Jan. 7, 1969 B. J. FREEDMAN ET AL **3,420,760**

PROCESS FOR DESCALING STEEL STRIP IN AN AQUEOUS ORGANIC CHELATING BATH USING ALTERNATING CURRENT

Filed April 30, 1965 Sheet 1 of 2

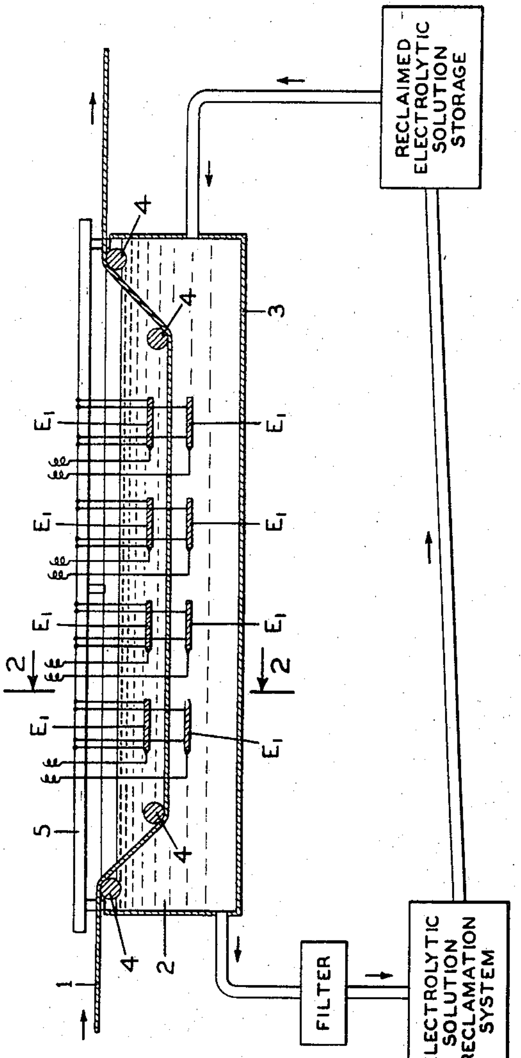

FIG.1.

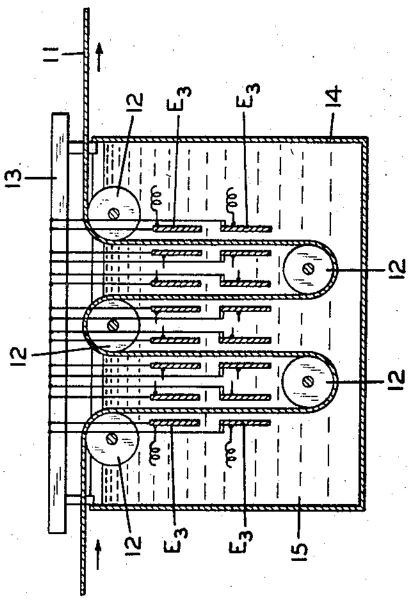

FIG.4.

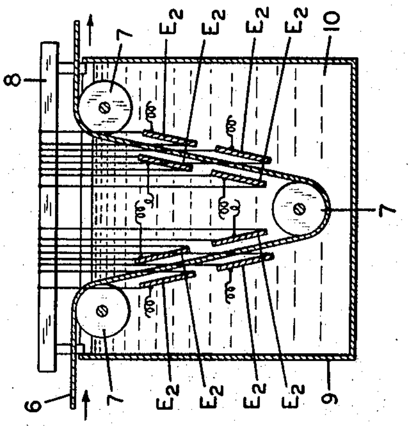

FIG.3.

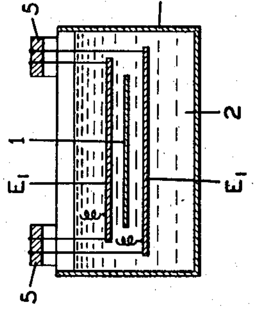

FIG.2.

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Filed April 30, 1965 Sheet 2 of 2

FIG. 5.

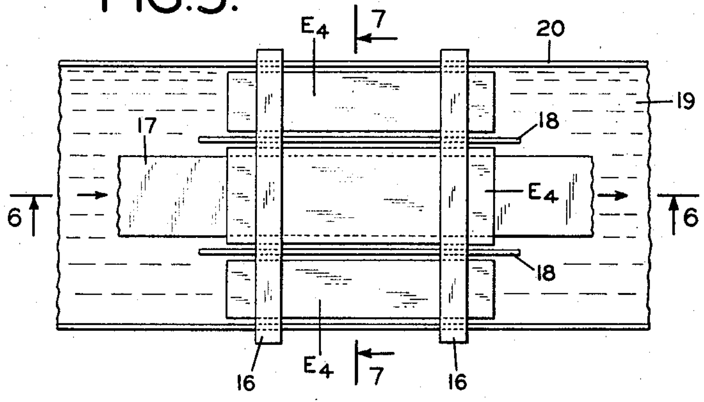


FIG. 6.

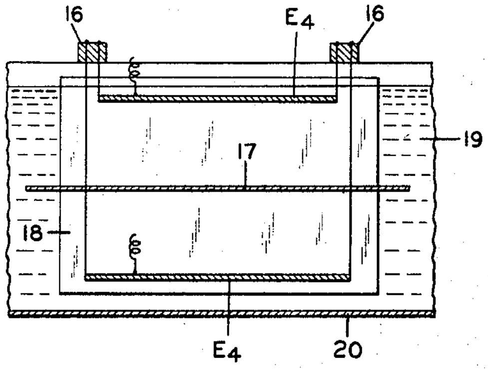


FIG. 7.

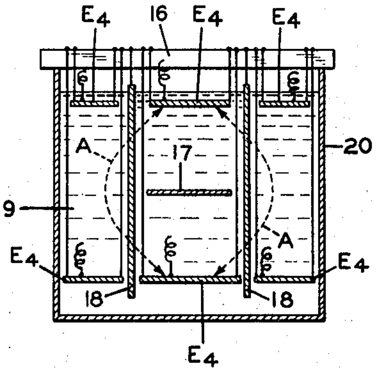


FIG. 8.

