

April 16, 1940.

L. H. WILSON
METHOD OF ELECTRICALLY PICKLING AND CLEANING
STAINLESS STEEL AND OTHER METALS
Filed May 23, 1936

2,197,653

2 Sheets-Sheet 1

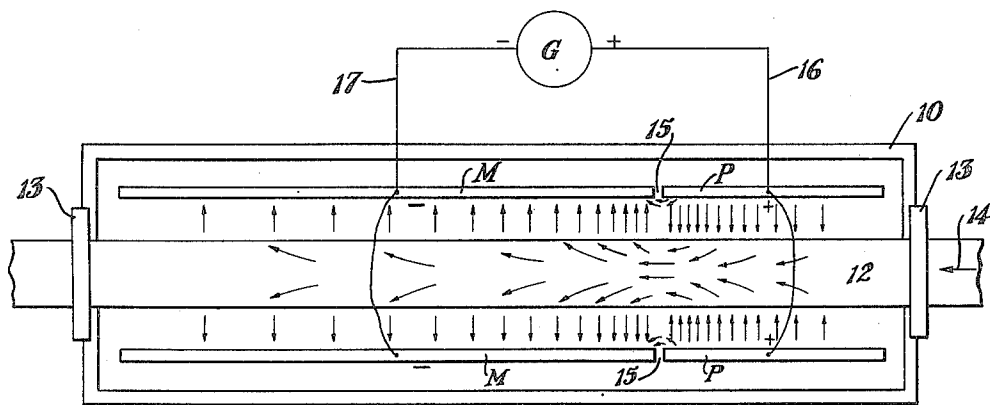


Fig. 1

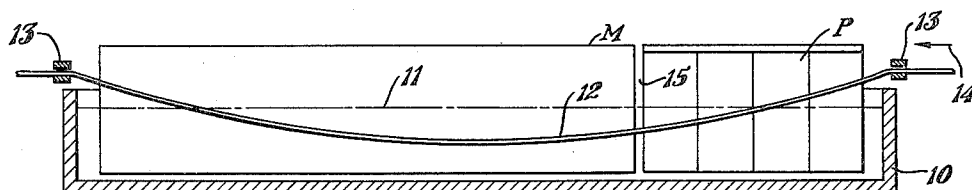


Fig. 2

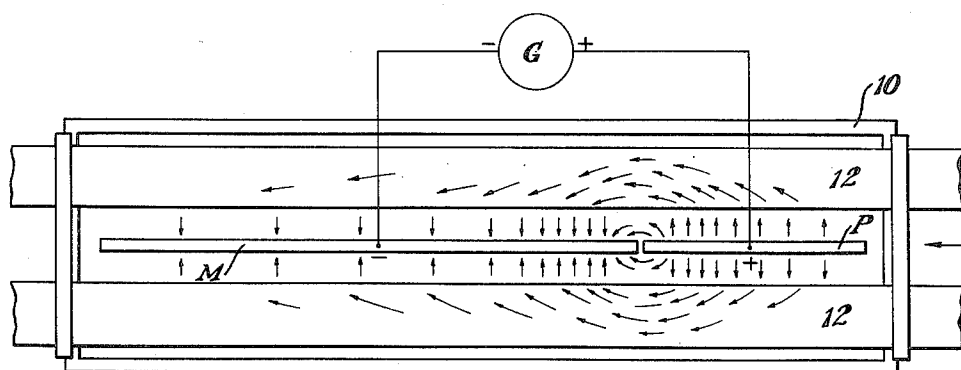


Fig. 3

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2 Sheets-Sheet 2

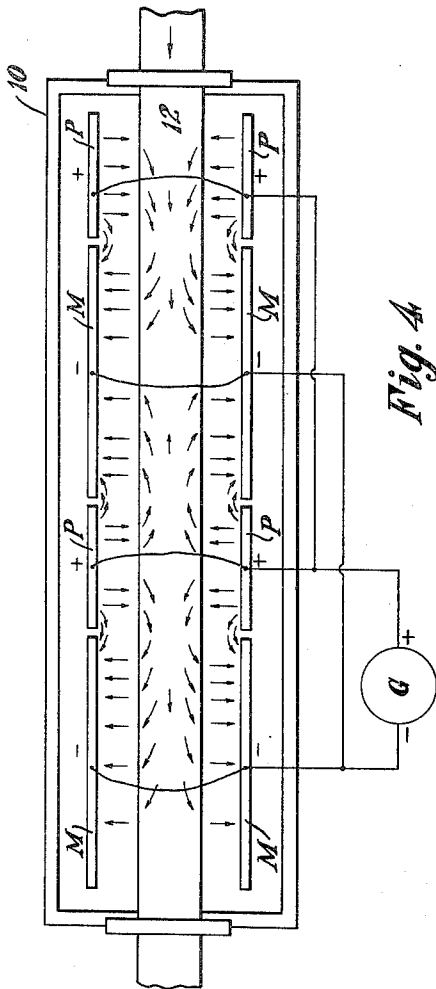


Fig. 4

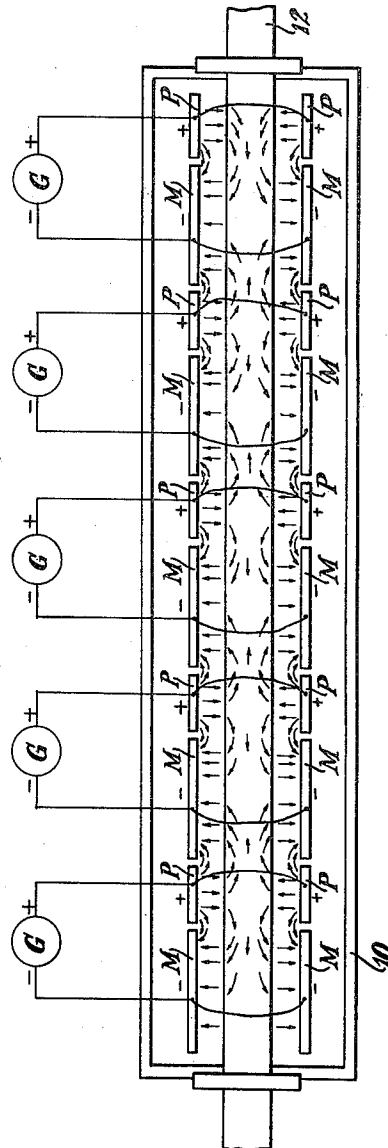


Fig. 5

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UNITED STATES PATENT OFFICE

2,197,653

METHOD OF ELECTRICALLY PICKLING AND
CLEANING STAINLESS STEEL AND OTHER
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Application May 23, 1936, Serial No. 81,461

23 Claims. (Cl. 204—1)

The invention relates generally to the art of pickling or cleaning metals for removing scale or oxides therefrom, and more particularly to the continuous electric pickling of metals and to the removal of scale or oxide film from annealed stainless steel strips, sheets and the like; and this application is a continuation in part of my copending application Serial No. 737,482, filed July 30, 1934.

Considerable difficulty has been experienced in commercially producing stainless steel in sheet or strip form which lends itself to ready polishing. The types of stainless steels particularly concerned are the high chromium steels containing from about 8% to about 40% of chromium, with or without other metals, such as between about ½% and about 30% of nickel.

Such stainless steels are commercially made into sheets, strips and the like, by hot rolling the cast ingot into stock perhaps ¼ inch in thickness, or even less, after which the stock is cold rolled to the desired thickness or gauge with or without intermediate annealing and pickling. The cold rolling hardens the steel and necessitates one or more annealings of the metal, particularly where the cold reduction is considerable and polished surfaces are desired.

For example, when hot rolled stainless steel strips about ¼ inch in thickness are to be cold rolled to a thickness of 20 gauge, or even to 0.005 inch or thinner, the steel is annealed several times during this reduction to remove hardness and restore ductility, and thus to permit further reductions without breakage. It is also desirable to anneal the steel after it has reached its final desired thickness, so that it can be readily handled in subsequent operations or uses.

Such annealing operations cause a scale or oxide film to form on the surface of the material annealed, and particularly in the cases of stainless steel, such scale or oxide film is quite difficult to remove while still retaining the surface polish or finish resulting from the cold rolling operations.

The removal of the scale which forms on metals, and particularly on iron and steel, during the treating thereof, by immersing the metal in a bath containing a solution of an acid or an acid salt, or an alkaline solution, has long been practiced.

When a strong solution is used with this method, the surface of the metal itself becomes etched or otherwise damaged, which requires subsequent tedious and expensive treatment or working in order to restore the surface of the metal and de-

velop the desired finish thereon. With a weak solution, which will not damage the metal, the method is very slow and expensive.

