Sept. 16, 1930. T. E. DUNN 1,775,671

ELECTROLYTIC METHOD OF CLEANING METAL

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Fig. 1

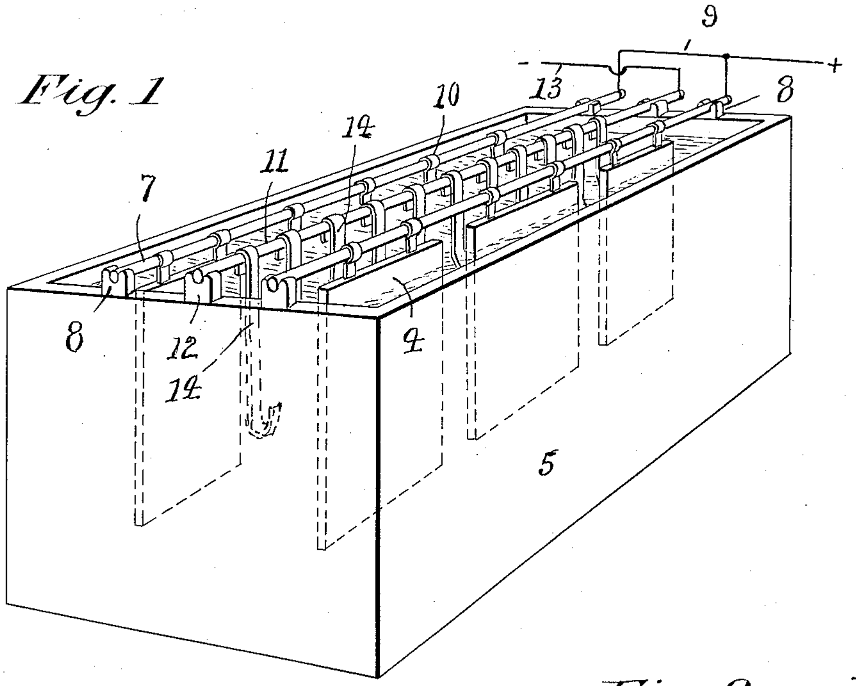


Fig. 2

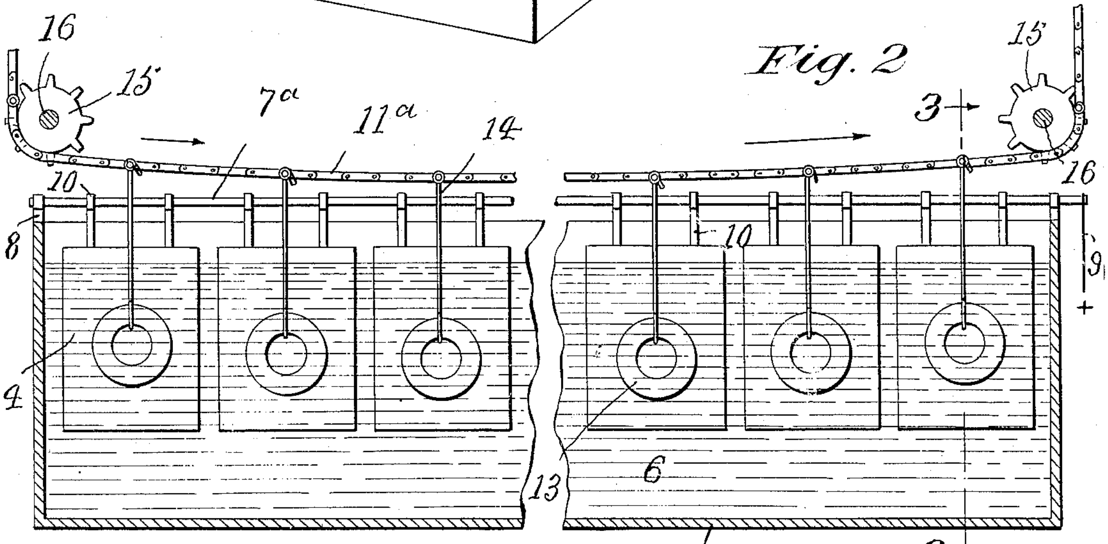
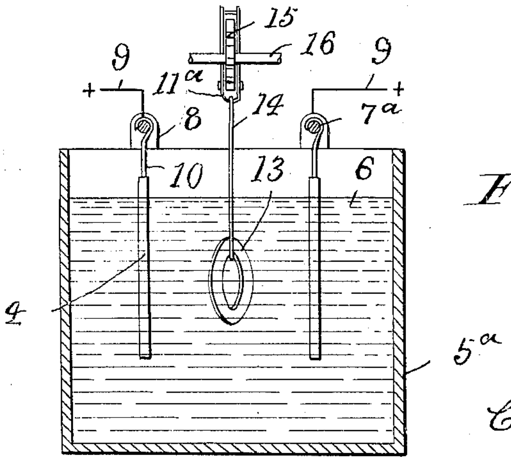


