opposite poles of a direct current supply source. Current is passed between the electrodes in adjacent chambers through the electrolyte and the strand while the strand is traveling through the chambers in the processing zone. The current flow is reversed in each succeeding adjacent chamber so that the polarity of the strand changes in each adjacent chamber. In this way, the strand is alternately made negative and positive as it travels through the processing zone. It should be noted, however, that certain important and critical processing conditions must be maintained in order to achieve successful and satisfactory strand cleaning. Thus, for example, it is necessary to maintain a current density of 40 to 50 times the surface area (in square inches) of all strands in each chamber. The temperature condition of the electrolyte is also critical and the sulfuric acid electrolyte used in accordance with the invention must be maintained at a temperature in the range 80 to 160° F. and the electrolyte concentration must be 12 to 30% acid by weight. The strand to electrode spacing is also desirably controlled to between ¼ to ¾-inch.

These and other aspects of the invention will be more fully understood by reference to the attached drawing and subsequent explanations.

The drawing is an isometric view, partly schematic, of an electrolytic cleaning apparatus according to one embodiment of my invention.

When strand speeds less than 100 feet per minute are intended to be used, a simple straight-line, tray-type processing unit may be employed in which a tray with grooved or perforated side walls is positioned over an electrolyte storage tank. The tray is divided into at least two processing zones at the bottom of each of which is positioned an electrode. Electrodes in adjacent processing zones or chambers are made to be of alternate polarity with an insulating barrier separating adjacent chambers. Electrolyte fills the processing zones and tray above the storage tank and a continuous electrolyte circulating system keeps the tray filled with electrolyte. The electrolyte used is sulfuric acid in the required concentration. If all the described critical processing conditions are observed, a simple unit of this type may effectively clean strands at line speeds of less than 100 feet per minute. However, if strand speeds of greater than 100 feet per minute and/or difficult scales must be removed, the electrolyte cross-flow apparatus described in the drawing is required.

The apparatus for electrolytically cleaning metal strands as shown in the drawing comprises an elongated receptacle or tank **10** and tray means **16** positioned and affixed to the top of tank **10**. Tray means **16** is defined by side walls **18** and **18***a*, end walls **20** and an insulated bottom **14** extending only over a portion of the tray means from side wall **18** to overflow weir **27**. The side walls **18** and **18***a* as shown are co-extensive with the sides of receptacle **10** to which they may be attached. The tray means **16** comprises the processing zone of the electrolytic cleaning apparatus and contains a plurality of electrolytic chambers **26** arranged in series. Each chamber is separated from the adjacent chamber or chambers by an electrically insulated barrier **28** which is a transverse wall member of substantially non-electrically conductive material. Apertures **19** and **29** are provided in the end walls of the tray and in the transverse wall members, respectively, and are aligned to enable a metal strand S to travel through the processing zone in a horizontal plane. In this way, the electrolytic apparatus may be incorporated in a continuous processing line for wire, rod, etc., without interfering or impeding line speed.

In the illustrated embodiment, the tray means **16** is shorter in length than the tank **10** and is disposed centrally thereof so that the tank extends beyond the tray means at both ends. This avoids the need for seals between the strand and apertures **19** and **29** since any electrolyte dripping out will merely fall into the storage tank.

The tray means **16** in the embodiment shown include an electrolyte reservoir **25** which extends the full length of the tray at one side thereof, and is defined by side wall **18** of the tray means **16** and an insulated inlet wall **23** which also extends the full length of the tray and is electrically insulated or formed of non-electrically conductive material. An overflow weir **27** is similarly positioned to extend the full length between end walls **20** or tray means **16**. Since tray bottom **14** extends between end walls **20** only from side wall **18** to overflow weir **27**, an open area exists between overflow weir **27** and side all **18***a*. Electrolytic chambers **26** are defined by the inlet wall **23** and overflow weir **27** at the sides thereof, and transverse walls **28** or end walls **20** at the ends thereof. Overflow weir **27** is made so that it is shorter in height than the insulated wall **23** and not as deep as end walls **20**, i.e. shorter in height, and electrolyte can flow over it as described below.

In each chamber **26** is positioned an electrode (**30** or **30***a*) having a large, effective (exposed) surface area. In the illustration, the electrodes in each chamber substantially cover the bottom of the chamber; however, the electrodes need not be as large as shown, but may be only large enough so that they cover the area of the chamber beneath the line of alignment of the apertures in the end walls and transverse walls through which metal strands travel through the processing zone. It is desirable, however, that the effective surface area of the electrode be at least three times, and preferably five times, the area of the strands treated in the electrolytic chambers. It is also necessary that the electrodes in each chamber have the capacity for carrying a current (in amperes) equivalent to 50 times the surface area, in square inches, of strands in each chamber. Further, it is desirable that the strand-to-electrode spacing be adjusted to between ¼ to ¾-inch. This serves to facilitate the passage of current through the electrolyte to the strands between the electrodes.