With certain alloy steels, such as stainless steels, the scale thereon may not be satisfactorily removed by ordinary pickling methods. Accordingly, it has been proposed to distort the metal just prior to the pickling operation, as by "grain breaking" in order to accomplish or aid the removal of the scale. This permits the pickling solution to get under the scale for removal thereof but also permits the pickling solution to attack the metal which produces etching or pitting and the like on the surface thereof.

This condition of the metal subsequently requires considerable additional rolling or other working to produce the desired finish, and prohibits the use of "grain breaking" on light gauge material, such as 0.010 inch stainless steel strips, and even thinner stainless steel strips, of which large quantities are being made and used.

Prior methods have been developed for electrically pickling metals, and particularly stainless steels, to remove scale therefrom. These methods have constituted in general, passing the metal through a pickling solution or electrolyte through which an electric current passes, the metal being treated acting as the anode or the cathode.

The electric current materially aids the pickling action and these prior methods have consequently enjoyed some measure of success, but many inherent difficulties, both electro-chemical and electro-mechanical, have been encountered, which have long been sought to be overcome.

Prior art electro-chemical difficulties

In certain of these prior methods, where the metal being pickled is made the anode in a solution of an acid or an acid salt, the scale is dissolved more rapidly than in the usual pickle bath; but the action is apt to be irregular, and activity of the acid ion frequently causes loss or pitting of the metal.

Where the metal being pickled is made the cathode in an electrolyte which is neutral, weak acid or alkaline, the removal of scale is relatively slow and irregular; and in neutral or alkaline solutions some of the scale is reduced to metal, which produces a rough irregular surface on the metal being pickled.

Various electrolytes have been tried out in connection with electric pickling, such as an aqueous solution of sulphuric acid, a solution of sulphuric acid and sulphur dioxide, a solution of

bisulphate of alkaline metal in water, a solution containing acid sulphate, a solution of bisulphate of an alkaline metal in dilute sulphuric acid, and a solution containing acid and acid sulphate. In using such solutions the temperature thereof must be maintained at a constant predetermined degree within relatively narrow limits in order to obtain satisfactorily results.

The methods employed with these various solutions have proven more or less successful, but they require excessive time and/or expense, and/or cause loss of the metal being pickled or injury to the surface thereof. Also, in many cases the pickling solution must be frequently replenished.

Prior art electro-mechanical difficulties

In all of these prior methods of electric pickling, the metal being treated is made either the anode or the cathode, and this requires mechanical-electrical contacts with the metal. In continuous electric pickling arcing occurs at the contacts, causing burning, warping, or otherwise damaging the metal strip. Thus it is necessary to control or restrict the amount of electrical energy used.

It is an established fact that the speed of pickling in any electric pickling process for any given electrolyte is dependent upon the electrical power input and the time the electric energy has to work on the material.