Fig. 3



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UNITED STATES PATENT OFFICE

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ELECTROLYTIC METHOD OF CLEANING METAL

Application filed November 1, 1926. Serial No. 145,462.

This invention relates to an electro-chemical cleaning process for cleaning metal and it has for its object to provide a process of removing the surface scale and other objectionable matter from forgings, castings or the like, preparatory to finishing the same and a further feature of the invention is to produce an improved quality of iron or steel by subjecting the same to cathode treatment in an acidified solution containing chlorides and sulfates of lead.

In the heat treatment of steel castings, machined tool parts, cast iron fittings and the like a hard adherent scale is usually produced on the surface of the steel or iron parts during the tempering or heat treating operation. This scale is very often extremely hard and unless removed will result in rapid wearing down of those steel parts coming into intimate contact with each other. This applies, for instance, to the case of gear wheels where all trace of scale must be removed from in between the teeth, in order to avoid rapid wearing away of the teeth.

In the past it has been customary to remove this scale by various processes. One of these consists in mechanical abrasion, using steel brushes and emery wheels. Another process consists in pickling the steel parts after heat treatment in strong mineral acids. This chemical process is difficult to control, is slow in operation and often results in sections of the steel being deeply pitted or eroded. Finally, there have been electrolytic methods proposed. In one of these electrolytic methods, the steel to be cleaned is made anode in a sulfuric acid solution. I have found that this process, although a little faster than the chemical pickling process, produces results very similar to the chemical pickling process, namely, lack of uniformity in the surface structure, parts of the surface being deeply pitted.

The object of my invention is to rapidly and completely remove surface scale and other foreign matter from metallic articles and especially those that have been heat-treated such as castings, gears, springs, etc. and simultaneously protect the articles against hydrogen embrittlement, pitting, etching, etc. by placing a coating on the surfaces thereof thus producing an improved product, having perfectly homogeneous surfaces, free from surface differences tending to produce local voltaic couples, said products being capable of being used as articles upon which subsequent surface treatment can most advantageously be done such as the depositing of metal thereon or which may be stored without surface deterioration such as corrosion.

My preferred electrolyte is an aqueous solution of the mineral acids, sulfuric and hydrochloric, together with a definite amount of a sodium salt, preferably the chloride or sulfate and containing lead in solution. Lead anodes are customarily used and in the presence of hydrochloric acid or chlorides, these are attacked and serve to replenish the lead content of the bath. The proportions of acids and sodium salt may obviously be varied within wide limits as may best suit the particular class of work to be handled. The solution can be used cold, but the cleaning operation is more rapid and more efficient if the solution is heated. As soon as the bath is put into service iron and lead salts are immediately introduced into the bath by the action of the bath on iron oxide scale carried by the work and on the lead anode. In operation with lead anodes the amount of lead in solution in the bath normally approaches the saturation point. Lead salts may also be added to the bath.

From a physico-chemical point of view the electrolyte is initially a solution containing ions of sodium, hydrogen, sulfate and chlorine, aside from the undissociated salts present. As soon as the electrolyte is put in service, the solution will contain also lead and iron, and sometimes a little antimony derived from the hard lead anodes. Potassium salts may be used in place of sodium salts but the latter are cheaper. The same bath can be used continuously for an indefinite period and its original efficiency maintained by the occasional addition of a little acid and sodium chloride.

In my process the work to be cleaned is made cathode in such a bath at a current density of approximately 75 to 100 amps./sq. ft. At lower current densities the operation proceeds more slowly. It is however impracticable to use such low current densities in my process as are customarily used in lead and copper plating. In carrying out my process I have discovered, contrary to general experience and the belief of those versed in the electro-plating art, that when using my high current densities I obtain a thin uniform continuous film of lead. It is well known that when exceedingly high current densities are used, such as I use, lead is deposited in a loosely adherent form but I have discovered that with these high current densities I can obtain a continuous adherent film of lead underlying the spongy lead and one which is homogeneous and practically free from pin holes and other defects. In order that cleaning be accomplished it is necessary that the hard adherent scale be blasted off by mechanical action. To do this I must use a current density such as those skilled in the electro-plating art consider exceedingly high, in order to secure an adequate supply of hydrogen gas so that in a single operation I can effect the complete removal of all foreign material—not only grease and rust but also indurated scale, heavy oxide, dirt, sand particles, emery grains and other foreign matters—and simultaneously deposit a coating of lead.

Scale, particularly scale formed as the result of heat treatment, often contains a relatively large amount of magnetite (Fe_3O_4). This is quite insoluble in acids and is a good conductor of electricity. With low current densities such as are generally employed in lead or copper plating the metal to be deposited is deposited on top of the scale. As a result no complete cleaning is obtained and the heavy scale is not removed nor are the particles of sand, etc., and the work does not present a clean surface uniformly covered with lead. Such results are of course entirely unsatisfactory; but I have discovered that by using exceedingly high current densities and a properly chosen electrolyte, I am able, by my process, to remove all of the scale including the magnetic iron oxide and to deposit a thin continuous adherent film of lead directly on the metallic iron. The anodes are cut from sheet lead, known in the trade as hard lead containing about 4% antimony. In place of anodes of antimonial lead, anodes of ordinary lead may be used. I have also tried out a number of other anodes notably of carbon or graphite, iron and tin. During my process of electrolytic cleaning, appreciable quantities of lead pass into solution due, very likely, to the presence of the chlorine ions which readily attack the lead, in comparison with the sulfate ions. The surface of the lead anode often has a thin coat of lead peroxide PbO_2. Whereas mechanical cleaning or acid dipping of heavily scaled steel parts may often require as much as one half to one hour, I find that with this new bath, the time can be cut down to 4 to 8 minutes. At the end of this time the steel parts, as they are taken out of the electrolytic cleaning bath, are covered over with a deposit of spongy lead, easily removed if desired in a subsequent washing with water. At the work which forms the cathode it is necessary in my process to have an ample supply of hydrogen ions and advantageously of sodium ions and also of ions of a less noble metal than that of the work such as lead ions. Accordingly when I use acetic acid instead of hydrochloric or sulphuric, I may regulate the supply of lead in the bath by using either a combination of carbon anodes and lead anodes or carbon anodes alone and add lead acetate to the bath from time to time. The mineral acids, however, have this advantage,—their greater stability and bettere electrical conductivity. Acetic acid, particularly in the presence of heat, is eventually decomposed by the action of the electric current, the end product being carbon dioxide. Such decomposition does not occur with hydrochloric or sulphuric acid.

I consider the function of the lead an important feature in the cleaning operation. I find that in the presence of the lead salts in the cleaning bath, the scale on a cathode is more rapidly loosened. This is particularly noticeable in the case of steel parts with deep recesses—for example, large toothed gear wheels. The scale between the teeth is more rapidly loosened and removed with the new bath than it is with any of the other baths heretofore proposed. Although it may appear poor practice to use lead anodes, I find that other anodes used in place of lead do not produce the same rapid efficient cleaning results. It appears from my experiments that the throwing power of the solution as applied to hydrogen is greatly improved by the introduction of lead into the bath. This is the more remarkable, in view of the lower potential difference between lead and hydrogen than iron and hydrogen. On the other hand, it is worthy of note that the hydrogen overvoltage for lead is very high as compared with the hydrogen overvoltage for iron. Now, during my cleaning process, as soon as the scale is reduced or removed at a point on the cathode or work to be cleaned nearest to the anode, lead will be deposited at this point and as the voltage at this point rises, due to the lead, the current is automatically turned towards parts of the work, such as recesses, further removed from the anode. This phenomenon is often referred to as "throwing power."

I merely offer the above interpretation as the most probable one to account for the remarkable phenomena during my cleaning process. I wish, however, not to be bound by this interpretation.

According to modern conceptions based on many carefully executed experiments "overvoltage" is the amount of the polarization which exceeds the reversible potential and I am using the word "overvoltage" with this meaning. It is a voltage in excess of the normal voltage of the particular cell under investigation, the excess voltage being attributed to the super-saturation of the surface of the electrode (or electrodes) with one or more products of electrolysis.

This super-saturation of the electrode surface results in a reaction which is opposite in effect (or sign) to that of the electric current passing through the solution. Accordingly, in order to overcome this counter-reaction or resistance and have the same electric current pass through the solution as at the very beginning of electrolysis, the electromotive force applied to the cell must be increased up to a certain value. The difference between this new voltage reading and the voltage of the cell at the very beginning of electrolysis (before polarization has set in) is called the overvoltage.

Example

	Volts
Current 5 amp. no polarization	3
Current 5 amp. polarization	4.5
Overvoltage	1.5

The higher the current density, the higher the overvoltage.

In the case in hand I am dealing with "cathodic overvoltage" and there are at least three metal and metal compound surfaces of the "work" that are to be taken into account.

As is well known, an electric current such as is used in electrolytic cells will always follow the path of least resistance, or the "shortest electrical path," even though this may be the longest path geometrically. Accordingly, it will be appreciated that the electric current passing through the solution and reaching the cathode will enter the cathode at those points or areas that offer the least electrical resistance, or, in other words, at those points or areas that form the "shortest electrical path" with the anode.

The resistance offered by the different metal or metal compound areas of the "work" is appreciably different: With my acid-sulfate-chloride bath the lowest resistance as a rule is offered by the oxide-filmed iron surface and then the cleaned iron surface; next in order is the lead (plated on iron) surface and then the lead-hydrogen compound surface. The presence of the oxide film on the iron surface may be regarded as a depolarizer and the resulting potential is lower than that required for the deposition of lead. Immediately the film is removed or reduced, the potential rises and lead is deposited. The lead, however, is rapidly saturated with hydrogen and the potential at this spot or area again rises, and, accordingly, the path of the electric current is diverted to other spots or areas of lower electrical potential. It is common knowledge that in the electrolytic production of hydrogen a lower potential is required with an iron cathode than with a lead cathode, the overvoltage on lead being markedly higher than on iron.

The great advantage of my process as compared with older processes is in the great speed of operation. Whereas it takes hours to clean certain steel parts by mechanical or by ordinary chemical means, by this new electrolytic method, iron and steel parts can be cleaned within a few minutes. The resulting surface produced after the removal of the spongy lead, which is easily accomplished with an ordinary brush and water, is a thin closely adherent uniform film of lead perfectly smooth and free from the pitting so familiar in the old wet methods.

Another advantage of my process is that flaws in the steel that may have developed during rolling, hammering or other mechanical operations, are readily revealed after this new electrolytic treatment. For example, scale or slag which has been worked into the surface of a forged or hammered piece is readily revealed after the electrolytic treatment. Finally, a distinct advantage of my process over the ordinary pickling process, aside from the factor of speed, is the absence of any change in the composition of the outermost layer of the steel under the scale, during the cleaning operation. In the case of ordinary pickling, I meet with selective dissolution, especially in the case of alloy steels. Iron and steel parts originally covered with scale cleaned by my electrolytic process as outlined above will be free from pits and other defects such as are commonly produced by other acid cleaning processes. Furthermore, the surface of the iron and steel parts cleaned by my process is remarkably free from the normal tendency to rust or corrode on contact with the atmosphere, and thus such iron or steel parts are better adapted to storage or subsequent surface treatment. In other words the removal of scale and the simultaneous deposition of lead produces a homogeneous surface free from local voltaic electrical couples which, as is well known, are the frequent cause of surface corrosion.

I have confined my process largely to the cleaning of iron and steel, including alloy steel. However, my process is likewise applicable to the cleaning of many nonferrous metals and alloys, including aluminum and its alloys. In each individual case the speed of scale removal, I believe, is dependent upon the proper control of the cathode overvoltages; that is to say, where a non-ferrous metal is to be cleaned the metal to be deposited thereon should, as in the case of cleaning a ferrous metal, differ sufficiently from said metal to be cleaned in hydrogen overvoltage to permit an excess of hydrogen to be electrolytically evolved on the article.

The metal to be cleaned may be suspended and stationarily supported between the anodes, or the work forming the cathodes may be suspended from a suitable traveling conveyor and drawn through the solution, between the anodes, as will later be again referred to. In both instances the two series of anodes would obviously be connected to the positive pole of a generator, whereas the work forming the cathodes would be connected to the negative side of the generator.

A preferable form of tank for carrying out my improved cleaning process is one made of wood or other suitable material proportioned and sized according to the particular class of work to be handled, and means for handling same.

Upon the accompanying drawing forming a part of this specification, I have illustrated my invention as being carried out in two different forms of apparatus—in one the work is stationary, suspended in the solution between two series of anodes, and in the second, the work is conveyed through the solution and between two series of anodes suspended in a long tank, the work being introduced at one end of the tank and removed as cleaned from the other. This may be called a continuous process.

With the above and other objects in view, an embodiment of the invention is shown in the accompanying drawing, and this embodiment will be hereinafter more fully described with reference thereto and the invention will be finally pointed out in the claims.

In the accompanying drawings:—

Fig. 1 shows a perspective view of a suitable form of tank containing the necessary solution, anodes and means for supporting the work therebetween;

Fig. 2 is a longitudinal central sectional view of a tank and conveyor, broken away, showing my improved method applied in connection with a movable work conveyor, and

Fig. 3 is a cross sectional view taken on line 3—3 of Fig. 2, better to illustrate the position of the work between the two lines of anode plates.

Referring in detail to the characters of reference marked upon the drawings, and more particularly to Figs. 2 and 3, 5 represents a tank, 6 solution within the tank, 7 two anode rods which are insulatively supported at 8 on top of the end portions of the tank and are connected to the positive side of low voltage direct-current generator by wires 9. The anodes 4, are preferably in the form of lead plates, and provided with attached hooks 10, by means of which they are hung from rods 7, which serve as conductors for carrying current. The third rod 11, positioned between the two anode rods 7—7, is also supported on suitable insulating blocks 12, secured to the top of the tank and serves as the cathode rod which is in contact with a current carrier which leads to the negative side of same low voltage direct-current generator.

The work herein shown is of ring form, and designated as 13, and may obviously be of steel, cast iron or the like, and supported by a simple form of hook 14, from the cathode rod 11. This work is supported in spaced relation to each other from these rods, and at equal distances between the two lines of anodes.

The tank 5^a, for the moving cathodes, shown in Figs. 2 and 3, may be similar to that illustrated in Fig. 1 except longer, and it is also true of the anode rods 7^a, upon which a greater number of anodes would be supported in substantially the same manner as that shown in Fig. 1. In this form of apparatus I propose to employ a suitable conveyor upon which the work may be hung or laid for the purpose of moving through the tank during the cleaning operation. For this purpose I have shown a simple form of sprocket chain 11^a which is supported at each end of the tank by sprocket wheels 15—15, mounted upon shafts 16—16 that can be operated by any suitable means. This chain would obviously be connected to carry negative current from generator and serves to support the work, designated as 13, through the medium of hangers 14. The work to be cleaned would be submerged in the left hand end of the tank, as shown in Fig. 2, and supported upon the chain, then gradually conveyed through the tank between the anodes and upon reaching the other end of the tank is removed in a finished or clean condition. In both apparatuses the work is suspended from the cathode rods between the lead anodes and is entirely submerged in the solution and comprises a negative cathode and positive anode. The circuit from the generator is closed and current flows from the positive lead anodes through the solution to the work suspended therein, forming the negative cathode.

The action of the current is to blast off the scale at the cathode with the accompanying simultaneous evolution of hydrogen and deposition of lead.

The chemical combination between the hydrogen and the oxygen of the scale to be removed from the piece or pieces to be cleaned serves as a cleaning action. In other cases I have observed that the hydrogen gas works its way under the scale and loosens same without complete reduction of the scale. Under proper working conditions this action will clean the surface of a piece of metal in a few minutes without pitting or etching, as is the usual result in the ordinary acid pickle, or in the acid pickle accelerated by electrical action wherein the work serves as the anode. The process is equally effective in a still, an agitated or moving cathode tank, and can be carried out with either high or low amperage.

I have used the word "attack" in the specifications and claims as including both hydrogen embrittlement and acid solution such as results generally in pitting and etching.

Metals are classified as more or less noble, the more noble metals being those of higher electric potential. I am using the words "higher electric potential" in the sense of meaning more noble metals as this is the definition adopted by the Bureau of Standards in 1922 and other authorities.

The words "foreign matter" are used herein as an all-inclusive term for such materials as scale, rust, grease, paint, etc., which are often found on the surfaces of manufactured iron or steel products.

I have used the word "iron" in the generic sense as including not only what is commonly called iron, but also steel and other ferrous alloys.

I have used the word "homogenize" as a verb meaning to make "homogeneous".

I have used the words "excessive hydrogen" and "exceedingly high" current densities as meaning quantities of hydrogen or current, as the case may be, greater than the amounts commonly used in the ordinary process of lead or copper plating, the evolution or use of which in these processes will be carefully avoided by the plater because it would result in the deposit of spongy lead plates, which are considered by those experienced in the art as improper and detrimental.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:—

1. The method of cleaning the surface of iron which consists in removing the surface foreign matter by the electrolytic production of an excess of hydrogen and simultaneously protecting the cleaned iron surface from attack by depositing lead thereon.

2. A cleaning process for metallic articles comprising the electrolytic generation of excessive hydrogen upon such an article as a cathode for the removal of the surface foreign matter therefrom with a concurrent deposition of a continuous coating of lead thereon.

3. A cleaning process for iron parts comprising suspending such parts as cathode in an acid solution and removing surface foreign matter therefrom by the electrolytic generation of hydrogen upon said cathode with the concurrent deposition of a continuous coating of lead thereon

4. The process of cleaning scaled metal which comprises mechanically detaching the scale by cathodic generation of hydrogen and concurrently homogenizing the cleaned surfaces by the deposition of lead thereon.

5. The process of cleaning metal which comprises mechanically detaching surface foreign matter by cathodic generation of an excess of hydrogen in an acid bath while concurrently homogenizing the cleaned surfaces by the deposition of a continuous metal film thereon.

Signed at Bridgeport, in the county of Fairfield and State of Connecticut this 25 day of October, A. D. 1926.

THOMAS E. DUNN.