The electrodes **30** and **30***a* are electrically connected by suitable means **32** and **32***a* to an electrical supply source which advantageously is a source of direct current and in the embodiment illustrated is a D.C. rectifier, although a D.C. generator could also be used. It is important that the adjacent electrodes, **30** and **30***a*, be connected to opposite poles of the D.C. supply source. In this way, a metal strand passing through the processing zone will be subjected to alternating polarities by the reversal of the current flow in each succeeding adjacent chamber.

In the operation of the apparatus, the tray means is flooded with electrolyte and no physical contact exists between the electrode and the metal strand traveling through the apparatus. At the higher strand speeds to which this embodiment of the invention is particularly well suited (and even at operation at lower speeds), it is also preferred to provide an insulating band **34** which may be ⅛ to ⅜-inch wide at about the center of electrodes **30** and **30***a* and extending across the electrode perpendicular to the direction of strand travel. The insulating band prevents electrical short circuiting at the high current densities employed in the cleaning operation. By preventing physical contact between the metal strand and the electrodes, the current is forced to flow through the electrolyte between the electrodes and moreover, arcing and mechanical wearing of electrodes is avoided.

Electrolyte is withdrawn from tank **10** through a conduit or pipe **8** by a pump **6** which also pumps the electrolyte through a heat exchanger **4** from which it is returned to the tray means through conduit or pipe **2** into the reservoir **25**. Electrolyte enters electrolytic chambers **26** from the reservoir through inlets **24** of inlet wall **23** and floods electrolytic chambers **26** to a sufficient level so that the metal strand will be immersed in electrolyte while the strand passes through the chambers. Electrolyte runs over overflow weir **27** and into tank **10** through the open area between the overflow weir **27** and side wall **18***a* at the side of the tray means opposite the electrolyte reservoir. The heat exchanger **4** is provided to control the temperature of the electrolyte, which for reasons discussed below is desirable.

It will be noted that in the apparatus described, electrolyte flows in a direction transverse to the line of travel of the metal strands through the processing zone. Continuous rapid movement of the electrolyte in the vicinity of the metal strands removes hydrogen electrolytically deposited on the strand surface and minimizes hydrogen embrittlement of the metal. Moreover, removing hydrogen as it deposits increases the efficiency of the electrolytic process by permitting constant regeneration without interference by accumulation. The effectiveness of the electrolytic treatment and the cleanliness of the resulting strand surface is greatly enhanced by the rapid removal of gases electrolytically deposited along the strand. Thus, the flowing electrolyte, by sweeping gases from the strand surface, accomplishes that which cannot be achieved in standard, i.e. batch-electrolyte, systems. Of course, alternative electrolyte-flow arrangements may be devised which fulfill the requirement of transverse flow (to the strand). For example, the reservoir may be omitted and replaced with a simple header or with individual pumping units supplying electrolyte to the electrolytic chambers.

As mentioned above, the electrolytic cleaning apparatus is operated at a current density 40 to 50 times the surface area of all strands in each chamber. If the current density is lower than 40 times, the cleaning time is increased by a factor of at least 5. When the cleaning time is so lengthened, the strand will absorb hydrogen and, as a result, the steel will lose its ductility due to hydrogen embrittlement. By employing a high current density, there is no loss in ductility because the strands are cleaned within a very short period of time, i.e. 1 second or less. In addition, at lower current densities, i.e. less than about

40 amps/in.^{2} averaged over the strand, the strand is only partially cleaned and a carbide soil is left on the strand surface. The accumulation of hydrogen along the strand accentuates this condition and also limits the operating current density which can be employed. There is no practical value to operating at a current density 50 times greater than the surface area, and furthermore, at unduly high current densities, the strands would be subjected to excessive heating which results in preferential electrolytic attack of the strand further resulting in a surface residue of iron carbide that would be detrimental in subsequent processing.

The electrolyte chosen for electrolytically cleaning influences the current density that can be used and therefore, the rate at which the work can be electrolytically cleaned. Electrolytes can be grouped into three general types: bases, salts and acids. The cleaning of oxide or scale by electrolysis in alkaline solutions has been found to be relatively expensive and suitable primarily for removal of light soils from the strand surface. Cleaning with salts has been found to be relatively slow and require voltages three to four times those necessary for acid solutions of equivalent concentrations.

Oxides (scales) and soils have been found to be most effectively removed by electrolyzing in acid solutions. Sulfuric acid, in addition to being an economically attractive electrolyte material, is required in the practice of the present invention because it has been found to be most effective, and when electrolyzed at the operating temperatures involved, decomposes only into water and is non-volatile. In contrast, chlorine containing electrolytes evolve considerable amounts of chlorine and hydrogen chloride gases.

