THESIS

THE ART OF RUST-PROOFING OF IRON AND STEEL

H. L. WATERBURY   J. D. ROBERTS

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An Investigation
of
The Art of Rust - Proofing of
Iron and Steel.

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By

[illegible] Lawrence [illegible]
H. L. Waterbury J. D. Roberts

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Iron and that form of iron called steel are being used increasingly as engineering materials. The tendency to rust is a characteristic inherent in the element iron impairing its usefulness both on account of reduction of strength and the offending appearance of rusty surfaces. It is probable that this rusting of iron and steel cannot be entirely overcome since no method is known by which to banish the agents which cause corrosion. The elements of this agency are those necessary to life itself and society would hardly consent to their removal were it possible.

Great expense falls annually upon manufacturers through the corrosion of iron and steel; great quantities of which are wasted through this baleful influence. The preservation of iron and steel is, therefore, one of the problems of highest importance before the world at present. The industries concerned must learn how to preserve the present supply for future generations.

It is known, however, that there is a great deal of difference between the manner and rapidity with which different specimens and types of iron and steel and their alloys are affected by corrosion. Some metals are more susceptible to corrosion than others. The proper control of unavoidable impurities, their homogenous distribution and careful heat treatment, will improve the rust resisting qualities of metal whether it is called iron or steel, and regardless of the method by which it is made. As the result of recent researches by a number of investigators, it is now very generally admitted that a state of stress or strain in the metal invites rapid corrosion. A similar effect is produced by a burnt condition of the metal leading to a high porosity and the presence of occluded gas and blow holes. The old hand forged metals are less easily corroded than are the modern metals.

In this Thesis an effort has been made to point out the causes of rust and the means and methods by which it may be prevented.

Information was obtained by research on the various causes and prevention of rust, as outlined by experts, and an investigation was conducted on the so called Parker Method of Rust Proofing.

The bibliography consulted for the purpose of securing information comprised the following references:

Corrosion and Preservation of Iron and Steel, by Cushman and Gardner,

Galvanizing and Tinning by Flanders.

Metalurgy of Iron and Steel, by Bradley Stoughton.

PART I.

Theories of Corrosion.

There have been three theories put forward to explain the corrosion of iron and steel; the carbonic acid theory, the hydrogen peroxide theory and the electrolytic theory.

The carbonic acid theory is the one which until recently was most generally accepted. The theory is best set forth in the words of a text book in analytical chemistry recently published.

"The process of rusting is a cyclical one, three factors play an important part; an acid, water and oxygen. This process of rusting is always started by an acid (even the week carbonic acid suffices); the acid changes the metal to a ferrous salt with evolution of hydrogen.

$2Fe$ plus $2H_2CO_3 = 2FeCO_3$ plus $2H_2$

"Water and oxygen now act upon ferrous salt causing the iron in this salt to separate out as ferric hydroxide, setting free the same amount of acid which was used in forming the ferrous salt.

$2FeCO_3$ plus $5H_2O$ plus $O = 2Fe(OH)_3$ plus $2H_2CO_3$

The acid which is set free again acts upon the metal forming more ferrous salt, which is again decomposed, forming more rust. Very small amount of acid, therefore, suffices to rust a large amount of iron. If the acid is lacking, the iron will not rust."

The above theory is a plausible explanation for rusting, and in spite of the fact carbonic acid and other acids do act a part in the ordinary rusting of iron it has been proven by the experiments of Dunstan and coworkers that rusting does take place when carbonic acid is absent with extreme rapidity. Hence it is plain that the carbonic acid theory does not furnish a complete explanation of the phenomenon of corrosion, but it does express partial truth in as much as hydrogen ions must be present before the attach on the surface of the iron can be made. The fact that even pure water provides a sufficient number of hydrogen ions to start the action shows that the roll of carbonic acid is only contributory and not the sole cause.

The peroxide theory of corrosion is based on the scheme of oxidation processes advanced by Traube. Thus the chemical action concerned in the formation of iron rust should be written.