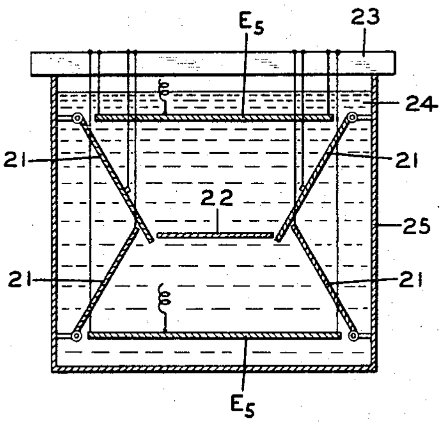
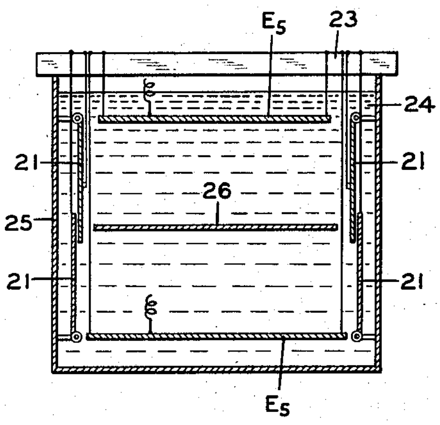


FIG. 9.



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3,420,760

PROCESS FOR DESCALING STEEL STRIP IN AN AQUEOUS ORGANIC CHELATING BATH USING ALTERNATING CURRENT

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U.S. Cl. 204—145 **16 Claims**
Int. Cl. C23b *1/00*

ABSTRACT OF THE DISCLOSURE

A process for electrolytically removing scale from a metal article. In the process, the article is immersed in an electrolyte and contacted with an alternating current, the object to be descaled being free of any electrical connections. The electrolyte used in the process is an aqueous solution of a salt of a chelating acid and an alkali metal hydroxide or a nitrogen base. The electrolyte should have a pH of about 3 to 7 when a nitrogen base is used and a pH of about 3 to 6 when an alkali metal hydroxide is used.

The present invention relates to the treatment of metal surfaces. More particularly, the present invention relates to a new and improved process for removing mill scale, referred to hereafter as scale, formed on ferrous materials in the course of high temperature operations such as strip rolling, sheet rolling, welding, annealing, finishing, normalizing, forging, stamping and the like.

The process of the present invention is applicable not only to the treatment of stationary objects but also to the treatment of continuously moving objects such as, for example, steel strip processed in a hot strip mill, in galvanizing or tinning lines or in other types of plating lines, and to semi-stationary individual objects such as plates, castings, extrusions, forgings and machined parts. The process is especially geared toward the steel industry and is particularly applicable for removing scale as heavy rolled-in scale from low carbon steel and low alloy steels and is particularly commercially acceptable for descaling metallic sheets or strips which in the steel industry usually have a maximum thickness of about one-quarter inch.

Steel and the like are commonly made in electric, basic oxygen and open hearth furnaces, with subsequent casting into ingots, blooms and billets followed by hot and cold working operations to produce plates, sheets, strips, bars, rods, wires, tubes, etc.

It is well known that when a ferrous metal is heated and exposed to the atmosphere and certain furnace gases, the surface of the metal becomes oxidized and the metal is thus coated with a scale consisting primarily of compounds of iron and oxygen, e.g. FeO, Fe_2O_3 and Fe_3O_4, which scale is frequently firmly adherent and extremely difficult to remove. This scale usually must be removed to obtain a desired quality of product and for proper performance of subsequent operations such as efficient welding, cold rolling, forming, coating and the like. It is impracticable, for example, to cold-draw or cold-roll a surface having scale thereon, since such procedure results in inclusions of scale in the finished product and hence a product of poor quality. The absence of scale, too, improves the corrosive-resisting qualities of the base metal, enables one to work with a base metal of exact dimensions, allows for inspection of the base metal for surface defects and affords the production of a base metal surface of pleasing appearance. Also in the steel industry it is highly desirable to form a coating on the base metal. This prevents exposure of the base metal to destruction

by corrosion and at times enhances the appearance and properties of the base metal. However for an efficient application of a coating, such as zinc, tin, lead, copper, etc. by means of electroplating or galvanizing and the like, or of enamel, paint, lacquer, etc. the removal of scale is necessary. Otherwise, scale can prevent the obtainment of coatings that are firmly adherent to a steel surface.

Aside from affecting the properties of the base metal itself, scale also has an injurious action on tools employed. For example, when an attempt is made to work the metals as by cutting, machining or grinding the involved metals, a scale surface produces undue burning and wear of the work tools thus shortening their life.

In the past the removal of scale has been accomplished by natural exposure; by mechanical methods; by chemical methods and by electrolytic methods. These methods involve a physical and/or chemical destruction of the bond between the scale and the surface of the base metal.

In the natural exposure method the objects to be descaled are exposed to corrosive atmospheric agents which provide for penetration, through the pores of the scale, of oxygen from the air and atmospheric humidity. These agents attack the steel underlying the scale and form a coating of rust. The rust then exerts a pressure on the scale which can be so great that the scale is mechanically detached. Removal of the scale by natural exposure of the object, generally requires an extremely long duration for an effective descaling and further involves a useless destruction of the metal.

Mechanical methods for descaling metals include a sand or shot blasting of the object to be descaled or a brushing, grinding or milling using an abrasive means. Scratches on the base metal surface can however result. Also, because of the human element involved, effects of texture on the surface of the base metal are not always uniform. Difficulties are further encountered in reaching recesses, corners, etc. of the objects to be so treated.

Chemical methods for descaling metals generally involve immersing the articles to be descaled in a bath containing an agent which causes the scale to dissolve in the bath itself or in a subsequent washing. In the practice of this method commonly known as "pickling," a dilute solution of a suitable acid, for example, phosphoric, sulphuric or muriatic acid is commonly employed as the pickling agent, although other baths such as an activated fused caustic alkali bath have been used.

The use of an acid results not only in the formation of a water soluble compound, e.g. soluble iron chlorides or sulphates, but also causes a portion of the scale to be dislodged mechanically from the surface. Such is brought about apparently through the mechanical action of the acid penetrating through the scale followed by the buildup of a certain pressure under the scale through the formation of hydrogen caused by the reaction of the acid on the base metal.