If a continuous metal strip is being pickled and the metal is acting as an electrode, the effective length of the bath is the length of metal strip immersed in the electrolyte at all times. Thus the time necessary for complete pickling is obtained by regulating the effective length of the bath and the speed at which the work travels through it.

Increasing the length of the bath increases the voltage required to force the current through the strip, so that the pickling speed cannot be materially increased beyond the limits determined by the requirements for low voltage.

In certain prior methods of continuous electric pickling, a single pickling tank is used with the metal strip acting as an electrode, requiring one or more mechanical-electrical contacts with the metal strip. With this construction, arcing occurs at the contacts and a voltage drop results at the contacts representing a loss of power.

Moreover, the contacts require adjustment for different sizes of strips, and they tend to bend light gauge strips. Still another difficulty presents itself when strips are pickled in multiple, because the contacts take up space and limit the effective width of the tank.

The strip between the contacts and the bath necessarily carries electric current, which causes additional voltage drop, and that portion of the strip tends to become heated, causing warpage and distortion thereof. Accordingly, if it is attempted to increase the speed of pickling by increasing the voltage, or if the effective tank length is increased; not only are the difficulties due to arcing increased and multiplied, but that portion of the strip between the contacts and the bath becomes increasingly hot and warps or distorts. This warpage or distortion may result in permanent disfigurement of the strip, especially in the case of light gauge material.

The present invention

I have discovered and developed an improved method of electrically pickling metals, by which

rapid, economical and complete pickling is accomplished without using the metal as an electrode, and by which substantially all of the foregoing difficulties are overcome.

The terms "electrode" and "electrodes" as used herein, mean the end or ends, such as a plate or plates of the conductors or wires leading from the generator or other source of current. These plates are immersed in and terminate in the electrolyte which is the medium conveying current to and from the material being treated.

It is a general object of the present invention to provide for electrically treating metals by passing the metal, while in a single bath of electrolyte, adjacent to, but not in contact with an electrode of one polarity, and then adjacent to, but not in contact with an electrode of opposite polarity, and simultaneously passing electric current from the one electrode through the bath to the other electrode and at the same time permitting current to pass from said one electrode through the bath to the metal, then through the metal, and thence through the bath to the other electrode.

A particular object of the present invention is to provide an improved method for the continuous electrical pickling of metals which will rapidly and completely remove the scale therefrom without damaging or materially affecting the surface of the metal.

Another object is to provide an improved method for continuous electric pickling which will satisfactorily remove the scale from special alloys such as cold rolled stainless steels.

A further object is to provide an improved method for continuous electric pickling which will completely and satisfactorily pickle metals in the form of light gauge strips or sheets without bending or injuring the strips or sheets in any way.

Another object is to provide an improved method for electric pickling which will satisfactorily and completely pickle metals without requiring any prior distortion or mechanical treatment thereof.

It is also an object of the present invention to provide for pickling stainless steel after annealing so that the pickled steel processes substantially the cold roll finish it possessed after the cold rolling and before the annealing.

Another object is to provide an improved method for electric pickling which is capable of utilizing a common and relatively inexpensive electrolyte, the concentration of which may vary considerably without affecting the pickling action.

A further object is to provide an improved method of electric pickling in which the temperature of the electrolyte utilized may vary between wide limits.

A further object is to provide an improved method of electric pickling in which the electrolyte utilized does not need frequent replenishing.

Another object is to provide an improved method for continuous electric pickling in which the speed of pickling may be increased and in which the voltage of the electric current may be varied, without having any deleterious effect upon the metal being pickled.

Another object is to provide an improved method for continuous electric pickling which requires no mechanical-electrical contacts with the metal being pickled.

Another object is to provide an improved

method for continuous electric pickling which is applicable to the pickling of metal strips in multiple.

Another object is to provide an improved method for continuous electric pickling in which the flow of electric current can take place whether or not the metal strip being pickled is in the electrolyte.

A further object is to provide an improved method of electrically pickling alloys such as stainless steels, which method may utilize an electrolyte which will not attack the alloy if the alloy is left in the bath with the current off.

A still further object is to provide an improved method for electric pickling which is applicable to a great variety of metals and alloys, including all ferrous or non-ferrous metals, and alloys, which are capable of conducting electricity.

These and other objects are accomplished by the improved methods comprising the present invention, as shown in the drawings, and hereinafter described and claimed.

In general terms, the present improved method of continuous electric pickling includes moving a preferably continuous strip of the metal to be treated into a single bath of preferably acid electrolyte containing successively arranged spaced electrodes of opposite polarity, moving the strip through the electrolyte first past, but not in contact with an electrode of one polarity, and then past, but not in contact with an electrode of opposite polarity, and simultaneously passing electric current from one electrode through the electrolyte to the other electrode and at the same time permitting electric current to pass from one electrode through the electrolyte to the strip, then through portions of the strip in the electrolyte, and thence through the electrolyte to the other electrode, whereby the strip is alternately subjected preferably to cathodic, neutral and anodic treatment in the electrolyte.

In the drawings forming part hereof:

Figure 1 is a diagrammatic plan view of a preferred form of apparatus which may be used for carrying out the improved method of electrically pickling a continuous strip of metal or alloy, showing a pickling tank having one pair of positive electrodes and one pair of negative electrodes;

Fig. 2 is a longitudinal sectional view thereof;

Fig. 3 is a diagrammatic plan view of apparatus for carrying out the improved method of continuously electrically pickling two strips, showing one anode and one cathode;

Fig. 4 is a diagrammatic plan view of apparatus for the continuous electric pickling of a continuous strip of metal or alloy, showing a series of two pairs of anodes and two pairs of cathodes, alternately arranged, the electrodes being connected to a single source of electric current; and

Fig. 5 is a diagrammatic plan view of the improved apparatus for the continuous electric pickling of one strip, showing a plurality of pairs of alternately arranged anodes and cathodes, and each series of one pair of anodes and one pair of cathodes being connected to a separate source of electric current.