Fe plus O_2 plus H_2O = FeO plus H_2O_2

$2FeO$ plus H_2O_2 = $Fe_2\ O_2\ (OH)_2$ = $Fe_2\ O_3$, H_2O

The excess of hydrogen peroxide immediately reacts with the iron, forming a further quantity of rust

Fe plus H_2O_2 = FeO plus H_2O

$2FeO$ plus H_2O_2 = $Fe_2O_2\ (OH)_2$ = Fe_2O_3 , H_2O

The theories of this explanation are interesting but they have never proved themselves or have they been supported by facts. Thus a further search must be made for a true explanation of the corrosion of iron.

The electrolytic theory is the one which has finally been accepted, as the true explanation of corrosion. In order to understand the above theory it will be necessary to give some attention to the theory of solution.

All soluable substances have a solution pressure which forces that substance into solution being opposed only by the osmotic pressure of

the water, When the two balance the disolving stops. Solution pressure varies over the surface of a piece of iron or steel causing some points to go into solution and rust while other portions remain bright. This rusting is an electrolytic action produced by positive and negative ions of solution. For instance, if we place a piece of iron in pure water, the iron has a definite solution tension, especially at certain points on the surface, which are electro positive to other points. The iron enters the solution as positive ferrous ions, the corresponding negative charges being assumed by hydroxyls. But immediately the oxygen of the air changes the ferrous ions to a ferric condition resulting in the hydrolytic formation of the insoluble ferric hydroxide or rust. Thus it appears that in order for rust to be formed iron must go into solution and hydrogen must be given off in the presence of oxygen or some other oxidizing agent. This presumes an electrolytic action as every iron ion that appears at a certain spot demands the dissapearance of a hydrogen ion at another, with a consequent formation of gaseous hydrogen. The gaseous hydrogen is rarely visible in the process of rusting, owing to the rather high solubility and great diffusive power of this element. Substances which increase a concentration of hydrogen ions, such as acids and acid salts, stimulate corrosion, while substances which increase the concentration of hydroxyls inhibit it.

It is further seen that solution tension is modified by impurities or additional substances contained in the metal and in the solvent. The effect of the slightest segregation of the metal or even unequal stresses or, strains in the surface, will throw that surface out of equilibrium, and the solution tension will be greater at some points than at others. The points or nodes of maximum solution pressure will be electro-positive to those of minimum pressure, and a current will flow, provided the surface points are in contact through a conducting film. If the film is water, or is in any way moist, the higher its conductivity the faster will iron pass into solution in the electro-positive areas, and the faster corrosion precedes.

By the use of ferroxyl, a solution for the indication of positive poles as well as negative poles, it was shown that the solution tension of iron is higher at certain points on the surface than it is at others. Or, in other words, certain surface points are, be it ever so slightly, electro-positive to others. Theseeffects which are produced in the ferroxyl indicator constitutes a visible demonstration of the electrolytic action taking place on the surface of iron and causing rapid corrosion at the positive nodes.

The ferroxyl test in the hands of a number of investigators has brought out with clearness a considerable body of evidence to show that the electrolytic theory is in accord with the observed facts when iron is undergoing corrosion.

Samples of rusted iron under the microscope show the formation of craters and mounds indicating the two poles of action in the electrolytic process. That is, when a positive center is surrounded by a negative area and when a negative center is surrounded by positive area. In the first case we find the metal is piled up in a crater formation, the metal being eaten out in the center. In the second case, the hydroxide is piled up in the center while the surrounding area is eaten away. The

foregoing examples confirm the conclusion that rusting is altogether a matter of electrolysis. Hence the iron that is most nearly free from other metals which will produce a difference in potential and hence an electrolytic action are the ones which will hold out the longest against rust. For instance there is a metal on the market at the present time which contains only five hundreths percent impurities which approaches in rust resistance the pure iron of our forefathers. Care should be taken, however, that in getting pure iron the metal be not spoiled by heat treatment. The physical properties of the iron may be changed to such an extent that the metal will be worthless or else it will have absorbed so much gas, principally hydrogen, that it will rust as readily, if not more readily, than it would have under the other conditions.

Experiements show that good homogeneous iron and steel rust about equally and that where iron and steel are connected together, the iron protects the steel which is negative to the iron.

Alloys of iron with other metals such as nickel, chronium, vanadium, tungsten, and silicon are all known to be resistant to corrosion, while manganese, if present in a large quantity, is resistant but if in combination with sulphur in small quantity it helps corrosion. Phosphorus retards corrosion and the fact that common iron does not rust as rapidly as the better grades has been attributed by some to the greater precentage of phosporus in it.

Owing to the nature of corrosion it is probably true that no satisfactory accelerating test for corrosion resistance can be devised. Corrison, in the natural process of rust formation, that is to say, in very slightly acid media, is a question of comparitively slow growth under special conditions and any effort to hasten the action changes all the conditions of equilibrium, producing an entirely different order of phenomena.

P A R T II

Preservation of Iron and Steel.

The problem of preservation has two phases. First, the manufacturing of a metal highly resistant to corrosion which has been discussed in the previous chapter. Second, protective coatings such as zinc, tin and lead, or oils, paints, varnishes, and bituminous materials and finally the production of a higher oxide on the surface.

Some authorities state that high carbon will protect the steel; that is, as the metal is eaten away the cemetite will come to the surface and protect it. However, there has not been sufficient experimentation and there is not enough data known to make this a positive statement.

Highly alkaline solution prohibits corrosion if it has an access of hydroxyl ions but if the solution is only dilutely alkaline rusting progresses very rapidly. As has been stated before, oxygen is necessary in the water to cause rusting. Now if something provents the oxygen from reaching the iron through the water, then no rusting will take place, thus natural water may contain properties which will prohibit rusting through preventing the oxygen from reaching the iron. Thus it is plain how in many cases iron will corrodue faster in clear water than in sewage, the amount of free oxygen is less and hence, the action is less. This theory also explains why it is that iron and steel immersed in water or imbedded in the earth below where the free oxygen from the air can reach it will last indefinitely without corroding to any great extent.

Any process for the prevention of rust requires that there be a clean surface on which to work and the cleaning of materials may be accomplished in three ways, pickling, tumbling and sand blast.

Pickling means the removing of scale or other foreign substances by the action of acids, sulphuric, muriatic and hydrofloric acids are all valuable agents for this purpose. Sulphuric acid solutions are used generally of strengths of one part sulphuric acid to twenty parts water at 150 deg. Fahrenheit. Muriatic acid is used in smaller plants in place of sulphuric acid; one part to four parts water. Care must be taken against overpickling which leaves the work seamed. Hydroflouric acid is very satisfactory for removing sand since it does not act on the metal. The formula for use is six gallons of hydroflouric acid, four gal. of muriatic acid and forty gallons of water. This should be used warm not hot. In order to obtain good results the work must be agitated in the liquid, being done to a large extent by hand, but mechanical power is coming into use with better results.

The tumbling process is a mechanical means of removing scale and dirt.

The water rolling process produces a smoother surface than the other processes. The castings are rolled in a tumbling drum loaded with stars and gravel and filled three fourths full of water. To this mixture is added fifteen pounds of muriatic acid, two pounds of grey ground sal amoniac. The whole is rolled from two and a half to five hours. The dry tumbling process polishes the casting as well as cleans them. In loading the drum put in first a layer of shot then a layer

of castings and continue in this manner. One third shot and two thirds castings is about the right proportion for ordinary tumbling.

The simplest definition of sand blasting is a stream of sand and air under pressure. The cutting value of the flow is greater when it strikes the object slant wise rather than straight. Different kinds of apparatus can be purchased for use in this work. The pressure of the air used in the sand blast is maintained at about 60 pounds per sq. in.

It has long been known that if iron has been made the anode in an electrolytic circuit it will not rust, providing the current passing is sufficient to protect it. Zinc is electro-positive to iron, and when the two metals are in contact and wet with a corroding medium, zinc will pass into solution and the iron will be protected.

There are three methods of galvanizing or plating with zinc, hot ~~dip~~ dipping process, "cold" or electro process, and sherardizing.

The hot dipping process is a process by which the materials are coated by dipping in a hot bath of spelter or slab zinc. After the work comes from the cleaning processes it goes thru the inspection and then is dipped in muriatic acid one to one liquid measure. The work is then dried either in an oven or on plates over the fire. The drying place should be near the dipping kettle as care must be taken not to dry too long or get too hot as it will burn the muriatic acid off and the piece will have to be dipped again. When properly dried the salts of muriatic acid should show on the surface of the work as a white powder. The work is dipped directly after drying and should not be allowed to get cold or stand over night as oxidation and rusting will again attack the clean surface.