With aqueous solutions of sulfuric acid as electrolytes, the conductivity increases as the solution concentration and temperature increase. However, it has been found that the electrolyte concentration must be maintained between about 12 and 30% acid by weight, preferably 15 to 25%. Below about 12%, the conductivity of the electrolyte is such that high voltages are required which result in preferential attack of the strand. In addition, the efficiency of scale removal is appreciably reduced at less than 12% concentration. Above about 30% it has been found that preferential attack also occurs, and the reason for this is not fully understood. Moreover, at higher acid concentrations, acid loss becomes excessive.

The effect of electrolyte temperature on cleaning time is also a critical feature in the effectiveness of the cleaning operation. It has been found that at all acid concentrations the cleaning time decreases with an increase in temperature up to 180° F. At temperatures below about 100° F., the time required for scale removal is increased. Nevertheless, electrolyte temperature as low as 80° F. may be used at some sacrifice of cleaning effectiveness and rate of scale removal. It should be noted, however, that as the cleaning time is increased, the embrittlement due to the absorption of hydrogen is increased. Thus, in accordance with the invention, temperature of the electrolyte must be maintained within the range 80° F. to 160° F. with optimum ranges 100° F. to 120° F. for higher carbon steels and 130° F. to 150° F. for the lower carbon steels. Strands of medium and high carbon steel, i.e. above about 0.3% carbon, are more susceptible to soiling at elevated temperatures and for these materials it is desirable to maintain the electrolyte temperature below about 120° F., preferably 100 to 120° F. However, scale on low carbon steel, i.e. less than about 0.3% carbon, is most effectively removed at higher temperatures, i.e. 120 to 160° F., preferably 130 to 150° F., and unlike medium and high carbon steel, is not soiled at this higher temperature range. A heat exchanger can be used to control the temperature within the required limits.

Direct current is preferred over alternating current for several important reasons. One advantage of direct current is that less dissolution of electrolysis is experienced.

We have found, for example, that with alternating current at 30 amps./in.^{2} a lead-1-percent-silver alloy electrode will lose 7.5 mils per hour through dissolution. In contrast, when direct current is used, either anodically or cathodically, under the same conditions as above, the electrode dissolution sharply decreases and an electrode loss of only about 0.011 mils per hour results. A second reason for using direct current is that the strand becomes increasingly soiled when the frequency of current reversal exceeds about 30 cycles per second. Current reversal frequency can be maintained within satisfactory limits with direct current.

In alternate-polarity descaling as used herein, scale is most quickly removed from the surface of the strand when the strand is cathodically connected and, by reversing the polarity of the strand, a thin layer of metal is removed which carries with it residual soil. Since the cathodic treatment leaves a carbon-bearing film on the surface the strand should be treated so that its final polarity is positive. In continuous operations using the alternate-polarity cleaning method, the polarity of the strand changes as it moves from one chamber to the next, simulating an alternating current. The strand speed and the length of each chamber determines the rate of polarity change.

The spacing of electrodes from the traveling metal strand has been found to be an influence on the power requirements and the voltage necessary to achieve electrolytic cleaning in as short a time period as possible. Optimum conditions have been found to be an electrode spacing of between ¼ and ¾-inch. However, satisfactory cleaning can be achieved even with greater spacings. Nevertheless, cleaning quality may be disadvantageously affected by unduly increasing electrode spacing. As the applied voltage is increased, the strand becomes hotter, the electrolytic descaling efficiency decreases with the result that the strand may be soiled and the scale may not be completely removed.

The total number and size of electrolytic chambers used in any particular application is a function of the speed at which it is desired to clean the metal strand. Should speeds greater than 100 feet per minute be required, more than two chambers would be used. However, the number of chambers (i.e. compartments) and the chamber dimensions are selected so as to provide a minimum current density on the strand of 40 amps/in.^{2} over full length of the cell. In order to achieve this condition in a two chamber cell, each of the electrodes is preferably less than 8-inches in length. In cells with more than two chambers, the first and last chambers are also preferably less than 8-inches and intermediate chambers are preferably less than 16-inches in length. Thus, for example, at speeds of 100 to 200 feet per minute, two 6-inch chambers and one 12-inch chamber would be desirable, with the 12-inch chamber being positioned in the middle. In such an arrangement, the electrode in the 6-inch chambers would be connected to the negative side of the rectifier, and the electrode in the 12-inch chamber connected to the positive side. For operating speeds of 200 to 300 feet per minute, two 6-inch chambers and two 12-inch chambers would be desirable with the 6-inch chamber being positioned at each end. Alternately, the electrodes in the first and third chambers would be connected to the positive side of the rectifier, the second and fourth electrodes connected to the negative side. By alternating the polarity of the electrodes in each chamber and by increasing the number of cells, strands at speeds up to 1000 feet per minute can be effectively electrolytically descaled if mechanically descaled first.