Although immersion in an acid such as sulphuric acid is a cheap method because of the relative low cost of the acids the scale removal tends to be slow thus requiring a large residence time in the acid of the objects to be descaled. Moreover, acid baths as hydrochloric or sulphuric acid baths because of the strong corrosive attack on the base metal in contrast to a slight etching of the base metal, leads to a roughened base metal surface with severe pitting, which may necessitate machining to produce an attractive, salable product. Naturally this can cause a considerable waste of base metal. This phenomenon is particularly noticeable when descaling steel strip in a continuous operation. The operation of continuous steel strip lines is performed at specific travel speeds with predetermined exposure time in the acid tanks. Stoppages are frequent for gauging, checking, inspection, adjustment, repair of equipment and other reasons. During such stoppage, when the strip is permitted to remain stationary in the acid bath severe pitting, discoloration and possibly complete dissolution of the base metal results. Similar pitting occurs when descaling steel containing heavy rolled-in scale which requires additional exposure in acid baths for removal of the scale.

Invariably, too, in conventional immersion methods the resultant metallic surfaces are covered with a black deposit of smut due to a disintegration of the surface. The smut adheres tightly to the surface of the metal and must be mechanically removed by scrubbing subsequent to any further treatment of the metal.

The roughened surface resulting from acid attack is further not conducive for subsequent coating operations or for resisting the formation of rust on the metal during storage and handling prior to such coating operations. In an attempt to prevent corrosive attack, inhibitors have been included in the baths but the necessary inclusion of inhibitors has proven costly and not entirely satisfactory.

Aside from the above disadvantages in acid immersion methods, waste or spent acid pickling baths of the type commonly used in the past normally cannot be discharged into sewage lines as such because of their high acidity. Thus it is necessary to include steps of neutralizing the free acid or recovering the free acid such as sulphuric acid as a sulphate. A normal practice required by most municipalities in which acid pickling solutions will be disposed necessitates a complete neutralization of the acid bath with caustic soda, after which the neutralized solution is passed to deep wells. From a standpoint of economics, the cost of neutralizing the spent acid descaling solution equals the cost of the acid alone. Too, such a neutralization step is not confined to the waste acid bath but must be performed on the metal itself subsequent to the pickling to remove the last trace of the acid.

Other problems incident to conventional acid pickling reside in the fact that obnoxious and highly irritating vapors having a deleterious effect on the health of the workmen are usually liberated from the bath. Also in view of the danger of acid burns to personnel during the normal operation, any leaks in the conventional and pickling baths can be disastrous to the personnel. Furthermore, mineral acid solutions tend to corrode the tanks, liners and associated equipment with which it comes into contact, thereby resulting in excessive maintenance. As a result, there is a considerable amount of replacement of equipment necessary in any acid descaling operation every year.

In the use of a fused caustic alkali in the bath it is generally necessary for any efficient operation to activate the bath with sodium hydride or a similar agent for reducing the iron oxides (scale) on the surface of the metal to a metallic state. With such a bath excessive removal of metal and uneconomical corrosive destruction of containers used to hold the bath are encountered. Moreover, the use of sodium hydride is not without an explosion hazard.

A modification of the immersion method is to coat the object to be descaled with a descaling solution. This can be done by applying a layer of the descaling solution by brushing, spraying, etc. Such modifications have not proved satisfactory from the aspects of time and equipment and further, are coupled with the disadvantages found in the immersion method.

Electrolytic methods for descaling metals have constituted in general passing the metal to be descaled through an electrolyte, such as a pickling solution used in the chemical immersion method, through which an electric current passes, the metal to be descaled being placed in the vicinity of one or more electrodes and/or being treated itself an an anode or the cathode. The electric current materially aids the descaling action and thus, under certain conditions, allows for descaling in a much shorter period of time than that normally required in the chemical immersion and coating methods. Moreover, as compared with conventional immersion descalings, electrolytic descaling has on certain steels proved more efficient. For example, said immersion descaling of certain steels has been attended by the drawback that even when the scale is rotted, thereby placing it in condition for removal, it is only by subsequent slow and tedious manual washing or scrubbing that the scale can be finally removed. This is due in part to the fact that when steel is hot-rolled the scale formed in the hot rolled operation is highly insoluble and extremely tenacious and adherent and thus difficult to remove by the acid immersion process.

Prior electrolytic methods for descaling metals are not, however, without disadvantages. When the conventional acid solutions employed in the chemical immersion method are used as the electrolyte, a severe attack upon the base metal almost invariably results. Moreover, disadvantages inherent in the use of an acid bath in the immersion method exist here. Noxious and toxic gases form and there is a rapid deterioration of the electrolytes. Solutions of weak acids made alkaline by the addition of excess base have been used but have not removed adequately the contaminating scale and further have been found to function slowly, requiring a long residence time. This is highly undesirable since it results in a very low production rate and is completely unacceptable in a continuous metal strip operation.

A conventional electrolyte bath is one formed by the fusion of a salt of an alkaline metal or a fused alkali. This bath requires a subsequent passing of the metal through a bath of hot water. In the hot water bath the film of alkaline metal on the base metal surface formed in the first bath reacts with such violence with the water as to remove scale from the metal surface. The use of such baths, however, has proven time consuming and also presents health hazards. Furthermore, the commercially available alkali metal hydroxide based salt baths for electrolytic cleaning of metals have operated unsatisfactorily after extended idling periods and the metal objects which result from the use of these baths after such shutdowns, have a dark gray or brown color and have an unattractive appearance. A further difficulty encountered with various molten alkali and/or salt electrolytic baths is that they require substantially high temperatures of about 950° F. for their operation and also leave a scum upon the work pieces which must be removed by brushing or other treatment. Moreover, when utilizing molten caustic baths, difficulties are encountered with the formation of excessive amounts of insoluble material in the bath which tends to settle out and form a sludge on the bottom of the bath container. Furthermore, excessive corrosion of metal parts in contact with the bath and deterioration of the container are encountered.

It is, therefore, a principal object of the present invention, in the elimination of the foregoing and related disadvantages, to provide a novel process for effectively and rapidly descaling metal surfaces.

Yet another object of the present invention is to provide a new process for electrolytically removing oxide scale from metal stock containing same.

A further object of the present invention is the provision of a new process for electrolytically descaling the surface of ferrous metal.

Still another object of the present invention is the provision of a novel process for electrolytically descaling the surfaces of iron and steel articles safely and effectively.

A further object of the present invention is to provide a new process for descaling metal surfaces with a single solution which will accomplish a removal of oxide material therefrom.

A further object of the present invention is the provision of a novel process for electrolytically descaling the surface of strip steel and the like on a continuous operation basis.

Another object of the present invention is to provide an electrolytic descaling system which eliminates the disadvantages of prior art electrolytic systems but yet provides for an efficient and rapid descaling of metals.

Yet another object of the present invention is the provision of a novel process for electrolytically descaling the surface of metal stock that will present no health or safety problem to personnel under all conditions.

A further object of the present invention is the provision of a novel process for electrolytically descaling metal articles which will place the surface of the metal stock in condition for receiving a surface coating thereon.

Yet another object of the present invention is the provision of a new process for electrolytically descaling the surfaces of metal articles which will permit the metal surfaces to be subsequently coated or otherwise treated thereafter without any neutralizing being required.

A further object of the present invention is the provision of a novel process for electrolytically descaling metal surfaces in which there will be a minimum of equipment replacement required due to the descaling solutions employed.

Still another object of the present invention is the provision of a new process for electrolytically descaling metal surfaces in which the cleaning solution employed therein may be effectively disposed of without expensive neutralization.

A further object of the present invention is the provision of an electrolytic descaling system in which heavy rolled-in scale can be removed safely without base metal attack.

Still another object of the present invention is the provision of an electrolytic descaling system that permits a shorter contact time for the work in the electrolytic bath thereby providing an increased production rate.

Yet another object of the present invention is the provision of an electrolytic descaling system that does not necessitate a mechanical pre-treatment to effect a breaking or loosening of the scale.

A further object of the present invention is the provision of an electrolytic descaling system for removing mill scale from ferrous materials that allows for a minimum electrolytic exposure time of the electrolyte, a low depletion rate, i.e., a high surface area of a metal such as steel descaled at a rapid rate before solution depletion, a high electrical conductivity, and a minimum electric power requirement, i.e. the voltage required to attain any desired current density.

Another object of the present invention is the provision of an electrolytic descaling system that allows for a minimum amount of insolubles being formed. This consideration is important in view of the sludge interference in descaling tanks in the past.

An additional object of the present invention is the provision of an electrolytic descaling system which allows for a practical and economical reclamation system.

Another object of the present invention is the provision of an electrolytic descaling system that eliminates the need of conduction rolls or similar devices with their attendant problems but yet allows for efficient electrical contact.

A further object of the present invention is to insure that the electrical potential of the workpiece to the ground is zero, thereby eliminating a possible safety hazard in areas of the strip external to the descaling tanks.

Yet another object of the present invention is to condition the surface of ferrous metals prior to a tinning or galvanizing operation.

Another object of the present invention is to provide a novel process for the even descaling of hot rolled steel strip. Hot rolled steel strip generally has an "edge ripple" which occurs when the edges of the strip are reduced more than its center or a "center buckle" which occurs when the center of the strip is reduced more than its edges.

A further object of the present invention is to provide a novel process for descaling hot rolled steel strip in the absence of any substantial burning damage to the strip caused by electrical arcing.

Other and additional objects will become manifest from the ensuing description and examples taken in conjunction with the accompanying drawings:

According to the present invention the foregoing objectives are accomplished by immersing the object to be descaled, preferably an object of whole or part of a ferrous metal with an aqueous electrolytic solution of a salt of a nitrogen base or an alkali metal hydroxide with an organic acid, the organic acid being such that a molecule of the acid can bind metal ions simultaneously through two or more positions so that multiple rings can be formed, or in other words can react with metal ions to form soluble complexes, such acids conventionally known as chelating agents and conducting current to the object to be descaled. The electrolytic salt solutions should have a pH of about 3 to 7 when a salt forming nitrogen base is used or a pH of about 3 to 6 when a salt forming alkali hydroxide is used. A preferred pH when a salt forming nitrogen base is used is 5 while a preferred pH when a salt forming alkali hydroxide is employed is 4. It is important in the process of the invention that the object to be descaled be free of any electrical connections during the process or in other words that said process comprise "indirectly contacting" the object to be descaled with a current via the electrolyte, i.e. an "Indirect-Electrolytic" process as opposed to any "Direct-Electrolytic" process wherein the object to be descaled is directly connected to an electrical connection and as such acts as an electrode.

The indirect electrolytic contact of the metal in association with the specific electrolytic solution set forth above with or without the inclusion as desired of other components such as nonionic surfactants, ionic surfactants, corrosion inhibitors, strong electrolytic ionic inorganic salts and the like, as desired, result in an efficient and economic descaling process.

Suitable organic acids include gluconic acid, tartaric acid, diglycolic acid and especially glycolic acid and citric acid. Citric acid is particularly preferred.

The term "nitrogen bases" as used in the specification is intended to include amines which give an alkaline reaction in aqueous solution and form salts with acids. Examples of nitrogen bases are ammonium hydroxide, alkanol amines such as ethanol amine and triethanol amine and alkyl amines such as ethylamines and triethylamine. Ammonium hydroxide is particularly effective. Salts of nitrogen bases, as compared with the use of other salt forming bases, require a minimum amount of electric power. In other words, the voltage can be at a minimum and yet a high current density can be had. Thus electric power costs are at a minimum.

Particularly effective alkali metal hydroxides are sodium hydroxide and potassium hydroxide. Alkali metal hydroxides allow shipments of the electrolyte in solid form, i.e. the solid salt, and thus makes for easy handling.

Perhaps a single most important economic advantage is that with the use of either type of salt, i.e. the salt of a nitrogen base or an alkali hydroxide, the electrolytes from the descaling process according to the present invention can be economically and conveniently reclaimed and used again in the process. Copending application Ser. No. 458,194 filed May 24, 1965 by J. A. Marriott, A. W. Petrocelli, A. Capotosto and J. F. Turco and assigned to the same assignee as the instant application describes a novel process for reclaiming the electrolytes.

The concentration of the acid component in the electrolytic solution should be about 5 to about 50 percent with a preferred percentage of about 25 to about 35 percent, the percent expressed in grams of acid component per liter of solution or in any other units corresponding to the same ratio. A 28 percent acid component when citric acid is used has been found to be especially suitable. Such a solution can be prepared by dissolving 280 grams of citric acid in water and adjusting the volume of the solution to one liter with a simultaneous adjustment of the pH to a desired value by the appropriate addition of base.