Similar reference characters indicate corresponding parts throughout the drawings.

The present improved method and apparatus will be described as applied to the continuous electric pickling of alloys such as stainless steels, but it is understood that the same may be applied to other metals or alloys by using different elec-

trolytes and/or electrodes of different material, and by making corresponding changes in dimension or arrangement of the parts of the apparatus; without departing from the scope of the invention as defined in the appended claims.

Referring first to Figs. 1 and 2, 10 indicates the pickling tank which may be of varying size or shape, but is preferably rectangular and considerably longer than wide, and the depth may be substantially the same as the width. The tank may be constructed of any material which is not attacked by the electrolyte and which is not a conductor of electricity, and since the electrolyte preferably used in pickling stainless steels is an acid solution, I prefer to use either a wooden tank or a brick tank.

The tank 10 contains the solution of electrolyte which is maintained substantially at the level indicated by the dot-dash line 11 in Fig. 2 during the improved pickling operation.

The continuous strip being treated is indicated at 12, and is moved longitudinally through the central portion of the tank 10 by any suitable means (not shown). Preferably, the strip passes through suitable guides 13 at the entrance and exit end of the tank, and is permitted to sag between the guides as shown, so as to immerse the strip in the electrolyte substantially throughout the length of the tank.

The guides 13 at the entrance end of the tank may be provided with means for applying tension to the strip, so that the amount of sag between the guides may be adjusted regardless of the gauge of the strip. The guides 13 at the exit end are adapted to act as a slicker or wiper for removing excess pickling solution and particles on the surface of the strip.

As shown in Fig. 2, the amount of sag is preferably adjusted so that the central portion of the strip between the guides is located substantially midway between the level of the electrolyte 11 and the bottom of the tank 10, so that the strip is in the most active part of the electrolyte while being pickled, and the under surface of the strip is subjected to substantially the same amount of pickling as the upper surface.

The electrodes are preferably relatively thin plates of large area composed of an insoluble material or of stainless steel, which may be and preferably is, substantially the same composition as the strip being treated. Preferably, the electrodes are arranged longitudinally of the tank, being spaced laterally of and at each side of the strip and stationarily extend into the electrolyte.

Although the electrodes can be disposed in various other positions such as horizontal, I prefer to dispose them vertically, because in that position they collect less sediment and are less likely to touch the strip; and the strip requires less mechanical guiding.

As shown in Fig. 2, the anodes P are preferably composed of a plurality of sections having their adjoining edges abutting each other, so that any section thereof may be replaced without replacing the entire anode; although these sections need not necessarily be abutted but may be spaced apart.

The cathodes M shown in Fig. 2, are indicated as being single plates, but the same may be composed of a plurality of sections similar to the sectional arrangement of the anodes P; and the cathodes M if made in sections, may have adjacent sections spaced apart if desired.

Laterally opposite electrodes should be of the

same polarity, that is, an anode should be laterally opposite an anode, and a cathode laterally opposite a cathode. If the strip 12 is moving in a direction indicated by the arrow 14 in Figs. 1 and 2, the best results are obtained by placing the anodes P at opposite sides of the entrance end of the tank 10, and the cathodes M at opposite sides of and extending substantially throughout the remainder of the tank. It is desirable to have the total electrode area substantially as long as the tank, and preferably the anodes are about one-third the length of the cathodes, although the anodes and cathodes may be of almost any proportion.

Each anode P is spaced longitudinally from the adjacent cathode M a relatively short distance indicated at 15, the shorter the distance 15 is without the electrodes touching, or without the occurrence of arcing, the lower the voltage drop at that point will be for any given current.

However, in some cases it may be desirable to space the anodes and cathodes a greater distance apart at 15 than the distance from many portion of the strip to any anode or cathode; although the diagrammatic showing of the drawings indicates a reverse relation. The efficiency of the operation of the equipment is controlled by varying the spacing 15 and the distance of strip 12 from anodes P and cathodes M.

Although only one strip is shown diagrammatically in Figs. 1, 4 and 5 of the drawings, such a strip may be wider or narrower than is shown, or a plurality of even six or more narrower strips may be simultaneously passed through the apparatus and quickly pickled by the improved method.

The source of electric energy G can be any practical electric current generator. I have obtained satisfactory results by using a 75 kw. D. C. generator, and operating it from a low voltage of say 2 volts to about 60 volts, and from a low amperage of say 10 amperes to 3000 amperes.

The anodes P are connected in parallel to the positive side of the direct current generator G by a conductor 16, and the cathodes M are connected in parallel to the negative side of the generator G by a conductor 17.

In the operation of the improved apparatus according to the improved method, as the strip 12 moves through the bath it first passes but does not contact with the anodes P, and then passes but does not contact with the cathodes M. At the same time direct current flows from the positive side of the generator G through the conductor 16 to anodes P. As indicated by the arrows in Fig. 1, direct current then flows through the electrolyte to the laterally adjacent portion of strip 12, through the strip to a position laterally adjacent the cathodes M, and then through the electrolyte to cathodes M, from which it returns to the negative side of generator G through conductor 17, and completes the circuit; and only the immersed portion of the strip carries current. At the same time, some current passes between the electrodes P and M directly through the electrolyte without entering the material.

Thus, a hot rolled stainless steel strip may be first cold rolled to reduce its thickness until such time as it may be necessary to anneal it; after which the strip is heated in an annealing furnace to between about 1300° F. and 2000° F., depending upon the composition of the steel. During such an annealing operation a scale or oxide film forms on the cold rolled surfaces of the strip,

which it is necessary to remove as by the present improved method.

During the pickling operation, the immersed portion of the strip is necessarily exposed to the action of the electrolyte. At places opposite to the anodes P, when current is being supplied to the same, the strip is cathodically treated; and at places opposite the cathodes M, the strip is anodically treated. In between or intervening such places, there is a region adjacent to the spaces 15, where the strip is neutral, that is, the strip is neither positively nor negatively charged with relation to the electrolyte; and at such a region the strip is exposed and subjected to the simple pickling action of the electrolyte, which may be termed "non-electrode pickling."

As the strip emerges from the electrolyte, the surfaces thereof are wetted with the electrolyte until the same is removed by wiping, scrubbing, washing, neutralizing, or the like; and where the strip is so wetted with the electrolyte it may likewise be subjected to any simple pickling action of the electrolyte which may occur, termed herein "non-electrode pickling."

The resultant action of the electric current and the electrolyte upon the strip 12 is to rapidly and satisfactorily pickle or remove the scale therefrom, without damaging or injuring the strip itself in any way, so that the use of an inhibitor is not required. No acid brittleness results because the pickling is performed so quickly that hydrogen cannot be absorbed.

Moreover, in the case of stainless steel the pickled strip has substantially the same surface as the strip had upon entering the annealing furnace prior to pickling; for instance, if the strip had a dull grey surface cold rolled or pickled surface upon entering the annealing furnace, it has a dull grey surface after being pickled, and if it had a mirror finish produced by cold rolling or polishing upon entering the annealing furnace, it has a mirror finish after pickling, provided the annealing operation is properly regulated to prevent too heavy a coating of oxide being formed on the strip.

Since there are no mechanical-electrical contacts with the moving strip to cause arcing or burning or voltage drop, and since the current-carrying part of the strip is always immersed in the electrolyte, the pickling speed may be varied almost at will. A raise in voltage enables the pickling speed to be increased for any given set-up. For the same reasons light gauge strips may be satisfactorily pickled without being distorted or damaged in any way.

Generally speaking the closer adjacent anodes and cathodes are together, provided they are not touching, the better are the results obtained. By slightly adjusting the space between adjacent anodes and cathodes, the working current may be adjusted for any given set-up. Also the distance between the electrodes and the strip has an effect upon electrical characteristics and pickling speed. The closer the strip passes to the electrodes without actual contact or the occurrence of arcing, the better are the results obtained.

I have found by experiment that in the improved method, better results are obtained with acid solutions as the electrolyte than with alkaline and salt solutions.

Any of the commercial acids, such as nitric or sulphuric or phosphoric can be used with excellent results.

Although the process will work satisfactorily

with almost any concentration of acid, I prefer to use a solution containing acid of two to twenty percent concentration by weight. The important factor is to use the concentration of acid having the best electrical conductivity.

Either nitric acid or sulphuric acid can be used alone, or the two can be combined to produce an electrolyte which gives very satisfactory results. While sulphuric acid is somewhat cheaper than nitric acid, I prefer to use the nitric acid because it does not give off objectionable fumes during the process, whereas sulphuric gives off obnoxious fumes, particularly at high pickling speeds, which may require a ventilating system; and while sulphuric acid attacks stainless steel, nitric acid attacks it only momentarily and then passivates it.

In carrying out the present improved method, if for instance, a solution of straight nitric acid of two to twenty percent concentration is used when pickling stainless steel, the nitric acid will not attack the stainless steel strip if the current is shut off with the strip in solution. Also, if the electrodes are of stainless steel, the nitric acid will not attack them when the current is off. Furthermore current can flow through the apparatus when the strip is not in the bath.

Moreover, the electrolyte solution does not need to be replaced except at long intervals. It may be desirable to replace the solution before it loses its ability to pickle, since the efficiency of the pickling solution is somewhat lessened by becoming dirty or otherwise contaminated.

Ordinarily, heating a pickling bath improves the pickling action, but the increased temperature causes the bath to give off fumes. I have found that by using an electrolyte solution of the above concentration of commercial acid in the present improved method, satisfactory results are obtained without heating the bath. The only requirement for controlling the temperature of the bath is that if the bath has been used for some time, and becomes warm due to the passage of electric current therethrough, it may give off more objectionable fumes and result in some loss of acid, so that it may be desirable to provide some conventional method of cooling the electrolyte, such as water cooled pipes or cascades.

In the pickling of stainless steel in a bath of commercial acid, any material which conducts electricity can be used for electrodes, but I prefer to use stainless steel electrodes because they are insoluble in the bath when the current is off, and because they do not cause any foreign matter to get into the tanks which would not be introduced by the material being pickled.

The cathodes M, which are attached to the negative side of the generator are not consumed by the pickling action and require replacing only at long intervals. The anodes P are consumed by the pickling action and require frequent replacement. However, since the anodes are preferably made only one-third of the length of the cathodes and are made in sections, the replacement of the anodes or sections thereof is relatively easy, and if the electrodes are stainless steel of substantially the same composition as the strip being treated, scrap stainless steel material may be used, involving little expense.

It is desirable to provide the surface of the electrodes away from the strip, or in other words, the sides of the electrodes adjacent the sides of the tank, with a non-conductive coating such as rubber to reduce electrical losses on the surface of the electrodes away from the strip. This coat-

ing, however, would have no effect upon the pickling action of the improved process.

When it is desired to simultaneously pickle two relatively narrow strips, the improved process may be carried out by means of the apparatus diagrammatically shown in Fig. 3. In this arrangement, the tank 10 has located in its longitudinally central portion a single anode P, and a single longitudinally adjacent cathode M.

The current flow is from the generator G to the anode P, and thence in the direction of the arrows through the electrolyte to and through each of the strips 12, and back through the electrolyte to the cathode M and thence to the generator G, some current passing directly from anode P to cathode M, as indicated by the arrows.

If it is desired to simultaneously pickle more than two strips in multiple, the same may be accomplished by merely increasing the width of the tank shown in Fig. 3 and providing longitudinally arranged electrodes between each pair of strips.

The electrode arrangement of Fig. 3 may be used in pickling a single strip, if the same is not too wide.

Although the working voltage can be varied between wide limits so as to regulate the speed of pickling without any damage or deleterious effect on the pickling action or material being pickled, it is usually desirable to hold the working voltage down as a matter of safety to the workman. Consequently, the apparatus may be arranged according to Figs. 4 and 5, in which there is a series of two or more pairs of anodes P longitudinally and alternately arranged with two or more pairs of cathodes M located in a tank 10, the strip 12 moving through the central portion of the tank between the opposite electrodes of each pair.

In the arrangement of Fig. 4, direct current flows from the positive side of generator G to each pair of anodes P, and from each pair of cathodes M to the negative side of the generator G. On opposite sides thereof current flows from each anode P through the electrolyte to the strip at a plurality of spaced places along the strip, through the strip, and then through the electrolyte to the adjacent cathode at a plurality of other places spaced apart along the strip and intermediate the first said places. This arrangement requires a working voltage of only about one-half of that used in the arrangement in Fig. 1, but the wattage and total current are about the same. Adjacent each pair of electrodes P and M the strip is cathodically and anodically treated, while at the intervening spaces the strip is exposed to the non-electrolytic pickling action of the electrolyte.

With a multiple arrangement of electrodes it may be desirable to have a separate source of current for each set of anodes and cathodes, as shown in Fig. 5. Here the tank 10 contains a series of five pairs of anodes P and five pairs of cathodes M alternately arranged in a longitudinal series, the strip 12 passing between laterally opposite electrodes through the longitudinal central portion of the tank.

In this arrangement, a generator G is provided for each series of one pair of anodes and one pair of longitudinally adjacent cathodes.

Obviously, a single row of longitudinally alternately arranged anodes and cathodes could be provided at one side of the strip instead of opposite sides as in Fig. 5.

In connection with all of the arrangements shown in the drawings, after the material has been pickled or treated, the same is preferably

mechanically or otherwise scrubbed and then washed and dried. In case the material being processed is strip material, the strips are usually inspected and then coiled after drying operation.

- 5 With the present improved method of electric pickling, any ferrous or non-ferrous metal, or any alloy, which is capable of conducting electricity may be completely pickled in a safe manner more rapidly than by any prior method, without requiring any mechanical treatment prior to the pickling operation for the purpose of cracking or loosening the scale.

Moreover, the improved method utilizes an electrolyte which may vary considerably in concentration and in operating temperature without affecting the pickling action, and which does not need frequent replenishing.

The improved method is equally applicable to the continuous electric pickling of one strip or of a plurality of strips simultaneously.

Obviously, the improved method may be applied to the pickling of separate units instead of a continuous strip, by providing suitable means for carrying the units past the electrodes without touching the same.

By using a caustic solution as the electrolyte, the improved method may be utilized for removing grease and oil from metals and alloys.

The present improved method of electric pickling may be made to accomplish pickling plus plating by making slight modifications in the improved apparatus. These modifications include reversing the direction of current flow, using a proper electrolyte, and using suitable electrodes.

For instance, if it is desired to copper plate stainless steel, copper anodes are preferably used, and the electrolyte may contain a solution of copper sulphate and sulphuric acid. The stainless steel to be plated is moved first past a cathode and then past an anode.

This system automatically pickles the material being plated before the plating action begins, so that little or no preparation of the material in the way of cleaning is required. Moreover, good distribution may be obtained with exceptionally low voltages.

The detailed description has had particular reference to the pickling or cleaning of cold rolled and annealed stainless steel, but it is of course understood that the same is equally applicable to pickling hot rolled stainless steel whether or not the same has been annealed prior to the pickling operation.

I claim:

1. The process of treating steel which includes the steps of passing cold rolled and annealed stainless steel, having an oxide film on the surfaces thereof, thru an electrolyte containing an acid, passing direct current thru said electrolyte to the steel at a plurality of spaced places along the steel, passing said current from said steel thru the electrolyte at a plurality of other places spaced apart along the steel and intermediate the first said places, and exposing the steel to the non-electrode pickling action of the acid in the electrolyte between said spaced places.

2. The process of treating steel which includes the steps of passing cold rolled and annealed stainless steel, having an oxide film on the surfaces thereof, thru an electrolyte containing a dilute acid, passing direct current thru said electrolyte and to the steel at a plurality of places on opposite sides of the steel, passing said current from said steel thru the electrolyte at a plurality of other places on opposite sides of the

steel spaced apart along the steel and intermediate the first said places, and exposing the steel to the non-electrode pickling action of the acid in the electrolyte between said spaced places.

3. The process of treating steel which includes the steps of cold rolling stainless steel thereby giving it a polished surface, annealing said steel in an oxidizing atmosphere thereby forming an oxide film on the polished surface thereof, and then removing said film without altering substantially the cold roll surface by subjecting the steel repeatedly to the anodic and cathodic actions of direct current in an electrolyte containing acid, repeatedly subjecting the steel to the non-electrode pickling action of the acid between said electrode treatments, mechanically scrubbing the steel, and washing and drying it, whereby, after such treatment, the steel possesses substantially the cold rolled finish it possessed after the cold rolling and before the annealing.

4. The process of treating steel which includes the steps of passing stainless steel, having an oxide film on the surface thereof, through an electrolyte containing an acid, passing direct current to and from the steel through the electrolyte at a plurality of alternately arranged spaced places along the steel, and exposing the steel to the non-electrode pickling action of the acid between said spaced places.

5. The process of treating steel which includes the steps of passing steel, having an oxide film on the surface thereof, through an electrolyte containing an acid, subjecting the steel to the cathodic action of a direct current at a plurality of places spaced along the steel, subjecting the steel to the anodic action of a direct current at a plurality of other places spaced along the steel between the first said places, and exposing the steel to non-electrode pickling action of the acid between said places where the steel is subjected to the anodic and cathodic action of the direct current.

6. The process of treating steel which includes the steps of passing stainless steel in thin elongated form and having an oxide film on the surfaces thereof, through an electrolyte containing an acid, subjecting opposed surfaces of the steel at a plurality of places spaced along the steel to the cathodic action of a direct current, simultaneously subjecting opposed surfaces of the steel at a plurality of other places spaced along the steel to the anodic action of a direct current, and simultaneously exposing the steel between the said places subjected to such cathodic and anodic action to non-electrode pickling action of the said electrolyte.

7. The process of treating steel which includes the steps of passing steel having an oxide coating on the surfaces thereof, through an electrolyte containing an acid, passing direct current through said electrolyte to an immersed place on the steel, then through the steel, and then from the steel through the electrolyte at another immersed place on the steel spaced from the first place so that only the steel immersed carries said current, simultaneously passing said current directly through the electrolyte adjacent to the space between said places, and exposing the steel to the non-electrode pickling action of the acid in the electrolyte at said space.

8. The method of electrically treating metal material in a single bath of electrolyte into which spaced electrodes of opposite polarity extend, which includes immersing the material in and subjecting it to the action of the electrolyte,

moving the material while immersed successively past, but not in contact with an electrode of one polarity and then past, but not in contact with an electrode of opposite polarity; and at the same time passing direct current from an electrode of one polarity through the electrolyte to portions of the immersed material, then through the immersed material, and thence from other portions of the immersed material spaced from said first portions through the electrolyte to an electrode of opposite polarity so that only the material immersed carries current, and simultaneously passing said current directly between said electrodes through the electrolyte between said spaced portions without entering the material.

9. The method of continuously electrically treating strip metal and the like in a single bath of electrolyte into which spaced electrodes of opposite polarity extend, which includes immersing a portion of a strip in and subjecting said portion to the action of the electrolyte, longitudinally moving the strip so that any moving portion of the strip while immersed successively passes, but does not contact an electrode of one polarity and then an electrode of opposite polarity; and at the same time passing direct current from an electrode of one polarity through the electrolyte to a part of the immersed moving strip portion, then through the immersed moving strip portion, and thence from another part of the immersed moving strip portion spaced from said first part through the electrolyte to an electrode of opposite polarity so that only the immersed portion of the strip carries current, and simultaneously passing said current directly between said electrodes through the electrolyte between said spaced parts without entering the strip.

10. The method of continuously electrically pickling stainless strip steel having an oxide coating thereon in a single bath of acid electrolyte into which spaced electrodes of opposite polarity extend, which includes immersing a portion of a stainless steel strip in and subjecting it to the action of the acid electrolyte, longitudinally moving the strip so that any moving portion of the strip while immersed successively passes, but does not contact an electrode of one polarity and then an electrode of opposite polarity; and at the same time passing direct current from an electrode of one polarity through the electrolyte to a part of the immersed moving strip portion, then through the immersed moving strip portion, and thence from another part of the immersed moving strip portion spaced from said first part through the electrolyte to an electrode of opposite polarity to pickle the strip so that only the immersed portion of the strip carries current, and simultaneously passing said current directly between said electrodes through the electrolyte between said spaced parts without entering the strip.

11. The method of continuously electrically pickling stainless strip steel having an oxide coating thereon, which includes immersing a portion of a stainless steel strip in and subjecting said portion to the action of a single bath of a nitric acid solution electrolyte into which spaced stainless steel electrodes of opposite polarity extend; longitudinally moving the strip so that any moving portion of the strip while immersed successively passes, but does not contact an electrode of one polarity and then an electrode of opposite polarity; and at the same time passing direct

current from an electrode of one polarity through the electrolyte to a part of the immersed moving strip portion, then through the immersed moving strip portion, and thence from another part of the immersed moving strip portion spaced from said first part through the electrolyte to an electrode of opposite polarity to pickle the strip so that only the immersed portion of the strip carries current, and simultaneously passing said current directly between said electrodes through the electrolyte between said spaced parts without entering the strip.

12. The process of treating steel which includes the steps of passing an annealed stainless steel strip having an oxide coating on the finished surfaces thereof, continuously through and subjecting it to the action of an electrolyte containing an acid, in which electrolyte electrodes of opposite polarity are located out of contact with said strip, passing direct current to and from the electrodes and the strip through the electrolyte at spaced immersed places along the strip, and simultaneously passing said current directly between the electrodes through the electrolyte at said spaces, whereby after such treatment the strip possesses substantially the surface finish it possessed before annealing.

13. The method of electrically treating metal material in a single bath of electrolyte into which a plurality of spaced electrodes of opposite polarity extend, which includes immersing the material in and subjecting it to the action of the electrolyte, moving the material while immersed successively past, but not in contact with an electrode of one polarity and then past, but not in contact with an electrode of opposite polarity; and at the same time passing direct current from the electrodes of one polarity at spaced places through the electrolyte to the immersed material, then through the immersed material, and thence from the immersed material at other spaced places through the electrolyte to the electrodes of opposite polarity so that only the material immersed carries current, and simultaneously passing said current directly between electrodes of opposite polarity through the electrolyte without entering the material.

14. The method of continuously electrically treating strip metal and the like in a single bath of electrolyte into which a plurality of spaced electrodes of opposite polarity extend, which includes immersing a portion of the strip in and subjecting it to the action of the electrolyte, longitudinally moving the strip so that any moving portion of the strip while immersed successively passes, but does not contact an electrode of one polarity and then an electrode of opposite polarity; and at the same time passing direct current from the electrodes of one polarity at spaced places through the electrolyte to the immersed moving strip portion, then through the immersed moving strip portion, and thence from the immersed moving strip portion at other spaced places through the electrolyte to the electrodes of opposite polarity so that only the immersed portion of the strip carries current, and simultaneously passing said current directly between electrodes of opposite polarity through the electrolyte without entering the strip.

15. The method of electrically pickling stainless strip steel having an oxide coating thereon in a single bath of acid electrolyte into which a plurality of spaced electrodes of opposite polarity extend, which includes immersing a por-

tion of a stainless steel strip in and subjecting it to the action of the acid electrolyte, longitudinally moving the strip so that any moving portion of the strip while immersed successively

5 passes, but does not contact an electrode of one polarity and then an electrode of opposite polarity; and at the same time passing direct current from the electrodes of one polarity at spaced places through the electrolyte to the immersed moving strip portion, then through the immersed moving strip portion, and thence from the immersed moving strip portion at other spaced places through the electrolyte to the electrodes of opposite polarity so that only the immersed portion of the strip carries current, and simultaneously passing said current directly between electrodes of opposite polarity through the electrolyte without entering the strip, to pickle the strip and remove the oxide coating therefrom.

20 16. The method of continuously electrically pickling stainless strip steel having an oxide coating thereon, which includes immersing a portion of a stainless steel strip in and subjecting it to the action of a single bath of a nitric acid solution, electrolyte into which a plurality of spaced electrodes of opposite polarity extend; longitudinally moving the strip so that any moving portion of the strip while immersed successively passes, but does not contact an electrode of one polarity and then an electrode of opposite polarity; and at the same time passing direct current from the electrodes of one polarity at spaced places through the electrolyte to the immersed moving strip portion, then through the immersed moving strip portion and thence from the immersed moving strip portion at other spaced places through the electrolyte to the electrodes of opposite polarity so that only the immersed portion of the strip carries current, and simultaneously passing said current directly between electrodes of opposite polarity through the electrolyte without entering the material to pickle the same and remove the oxide coating therefrom.

45 17. The method of electrically treating metal material in a single bath of electrolyte into which a plurality of spaced electrodes of opposite polarity extend, which includes immersing the material in and subjecting it to the action of the electrolyte, moving the material while immersed past, but not in contact with said electrodes; and at the same time passing direct current from the electrodes of one polarity at spaced places through the electrolyte to the immersed material, then through the immersed material, and thence from the immersed material at other spaced places through the electrolyte to the electrodes of opposite polarity so that only the material immersed carries current, and simultaneously passing said current directly between electrodes of opposite polarity through the electrolyte without entering the material.

18. The process of treating steel which includes the steps of passing annealed stainless steel, having an oxidized surface, through and subjecting it to the action of an electrolyte containing between about 2% and about 20% of acid, passing direct current of a low voltage up to about 50 volts at a low amperage up to about 600 amperes through the electrolyte to the said oxidized surface of the steel from a plurality of anodes spaced along the path of travel of the steel, conducting current from the oxidized surface of said steel through the electrolyte to a plurality of cathodes arranged between but

spaced apart from said anodes along said path of travel, and thereafter removing particles of foreign material from the said surface of said steel, whereby the thus treated steel possesses substantially the same surface it possessed in unannealed state.

19. The process of treating stainless steel which includes the steps of passing stainless steel having an oxide coating on the surfaces thereof through and subjecting it to the action of an electrolyte into which vertically arranged longitudinally spaced electrodes of opposite polarity extend out of contact with said steel, passing direct current to and from the electrodes and the steel through the electrolyte at alternately arranged spaced places along the steel, and simultaneously passing said current directly between longitudinally adjacent electrodes through the electrolyte between said spaced places without entering the steel.

20. The process of treating stainless steel which includes the steps of passing stainless strip steel having an oxide coating on the surfaces thereof through and subjecting it to the action of an electrolyte into which spaced electrodes of opposite polarity extend out of contact with said strip by permitting the strip to sag into and become immersed in the electrolyte, passing direct current to and from the electrodes and the immersed sagging portion of the strip through the electrolyte at alternately arranged spaced places along the strip, and simultaneously passing said current directly between said electrodes through the electrolyte between said spaced places without entering the strip.

21. The process of treating stainless steel which includes the steps of passing stainless strip steel having an oxide coating on the surfaces thereof through and subjecting it to the action of an electrolyte into which vertically arranged longitudinally spaced electrodes of opposite polarity extend out of contact with said strip by permitting the strip to sag into and become immersed in the electrolyte, passing direct current to and from the electrodes and the immersed sagging portion of the strip through the electrolyte at alternately arranged spaced places along the strip, and simultaneously passing said current directly between said electrodes through the electrolyte between said spaced places without entering the strip.

22. The process of treating stainless steel which includes the steps of passing stainless strip steel having an oxide coating on the surfaces thereof through and subjecting it to the action of an electrolyte into which spaced pairs of electrodes extend, said pairs of electrodes being successively arranged with opposite electrodes of each pair having the same polarity and successive electrodes having opposite polarity, maintaining the strip in the electrolyte between, but out of contact with the electrodes of each pair, passing direct current to and from the steel through the electrolyte from said electrodes at alternately successively arranged spaced places along the strip, and simultaneously passing said current directly between adjacent successive electrodes through the electrolyte between said spaced places without entering the strip.

23. The method of electrically treating strip metal having an oxide coating thereon in a single bath of electrolyte, which includes immersing a strip in and moving it through the electrolyte into which electrodes of opposite polarity extend out of contact with said strip at places

spaced from each other and from the strip, passing direct current to and from the electrolyte and said electrodes, and at the same time subjecting the immersed moving portion of the strip to the action of the electrolyte, whereby the strip acts as a bipolar-electrode and the oxide

coating is removed therefrom without passing current through any unimmersed portion of the strip and without contacting the strip with any of said electrodes.

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