The most important thing about a galvanizing process is the firing of the kettles. A layer of about six inches of lead is placed in the bottom for the protection of the kettle; above this is the molten spelter and at the top a flux of salamoniac.

The temperature of the zinc cannot have definite rules laid down. These things must be learned by experiment and practice. The temperature ranges from 750 deg. to 925 deg. F. The article to be dipped is dropped thru the flux into the molten zinc and kept there until it is the temperature of the zinc. It is then rinsed or washed around in the metal in such a way that the flux will come in contact with all parts of it.

When the article is thoroughly coated clear a space on the surface of the metal with the skimmer, sprinkle on a little dry salamoniac and draw the article slowly from the metal. Hold the article in such a position as to cause the surplus metal to flow to one point and just as the drop starts to harden remove it with a stiff brush or old file. Expose the article to the air until crystals appear and rub lightly with a brush wet with clear water. Do not dip light castings in water.

The Schoop metal spray process has been perfected by three stages of development; the liquid metal process, involving a tank for hot metal weighing about one ton was non-portable; the next stage consisted of apparatus which was portable and galvanizing was accomplished by spraying zinc dust thru a flame. The metal in the pastic condition produced a coating and is yet the most economical method of coating with zinc; the last invention is the gun, weighing about four pounds, which is fed by means of a metal wire and sprays the hot molten metal upon the surface to be plated. The thickness of a single coating is about one thousandths of an inch. The operator easily can distinguish the places where there is no coat also the difference between the first and second coat. Two thousandths of an inch well impacted on a surface is just as effective as a thicker coat and since the cost increases as the thickness, care should be taken not to put on more than necessary. For metal spraying the work should be thoroughly cleaned and pores opened by preliminary sand blasting, since the action of the metal spray, with the exception of the few cases when there is chemical affinity, is a purely mechanical one and restricted to superficial pores of the object. However, with a thoroughly cleaned opened surface, a durable, adherent protective coating is obtained. In general the application of the metal spray process may be divided into five groups; protective coatings, bonding or junction coatings, electrical coatings, decorative coatings, detachable coatings or copies of the objects.

The tinning of objects is a hot dip process similar to galvanizing. All work must be cleaned by some one of the methods as hitherto described. All paint or grease must be removed before processing. The sand blast may be used for this or a strong solution of caustic soda or soda ash. Immerse the object in the hot liquid and when free from matter remove and rinse. This process should precede pickling.

When the work has been made perfectly clean from sand, scale, rust, grease or paint by some one of the treatments described, it is ready for the final operations. It should now be put in the alkali solution and be allowed to remain there for several minutes. From the alkali solution the work is to be passed into the rinsing tank, where care should be taken that all traces of the alkali are removed.

When this is accomplished the work is to be given a few minutes immersion in muriatic acid and water. The object of this dip is to remove any trace of rust that may have formed in the work. After this dip muriatic acid and water, which should never be omitted, the work is to be dipped in muriate of zinc, which is the last dip previous to dipping in molten tin. If roughing and finishing kettles are to be used remove the work from the muriate of zinc solution and put directly into the roughing kettle. After the work has remained in the roughing kettle take the wire by which the work has been handled in the left hand and with a skimmer in the right hand, clear a space on the surface of the tin large enough to permit the wire full of work being removed without any of the dross or flux adhering to it. Remove the wire full of work and immerse it in the second kettle. Allow the work to remain in the second kettle for a fraction of a minute until the heat of the work attained in the first kettle is reduced to about the temperature of the tin in the second kettle, which, for most purposes should be about 400 deg. Fahrenheit. When the work has about reached the heat of the metal draw it quickly from the tin and after a few rapid swinging motions to free it of surplus metal plunge it into a tank of kerosene oil. It should be allowed to remain in the oil long enough to set the layer of tin. It should then be immersed in water and thrown in dry sawdust to dry and remove the oil. For special design objects such as wire and the like there are special contrivances used but this gives the method of tinning as it has been developed.

The art of electro galvanizing and its industry is not the result of an invention but was simply created within the last twenty years. The force of necessity in protecting such articles as springs, small wire nettings, screws, bolts, nuts and the like which could not up to that day be satisfactorily galvanized by the hot process brought about electro galvanizing. The cold galvanizing has its advantages being suitable for treating the larger objects especially goods that have been hardened and tempered and all kinds of machine parts, perferationsand threads. Zinc~~k~~ing is affected by electro deposition from a bath, containing salts of zinc and aluminum and the ease with which it may be applied has made this industry during the last ten or twelve years grow very rapidly. Electro zincing is now being applied to many iron and steel articles which could not as readily be treated in any other way. The fundamental basis of this process is a tank containing the plateing solution or an electrolyte and an anode and cathode. The anode is the positive element from which the metal is taken to go in solution taking the place of that being plated upon the cathode or casting.

A cast anode is better than the plate form of zinc as the structure is more open and crystaline and is more readily disintegrated under the action of current. The shape of the anode can be either eliptical, round, or flat.

The cost of this process is greater in first cost than the cost of the other processes, due to the increase size of plant owing to the slower process. The cost of one cubic foot of electrolytic bath, however, is but a fraction of one cubic ft. of galvanizing bath and the

cost of the tanks is less.

The materials to be electro galvanized are cleaned in the same manner as hitherto described. Work to be electro plated must be cleaned better than for the hot process, that is in electro-plating a surface upon which any dirt or oil is adhering, while the hot method will plate if the work is not absolutely clean, although it is not a perfect rust preventative.

There are many different formulas for the galvanizing solutions or electrolytes, one of which is as follows; zinc sulphate 200 pounds, sulphate of sodium (crystal) 20 pounds, sulphate of aluminum 10 pounds, Borax acid three pounds, water to make 100 gallons.

Sherardizing, or dry galvanizing is a process whereby articles of iron and steel are rendered rust proof by applying a coating of zinc dust. The coating produced by this process is first an alloy with the underlying metal. After this alloying action is completed the outer layer of zinc is deposited, the zinc penetrating into every crevice and cavity radically different from any other zinc coating. Briefly stated this coating is not a pure layer of zinc but a zinc iron alloy. Sherardizing may be defined as a process of sublimation and adhesion when considered in connection with the theory of ions. The process of passing directly from the solid to the gaseous and from the gaseous to the solid state, in both cases stepping over the liquid state, is called sublimation.

In this process the sublimation is accomplished by placing the object to be coated and the zinc dust in a drum and heating, causing the zinc to sublime on the outer surface of the object.

As in all previous processes the object to be coated must be thoroughly cleaned. It should be placed in the sherardizing drum as soon as possible after cleaning to prevent oxidation.

To load the sherardizing drum put in alternate layers of zinc dust and material until within a few inches of the cover to allow for expansion. From three to five pounds of zinc dust should be used to each 100 pounds of material. The cover should be made dust tight not air tight, and the container placed in the furnace.

If common or blue dust is used, the total run is to be about 5½ hours of which about two hours must be allowed for attaining a maximum furnace temperature of 440 deg. C and about 3½ hours for a temperature of 440 to 450 deg. C. The metallic percentage of zinc should be from 35 to 45 per cent. The drum should be rotated throughout the whole run at about ½ R. P. M. At the end of the run the container, if blue dust is used, should be removed from the furnace and not opened until the temperature has dropped to 100 deg. C. This will require from eight to twenty four hours, depending upon the outside temperature.

The painting of material to prevent rust is the one that is used almost universally in construction work. Since water is necessary for electrolysis a pigment to be inhibited must either be a water shedder or neutralize the effect of water. It has been found by experiment that certain salt, such as bichromates of soda and pot ash are inhibitives to corrosion. Experiments have been found which have discovered certain kinds of these salts which can be used as pigments. A series of these compounds were prepared and tested; but it soon became apparent that while some afforded protection. to steel others did not. The raw materials used, the method of preparations, the amount and character of the contained impurities, together with other factors, had a marked influence upon the efficiency of these compounds. It was even found that a series of chrome salts, all of which theoretically should have possessed inhibited value, were in many cases actually stimulative.

Not only in the nature of the pigment itself, but also the amount and quantities of impurities in it decides its value as a corrosive preventative. The solubility of the pigment, and the ease with which it is ionized when brought into contact with water are also important considerations. If the pigment is of a basic nature, and therefore tends to increase the number of hydroxyl ions, it is sufficiently high to furnish protection. If the pigment is acid in nature, or contains any free acid which is easily hydrolized it is quite certain to appear in the stimulation groups.

If the immunity from rust of painted surfaces depends mainly upon the pigments with which the steel is coated, it is fair to believe that this immunity from attack will be reinforced by providing that the ~~simpl~~ principal base content of the pigment shall be a good non-conductor of electricity. The use of a paint inhibitive in both pigment and vehicle antagonizes the forces that cause corrosion, the greater the inhibitive value of the pigment and the vehicle greater will be the defensive action working against the factors which produce corrosion and rapid decay.

The Parker Method of Rust Proofing is a process of coating the outside of the metal with a chemical compound of iron phosphates and manganese iron which are supposed to be immune to rust. Material is first cleaned by one of the processes previously given and then placed in a bath containing manganese dioxide, phosphoric acid and water, all heated to a temperature of 210 deg. Fahr. The metal is

allowed to remain in this bath until all effervescing stops or about 2½ hours. The work is then removed and given an oil coating, Since this is the one to which special attention has been given, the next chapter will be devoted to this method.

The probable reaction of the phosphoric acid with the iron is as follows:

$$4CaH_4\ (PO_4)_2 \text{ plus } 8Fe \text{ plus } 2O_2 = 2CA_2H_2\ (PO_4)_2 \text{ plus}$$
$$Fe_3\ (PO_4)_2\ Fe_3\ O_4\ Fe_2\ (PO_4)_2 \text{ plus } 6H_2$$

PART III

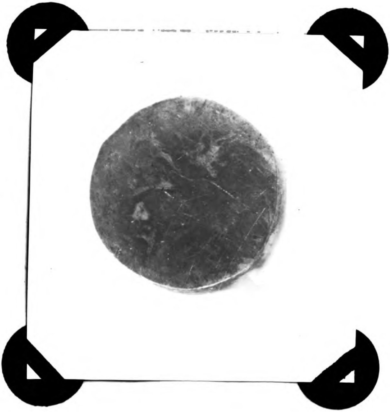
Four samples of metal, tool steel, cold rolled, cast iron and wrought iron were selected and sent to the Parker Co. to be rust proofed. Upon being treated these samples were broken and the surfaces buffed and placed under a microscope. No satisfying results were to be obtained from the microscopic structure as to any change in the surface of these samples. The sample of wrought iron was then etched with sulphuric acid without any result.

After again polishing the sample, iodine was used to etch the surface for a phosphorus test. The result of which is shown in cut one. No satisfying results were to be obtained by this treatment. Either the iron phosphate forms in such a thin layer at the outer surface of the sample that it is not made apparent by this test or else the phosphate combinations are not formed.

By means of a file a thin layer of the outer surface of the samples was removed. One portion of these filings was dissolved in nitric acid (Sp. gr. 12) until it went into solution. The volume was increased three times with water and brought almost to the boiling point. 5 grms. $Pb_3 O_4$ was added cautiously and boiled for about 5 minutes. The mixture was then allowed to stand in the dark. The lead settled to the bottom while the liquid above became dark purple showing the presence of manganese in large quantities.

Another portion of the filings was dissolved in a solution of nitric acid and evaporated to nearly dryness, then made strongly acid again with nitric acid and boiled down as before. The solution was then diluted with water to the original volume and warmed. A

Figure One.



few C. C. of ammonium molybdate was added and a yellow precipitate $(NH_4)_3 PO_4 \quad 12 M_oO_3)$ was formed denoting the presence of iron phosphate in large quantity.

Two samples which were rust proofed by Parker Co. for exhibition purposes were tested for their rust resisting qualities. One piece was placed half immersed in water. The other in the open air only. The test, covering two months duration, showed that the piece half immersed in water rusted while the piece in air was free from rust.

The conclusion then from our limited observation is that the phosphate and manganese compounds are formed only to an exceedingly thin depth at the other edge and that rusting action does take place to a more or less degree. Thus where conditions for rusting are favorable the outer surface is soon eaten away and rusting action will progress very rapidly.

The Parker method, therefore, though not being proved absolutely inadequate by such limited experiments, should be investigated further by those interested before adopting the method for use very extensively.

KW 2/17/14