The pH of the electrolytic solution and the concentration of the acid component in the electrolytic solution are essential for the process of the present invention. Important properties of the descaling solutions which dictate the selection of usable and preferred pH's are the amount of insoluble sludge formed during descaling, (a minimum amount with the ranges of the present invention) a good descaling ability (a minimum of exposure time of the article in the electrolyte required for efficient descaling) a good electrical conductivity of the electrolyte and a long life of the electrolyte before depletion of its activity. Electrolytes having a pH outside the stated range, but yet identical in all other aspects have been found to be inferior for the process of the present invention. For example, two liters of a basic aqueous sodium citrate within the stated range of acid component, according to the process of the present invention, will descale 2 square feet of steel in an average time of five minutes. On the other hand, when the pH of that solution is 4, 35 square feet of steel is descaled in an average time of thirty seconds, in both cases the current being at constant current density. On the other hand, the electrical conductivity of an aqueous 28 percent potassium citrate solution with a pH of 2 at 212° F. is 30,000 micromho-cm. While the electrical conductivity of an aqueous 28 percent potassium citrate solution with a pH of 3 at 212° F. is 10,000 micromho-cm. Thus the voltage required to attain the same current density with a pH of 2 is 3.5 times as great as with a pH of 3. This increase in voltage corresponds to a 3.5 times increase in electrical power requirements and costs and results in a required operational voltage which constitutes a safety hazard, i.e. approximately 100 volts or greater.

Significant properties of the electrolytes which dictate the selection of usable and preferred electrolytic solution concentrations are the high electrical conductivity, the long life of the electrolyte before its depletion and the minimum amount of insolubles formed in the descaling process. With good electrical conductivity, electrical power requirements is minimized (i.e. the voltage required to attain any desired current density is a minimum). To illustrate an ammonium citrate solution of pH 6.0 at 205° F. will have a conductivity of 210,000 micromho-cm. at about 55 percent acid concentration. On the other hand, the same ammonium citrate solution with a pH of 6 but having an acid concentration of 28 percent has a conductivity of 32,000 micromho-cm.

Variations in the indirect-electrolytic method are within the scope of the present invention. Thus in what is termed a "perpendicular" setup, the current flow is between working electrodes located on opposite surfaces of the metal object being descaled while in what is called a "parallel" setup the current flow is between working electrodes located on the same side of the metal object.

The potential impressed on the electrodes may be either direct current or alternating current although the use of alternating current contributes certain distinct advantages over the use of direct current. Thus, for example, while the use of direct current has been found to have a serious detrimental effect on the life of the electrolyte used herein, the use of alternating current in comparison has no such effect. Good descaling has been obtained by using at least one pair of spaced electrodes connected to opposite sides of an A.C. source and by simply placing the object to be descaled in the path at a point substantially midway between the electrodes, free of any electrical connections. It is advisable in the parallel indirect and perpendicular indirect systems, when using direct current, to have an equal number of sets of anode (+) plus cathode (−) with alternate sets reversed in orientation with respect to the particular metal surface to be descaled, the reason being that most of the descaling occurs on the surface of the strip which is beneath or above the anodes. In the perpendicular indirect system providing equal anode area on both surfaces of the strip will allow equal descaling on the top and bottom surfaces although when using alternating current there is no need for reversed orientation of electrodes since with alternating current descaling is equivalent under both electrodes, cathode and anode, in each set.

The flexibility and efficiency of the electrolytic line can be increased by using segmented electrodes. In this arrangement, electrode segments will allow metallic strips of various widths to be processed at proportionately equivalent power consumption. For example, one segment of the electrode (anode plus cathode) would be adequate for descaling a metal strip having a width equal to that segment. On the other hand, more than one segment of electrode will allow adequate descaling of a metal strip having a width corresponding to the total width of the electrode segments taken with the intervals between said segments. Thus a center electrode segment could be used to descale a strip of metal of a width corresponding to the center metal segment. On the other hand, three electrode segments alongside of each other could be used with a strip of metal having a width running from the beginning of the width of the first segment to the end of the width of the third segment.

In order for maximum benefits to be derived from the segmented electrode concept, an insulated baffle system is advisably used to minimize stray currents. Otherwise in descaling a metallic strip having a width corresponding to only a center electrode segment of a three electrode segment system, considerable electric current will be wasted if not substantially all the current is channeled through the metallic strip. To allow for such channeling, baffles of a suitable material, e.g. rubber-covered steel and reinforced fiberglass, are inserted between the center electrode segment set and sets of outer electrode segments. Alternatively, the baffles are arranged to pivot inward from the edges of the bath to approximately meet the strip to be descaled, thus preventing a current flow to any great extent around the edges of metallic strip. In the segmental arrangements current density on the strip surface could be held constant for varying strip width by adjusting the total current flow between electrodes, i.e. total current flow would be sensitive to and proportioned to strip width.

The electrolytic descaling process can be performed with the plane of the metallic object and the electrodes in a horizontal, vertical or inclined position. Equipment for the electrolytic descaling process can include a tank for containing the electrolyte, immersion electric heaters or otherwise for the electrolytic solution, heat exchangers to collect heat generated during the process, electrodes and a low-voltage electric power source. The electrodes may be made of any suitable electrically conducting material, such as, for example, mild steel, carbon, titanium, etc., and may be of a solid or perforated sheet or rod type. Perforated sheet is preferred to solid sheet electrodes, since the perforations will allow a better solution circulation. An electrically insulating coating such as epoxy resinous or a fiberglass coating on the back surface of the electrodes is also advantageous since it minimizes stray paths of electric current. It is further desirable to maximize the electrode surface area per given area of object or strip to be descaled since a maximum electrode surface area minimizes the current density on the electrode surface. This reduces both the electrode erosion and the gas evolution on the electrode, the latter being a function of the current density. A reduction of the gas evolution will also reduce the amount of gas-caused foam in the descaling tank.

The tank for the electrolyte is of basically conventional design and material, e.g. rubber covered steel, reinforced fiberglass and the like. The dimensions of the tank should be sufficient to easily and adequately accommodate the object to be descaled and a plurality of tanks for the electrolytic bath can be used in the electrolytic process. In general, the width of the tank baths and electrodes can be as great as necessary to accommodate various widths of metal objects to be descaled and the depth of any tank is that necessary to immerse the electrodes and the object to be descaled regardless of whether a continuous or intermittent operation is to be performed. With a continuous moving strip of metal to be descaled the length of the tank or number of tanks employed and the lengths of the electrodes in the tank or tanks are governed primarily by and are proportional to the linear speed of the strip as its passes through the bath.

A filtering system may be included in the equipment for the process, a magnetic filter separator being particularly desirable. With a filter system, any undissolved scale that has not yet reacted with the electrolyte but has come off of the surface of the metal can be readily removed.

Current density employed in the process according to the present invention can vary from approximately 100 to 1300 amps per square foot with a normal operational density of 300 amps per square foot. The electrolytic exposure time is inversely proportional to the current density. For example, when an aqueous solution of ammonium hydroxide and 28 percent citric acid at a pH of 6 is employed for descaling a strip mild steel sheet, according to the present invention, the following was had:

Current density amps/ft.^{2}:	Electrolytic exposure time (sec.)
390	30
590	20
1000	13
1300	9

Convenient operating temperature for the electrolytic solution is normally between 200° F. and the boiling point of the electrolytic solution which is about 215° F.

Electrolytic exposure time according to the process of the present invention will vary from a few seconds to sixty seconds, a suitable operational exposure time for removal of scale being about 15–30 seconds. It has been found, when maintaining a fixed current density, that the voltage and electrolytic exposure time are inversely proportional to solution temperature of the electrolytic bath. Thus when descaling a sheet of mild steel with an aqueous electrolytic solution of 28 percent ammonium citrate with a pH of 6 and maintaining a current density of 1300 amps per square foot these results were had:

Solution temperature, °F.	Volts	Electrolytic exposure time (sec.)
125	14	25
135	13	23
145	11.8	20
155	11.8	18
165	10.8	15
175	10.2	13
185	10.0	12
195	9.9	12
205	9.6	9

In the process of the invention the distance between any immersed electrodes and the metal to be descaled may be varied to facilitate the operation of the process and the closer such electrodes are positioned to the metal object and to one another, the lower generally will be the voltage necessary to provide the required current density or the higher will be the current density at a fixed voltage. If desired, agitator or circulating means may be utilized to circulate the electrolyte in the bath during the descaling.

In the case of descaling a continuously running metal strip, a rubber covered guide roll can be positioned adjacent the top edge of the tank bath. Sinker rolls, preferably of rubber covered stainless steel, can be used to insure a substantially uniform movement of the metal strip in properly spaced relationship. The inherent flexing action and vibration setup in the strip as it travels through the descaling tank assists in lifting off the scale from the strip.

Washing nozzles may be appropriately arranged to enable a rinsing of the metal object to remove any residual cleaning solution that may be present thereon and if desired, a water or rinse tank may be employed to effect a rinsing of the metal object. In the case of a continuously moving metal strip, this may be accomplished by providing a tank of water having suitable rollers which will permit the metal strip to continuously pass through the water bath and out for drying, storage, or use.

Brushes can be used to assist in removing loosened scale from the surface of the object being descaled. Such brushes may be located in or subsequent to the descaling tanks.

The invention will be better understood by reference to the annexed drawings which set forth in detail certain illustrative embodiments of the invention. These embodiments should not, however, be construed as limiting the invention, it being understood that the invention may be variously modified and embodied within the scope of the appended claims.

In said annexed drawings:

FIGURE 1 is a side view, partially in section, of a "horizontal strip path" apparatus especially suitable for descaling a continuously moving steel strip according to the process of the present invention;

FIGURE 2 is a cross-sectional view taken along line **2—2** of FIGURE 1 in the direction of the arrows;

FIGURE 3 is a side view, partially in section, of another type of apparatus, an "inclined strip path" apparatus, for carrying out the process of the invention;

FIGURE 4 is a side view, partially in section, of a third type of apparatus, a "vertical strip path" apparatus for carrying out the process of the present invention;

FIGURE 5 is a plan view of an embodiment of the invention showing the employment of segmented electrodes;

FIGURE 6 is a cross-sectional view, taken along line **6—6** of FIGURE 5;

FIGURE 7 is a cross-sectional view taken along line **7—7** of FIGURE 5 (but with the outer electrodes of FIGURE 5 not in use) in the direction of the arrows;

FIGURE 8 is an end view, partially in section, of another embodiment of the invention; and

FIGURE 9 is an end view similar in nature to the view of FIGURE 8 but showing a wider strip of metal than in FIGURE 8.

Referring to FIGURES 1 and 2, a steel strip **1** continuously moves through electrolyte **2** in tank **3** via rollers **4**. Electrodes E_1 are inserted in the tank by means of longitudinally extending bars **5** and suitable supporting wires or rods. The electrolyte, in counterflow movement to the travel of the strip allows for the dissipation of foam and gas developed in the process. Current is caused to flow through the moving metal strip via the electrodes E_1 disposed above and below the path of movement of the strip, those above and those below the path of movement of the strip being connected with opposite terminals of the current source. Provision is made for removing insolubles from the electrolyte discharged from the tank and for its storage prior to its return to the tank.

FIGURE 3 shows the movement of strip **6** via rollers **7** in an inclined position between electrodes E_2 secured by wires or rods extending downwardly from crossbar **8** extending longitudinally of the top of tank **9** containing electrolyte **10**, while FIGURE 4 shows the movement of strip **11** via rollers **12** in a vertical position between vertically disposed electrodes E_3, suspended from crossbar **13**, into tank **14** containing electrolyte **15**. In each instance the electrodes are disposed parallel with the strip being treated.

Although in FIGURES 1 and 4 the strip shown as being processed with the transverse plane of the strip parallel to the ground (FIGURE 1) or to the side of the tank (FIGURE 4), it is possible to process the strip on "edge" with the transverse plane of the strip perpendicular to the ground in FIGURE 1 or to the tank side in FIGURE 4. Moreover, although FIGURES 1, 3 and 4 show the processing of a continuously moving metal strip, the embodiments therein can be readily adapted for the descaling of stationary metal objects. For example, in FIGURE 4, stationary metal objects can be suspended from the crossbar **13** between electrodes E_3 and the descaling may be carried out by electrodes having surfaces opposite to those of the object which are spaced a predetermined distance from the latter in all regions.

In order to obtain uniform descaling over the entire surfaces of the work piece, especially when descaling stationary objects according to the process of this invention, it is advisable that the electrodes be so constructed and/or spaced to insure that the current will substantially extend over the entire length and width of the surfaces of the work piece.

FIGURES 5, 6 and 7 show the segmented electrode concept with employment of baffles to prevent the straying of current in descaling metal strip **17**. Three electrodes suspended from crossbars **16** are shown at E_4 (FIGURE 5) above the metal strip, and three slightly longer electrodes E_4 are similarly suspended and held in a position below the metal strip (FIGURES 6 and 7). Metal strip **17** if narrow may correspond in width to the width of the middle electrodes. Current may then be delivered to only these middle electrodes. Baffles **18** prevent current movement through electrolyte **19** in tank **20** in directions away from strip **17** (such current movement being hypothetically shown by dotted lines A in FIGURE 7 in the absence of such baffles). If it is desired to descale a strip having a width corresponding to but one of the outer electrodes and the middle electrode in the three segmented arrangement, the baffle **18** extending between the two electrodes being used can be removed or omitted and the operation readily carried out. It will be understood that electrical connections from a suitable power source may be made to only those electrodes which are being used at a particularly time or that the power may be cut off to those electrodes not being used at a particular time.

In FIGURE 8, through the use of hinged baffles **21**, a strip **22** which is between the hinged baffles can be conveniently descaled with use of electrodes E_5, suspended from crossbar **23**, the electrodes acting through only a portion of electrolyte **24** in tank **25**.

In FIGURE 9, a strip **26** of width wider than strip **22** can be readily descaled, the baffles **21** now being in an inactive position.

The following examples are given to aid in understanding the invention but it is to be understood that the invention is not restricted to the specific examples. The examples are illustrative only and should not be construed as limiting the invention which is properly delineated in the appended claims.

EXAMPLE 1

Using an apparatus of the type shown in FIGURE 4, a strip of hot rolled mild steel with tightly adherent oxide mill scale was placed in the tank containing as the aqueous electrolyte, an aqueous solution which aqueous solution contained 28% citric acid adjusted to about a pH of 4 with sodium hydroxide. The temperature of the descaling bath was maintained at 215° F. The surface of the steel strip was completely descaled in 30 seconds at a current density of 300 amps per square foot of steel surface, with a potential of 28 volts alternating current between electrodes.

EXAMPLE 2

Using the solution and procedure outlined in Example 1, complete descaling was attained in 20 seconds at a current density of 600 amps per square foot and 25 volts alternating current.

EXAMPLE 3

Using the procedure outlined in Example 1 and with the pH of the solution adjusted to approximately 6.0 complete descaling was attained in 2 minutes at a current density of 600 amps per square foot and 22 volts alternating current.

EXAMPLE 4

The procedure outlined in Example 1 was followed. The electrolyte comprises an aqueous solution containing 7% citric acid with the pH of the solution adjusted to approximately 4.5 with sodium-hydroxide. Complete descaling was attained in 35 seconds, at a current density of 400 amps per square foot and 30 volts alternating current.

EXAMPLE 5

Using the procedure outlined in Example 1 and with an aqueous solution containing 42% citric acid with the pH of the solution adjusted to approximately 4.0 with sodium hydroxide, complete descaling was attained in 50 seconds at a current density of 300 amps per square foot and 32 volts alternating current.

EXAMPLE 6

Using the procedure outlined in Example 1 and an aqueous solution containing 28% citric acid with the pH of the solution adjusted to approximately 3.0 with ammonium hydroxide, complete descaling was attained in 26 seconds at a current density of 300 amps per square foot and 38 volts alternating current.

EXAMPLE 7

The procedure of Example 6 was followed, but with the pH adjusted to approximately 5.0 with ammonium hydroxide. Complete descaling was attained in 35 seconds at a current density of 300 amps per square foot and 16 volts alternating current.

EXAMPLE 8

The procedure of Example 6 was followed, but with the pH adjusted to approximately 7.0 with ammonium hydroxide, complete descaling was attained in 50 seconds at current density of 300 amps per square foot and 15 volts alternating current.

EXAMPLE 9

The procedure outlined in Example 1 was again followed. The electrolyte comprised an aqueous solution containing 28% citric acid with the pH of the solution adjusted to approximately 4.0 with potassium hydroxide. Complete descaling was attained in 30 seconds at a current density of 300 amps per square foot and 30 volts alternating current.

EXAMPLE 10

As in Example 9, but with the pH adjusted to approximately 6.0 with potassium hydroxide, complete descaling was attained in 60 seconds at a current density of 300 amps per square foot and 16 volts alternating current.

EXAMPLE 11

Using the procedure outlined in Example 1 and with an aqueous solution containing 28% glycolic acid with the pH of the solution adjusted to approximately 6.3 with ammonium hydroxide, complete descaling was attained in 45 seconds at a current density of 600 amps per square foot and 15 volts alternating current.

EXAMPLE 12

The procedure outlined in Example 1 was practiced. With an aqueous solution containing 28% citric acid with the pH of the solution adjusted to approximately 6.0 with ammonium hydroxide, and with direct current electric power, complete descaling was attained on the surface of the steel beneath the anode in 24 seconds at a current density of 600 amps per square foot and 13 volts direct current.

EXAMPLE 13

Employing a "horizontal strip path" apparatus of the type shown in FIGURE 1 and using an aqueous solution containing 20% citric acid adjusted to approximately pH 6.0 with ammonium hydroxide and at 200° F., a sample of hot rolled mild steel strip with tightly adherent oxide scale on the surface was descaled in 20 seconds at a current density of 600 amps per square foot of steel surface, with a potential of 19 volts alternating current between electrodes, a continuous steel strip being circulated between the electrodes in the direction of the arrows as shown in FIGURES 1.

EXAMPLE 14

Using the procedure outlined in Example 13, and an aqueous solution containing 28% citric acid with the pH of the solution adjusted to approximately 4.0 with sodium hydroxide and at 212° F., complete descaling was attained in 26 seconds at a current density of 200 amps per square foot and 30 volts alternating current.

While there have been described herein certain embodiments of the invention, it will be obvious to those skilled in the art that modifications and changes may be made therein without departing from the essence of the invention. It is, therefore, to be understood that the exemplary embodiments and drawings are illustrative and not restrictive of the invention, the scope of which is defined in the following claims, and that all modifications that come within the meaning and range of equivalency of the claims and would be obvious to those skilled in the art, are intended to be included therein.

Also the terms and expressions which have been employed in the specification are used as terms of description and not of limitation, and there is no intention, in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, since it is recognized that various modifications are possible within the scope of the invention claimed.

Having described the present invention in some detail, that which is sought to be protected is set forth in the following claims.

What is claimed is:

1. A process for electrolytically removing scale from a steel article which comprises immersing said article in an electrolyte and indirectly contacting the steel article with an alternating current while so immersed, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic acid, citric acid and mixtures thereof, and a base selected from the group consisting of an alkali metal hydroxide and a nitrogen base, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a pH of about 3 to 7 when the base is a nitrogen base and a pH of about 3 to 6 when the base is an alkali metal hydroxide, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

2. A process for electrolytically removing mill scale from a steel strip which comprises immersing the strip in an electrolyte and indirectly contacting the strip with an alternating current while so immersed, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic said, citric acid and mixtures thereof, and a base selected from the group consisting of an alkali metal hydroxide and a nitrogen base, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a pH of about 3 to 7 when the base is a nitrogen base and a pH of about 3 to 6 when the base is an alkali metal hydroxide, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

3. A process for electrolytically removing mill scale from a strip of hot rolled mild steel which comprises immersing the strip in an electrolyte and indirectly contacting the strip with an alternating current while so immersed, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic acid, citric acid and mixtures thereof, and a base selected from the group consisting of an alkali metal and a nitrogen base, said electrolyte containing about 5 to about 50 percent acid components, said electrolyte having a pH of about 3 to 7 when the base is a nitrogen base and a pH of about 3 to 6 when the base is an alkali metal hydroxide, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

4. A process for electrolytically removing mill scale from a moving horizontally disposed continuous steel strip which comprises moving a continuous steel strip in a horizontal direction through an electrolyte while indirectly contacting the steel strip while so immersed with an alternating current, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic acid, citric acid and mixtures thereof, and a base selected from the group consisting of an alkali metal hydroxide and a nitrogen base, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a pH of about 3 to 7 when the base is a nitrogen base and a pH of about 3 to 6 when the base is an alkali metal hydroxide, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

5. A process for electrolytically removing mill scale from a moving continuous steel strip which comprises continously moving said strip along a vertically inclined path through an electrolyte while indirectly contacting the moving steel strip while so immersed with an alternating current, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic acid, citric acid and mixtures thereof, and a base selected from the group consisting of an alkali metal hydroxide and a nitrogen base, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a pH of about 3 to 7 when the base is a nitrogen base and a pH of about 3 to 6 when the base is an alkali metal hydroxide, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

6. A process for electrolytically removing scale from a steel article which comprises immersing said article in an electrolyte and indirectly contacting the steel article with an alternating current while so immersed, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic acid, citric acid and mixtures thereof, and an alkali metal hydroxide, said electrolyte contacting about 5 to about 50 percent acid component, said electrolyte having a pH of about 3 to 6, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

7. A process for electrolytically removing scale from a steel article which comprises immersing said article in an electrolyte and indirectly contacting the steel article with an alternating current while so immersed, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic acid, citric acid and mixtures thereof, and a nitrogen base, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a pH of about 3 to 7, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

8. A process for electrolytically removing mill scale from steel which comprises immersing the steel in an electrolyte and indirectly contacting the ferrous metal with an alternating current while so immersed, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of ammonium citrate having a pH of about 3 to 7, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

9. A process for electrolytically removing mill scale from steel which comprises immersing the steel in an electrolyte and indirectly contacting the ferrous metal with an alternating current while so immersed, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of sodium citrate having a pH of about 3 to 6, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

10. A process for electrolytically removing mill scale from steel which comprises immersing the steel in an electrolyte and indirectly contacting the steel with an alternating current while so immersed, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte consisting essentially of an aqueous solution of potassium citrate having a pH of about 3 to 6, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

11. A process for electrolytically removing oxide mill scale from a moving continuous strip of hot rolled mild steel which comprises moving the continuous hot rolled mild steel strip through an electrolyte, said electrolyte consisting essentially of an aqueous solution of sodium citrate having a pH of about 3 to 6 of an acid component concentration of about 28 percent, while indirectly contacting the hot rolled steel strip while so immersed with an alternating current, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

12. A process for electrolytically removing oxide mill scale from a moving continuous strip of hot rolled mild steel which comprises moving the continuous hot rolled mild steel strip through an electrolyte, said electrolyte consisting essentially of an aqueous solution of ammonium citrate having a pH of about 3 to 7 and an acid component concentration of about 28 percent, while indirectly contacting the hot rolled steel strip while so immersed with an alternating current, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

13. A process for electrolytically removing oxide mill scale from a moving continuous strip of hot rolled mild steel which comprises moving the continuous hot rolled mild steel strip through an electrolyte, said electrolyte consisting essentially of an aqueous solution of potassium citrate having a pH of about 3 to 6 and an acid component concentration of about 28 percent, while indirectly contacting the hot rolled steel strip while so immersed, with an alternating current, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

14. A process for electrolytically removing oxide mill scale from a moving continuous strip of hot rolled mild steel which comprises moving the hot rolled continuous mild steel strip through an electrolyte, said electrolyte consisting essentially of an aqueous solution of ammonium glycolate having a pH of about 3 to 7 and an acid component concentration of about 28 percent, while indirectly contacting the hot rolled steel strip while so immersed with an alternating current, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

15. A process for electrolytically removing oxide mill scale from steel strips of various widths which comprises immersing a steel strip in an electrolyte and indirectly contacting the strip while so immersed with alternating current from a selected number of electrodes, the exact number of electrodes depending on the width of said strip, and providing baffle means to cause the passage of substantially all the current to the strip undergoing the descaling, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic acid, citric acid and mixtures thereof, and a base selected from the group consisting of an alkali metal hydroxide and a nitrogen base said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a pH of about 3 to 7 when the base is a nitrogen base and a pH of about 3 to 6 when the base is an alkali metal hydroxide, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

16. A process for electrolytically removing oxide mill scale from moving continuous steel strips of various widths which comprises moving a continuous steel strip immersed in an electrolyte while indirectly contacting the strip with alternating current from a selected number of electrodes, the exact number of electrodes depending on the width of said strip, and providing baffle means to cause the passage of substantially all the current to the strip undergoing the descaling, said electrolyte consisting essentially of an aqueous solution of a salt of a chelating acid selected from the group consisting of gluconic acid, tartaric acid, diglycolic acid, glycolic acid, citric acid and mixtures thereof, and a base selected from the group consisting of an alkali metal hydroxide and a nitrogen base, said electrolyte containing about 5 to about 50 percent acid component, said electrolyte having a pH of about 3 to 7 when the base is a nitrogen base and a pH of about 3 to 6 when when the base is an alkali metal hydroxide, said alternating current having a current density of from about 100 to 1300 amp per square foot, said electrolyte having a temperature between 200° F. and the boiling point of said electrolyte.

References Cited

UNITED STATES PATENTS

2,146,488	2/1939	Sykes	204—145
2,165,326	7/1939	Yerger et al.	204—145
2,685,564	8/1954	Emmett et al.	204—145
3,304,246	2/1967	Fukui et al.	204—145

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