Electrolytic cleaning, according to the invention, is most effectively used in combination with prior mechanical treament for breaking scale on the surface of the metal strand. As indicated previously, in certain operations prior mechanical treatment is essential for satisfactory electrolytic cleaning. The current is carried to the strands in each chamber through the electrolyte. The strands at no time directly contact a metal electrode, which at the high operating current densities would cause arcing. The current takes the easiest path flowing from the lead cathode, through the electrolyte, and to the strand in this chamber. The surface of a strand treated according to the invention is not affected because hydrogen absorption (embrittlement) is negligible. Each strand is cleaned with the same electrolytic treatment and the result is a more uniform high-quality product.

I claim:

1. A method of electrolytically cleaning a strand of an electrically conductive ferrous metal composition comprising passing said strand at a speed sufficient to minimize hydrogen embrittlement in a horizontal plane through sulfuric acid electrolyte having an acid concentration of 12 to 30% by weight in a processing zone divided into a plurality of electrolytic chambers, passing direct current at a current density of 40 to 50 amps/in.^{2} of strand surface between electrodes in adjacent chambers through said electrolyte and said strand during travel of said strand through said chambers in said processing zone, reversing the current flow in each succeeding adjacent chamber so as to change the polarity of said strand in each of said adjacent chambers thereby subjecting said strand to alternating polarities, maintaining the temperature of said electrolyte at about 80 to 160° F. and withdrawing said strand in a horizontal plane from the last of said chambers in said processing zone.

2. A method according to claim **1** wherein said sulfuric acid electrolyte has an acid concentration of 15 to 25% by weight.

3. A method according to claim **1** wherein said electrodes are about ¼-inch and ¾-inch from said strand.

4. A method according to claim **1** wherein said strand is treated so that its final polarity is positive.

5. A method according to claim **1** wherein said strand is steel with a carbon content of less than about 0.3% and the electrolyte temperature is maintained at 130 to 150° F.

6. A method according to claim **1** wherein said strand is steel with a carbon content above about 0.3% and the electrolyte temperature is maintained at 100 to 120° F.

7. A method of cleaning a strand of an electrically conductive ferrous metal composition comprising mechanically breaking the scale on said strand at a speed sufficient to minimize hydrogen embrittlement, passing said strand in a horizontal plane through aqueous sulfuric acid electrolyte having an acid concentration of 12 to 30% by weight in a processing zone divided into a plurality of electrolytic chambers, maintaining said electrolyte at a temperature of about 80 to 160° F., passing direct current at a current density of 40 to 50 amps/in.^{2} of strand surface between electrodes in adjacent chambers through said electrolyte and said strand during travel of said strand through said chambers in said processing zone, said electrodes being about ¼-inch to ¾-inch from said strand, reversing the current flow in each succeeding adjacent chamber so as to change the polarity of said strand in each of said adjacent chambers thereby subjecting said strand to alternating polarities and withdrawing said strand in a horizontal plane from the last of said chambers in said processing zone.

8. A method of cleaning a strand of an electrically conductive ferrous metal composition comprising mechanically breaking the scale on said strand at a speed sufficient to minimize hydrogen embrittlement, passing said strand in a horizontal plane through aqueous sulfuric acid electrolyte having an acid concentration of 12 to 30% by weight in a processing zone divided into a plurality of electrolytic chambers, flowing said electrolyte transverse to the direction of strand travel, maintaining said electrolyte at a temperature of about 80 to 160° F., passing direct current at a current density of 40 to 50 amps/in.^{2} of strand surface between electrodes in adjacent chambers through said electrolyte and said strand during travel of said strand through said chambers in said processing zone, said electrodes being about ¼ inch to ¾ inch from said strand, reversing the current flow in each succeeding adjacent chamber so as to change the polarity of said strand in each of said adjacent chambers thereby subjecting said strand to alternating polarities and withdrawing said strand in a horizontal plane from the last of said chambers in said processing zone.

References Cited

UNITED STATES PATENTS

2,197,653	4/1940	Wilson	204—145
2,876,132	3/1959	Worden et al.	204—145
3,224,953	12/1965	Russell	204—212
3,287,238	11/1961	Latawiec et al.	204—140.5

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,338,809 August 29, 1967

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 49, for "all" read -- wall --; column 7, lines 45 and 46, strike out "at a speed sufficient to minimize hydrogen embrittlement" and insert the same after "strand" in line 47, same column 7; column 8, lines 18 and 19, strike out "at a speed sufficient to minimize hydrogen embrittlement" and insert the same after "strand" in line 19, same column 8.

Signed and sealed this 30th day of July 1968.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents