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PASSIVATION OF FERROUS METALS

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This invention relates to the passivation of ferrous metals such as iron and steel having a tendency to rust, and more particularly to a process for treating a surface of such a metal to provide highly advantageous rust resisting and rust inhibiting properties.

Because of the great commercial importance of iron and steel intensive scientific investigation has been devoted to the determination of methods for increasing the resistance to rusting of such metals. It is found that under certain conditions a surface of such a metal may become "passive" or resistant to rusting. It appears that passivation is caused by the protective action of a continuous film of a suitable oxide formed on the surface, which film is so thin that it does not even exhibit interference colors. Various processes have been proposed for passivating the surfaces of iron and steel, but in most cases such processes are complicated or expensive, or do not provide surfaces which will resist rust as completely or for periods as long as desired .

The present invention provides a process for treating surfaces of ferrous metals such as iron and steel having a tendency to rust which process is simple, inexpensive and provides excellent rust resisting properties which are effective for periods considerably longer than are usually obtainable.

According to the present invention, a surface of such a ferrous metal is first treated to cause recrystallization, roughening, and occlusion of hydrogen by the metal and is then exposed to hydrogen peroxide in substantial concentration for a period long enough to cause highly effective passivation of the metal surface.

Further details of the process of the invention will be provided in the following discussion which also points out other advantages of the invention.

Highly advantageous results are provided by the process of the invention when the surface of metal to be treated is initially clean and free from rust, dirt, grease, etc., although beneficial results in rust inhibition are provided by the process even if the surface of the metal before treatment according to the process is contaminated with such foreign materials, since the treatment of the invention largely if not entirely removed such contaminating materials. Best results are provided when the surface of metal treated according to the invention is also free of deep scars, cracks, pits or segregated impurities, since these tend to interrupt the continuity of the passivating film on the surface and provide

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focal areas for the commencement of rusting; however, beneficial results are provided even if the metal surface has these defects.

According to the present invention it is important that the metal surface prior to exposure to the hydrogen peroxide be in the roughened, recrystallized state and contain occluded hydrogen; however, in the treatment prior to exposure to the hydrogen peroxide it is not necessary that the recrystallization, roughening and hydrogen occlusion be accomplished in any particular order or even in individual steps.

The treatment of the metal surface prior to its exposure to the hyrogen peroxide must involve a heating of the metal of the surface to a temperature and for a time sufficient to cause recrystallization of the metal; the lowest temperature at which recrystallization of pure iron occurs is about 450° C. while that for steels is somewhat higher because of their contents of carbon or other metals; in general, temperatures are preferred which are substantially above the lowest crystallization temperatures but, of course, less than the temperatures at which the metal may be damaged.

Said prior treatment will also involve treatment of the metal of the surface to cause occlusion of a substantial amount of hydrogen therein; this may be accomplished by heating said surface metal in gaseous hydrogen to a temperature sufficient to cause hydrogen occlusion; or by pickling or etching the metal in a suitable solution. In causing hydrogen occlusion by heating the metal in hydrogen, the metal may be heated to a temperature between about 300° C. and more elevated temperatures which are not sufficient to damage the metal, shorter times of heating being required when higher temperatures are employed; advantageous results are obtained when temperatures between about 850° C. and 950° C. are employed since substantial hydrogen occlusion as well as recrystallization is obtained in a few minutes. In causing hydrogen occlusion by pickling or etching, the metal may be exposed to a suitable pickling or etching solution chosen from those well known for such a purpose; in general, a solution of a suitable non-oxidizing acid which forms soluble salts upon reaction with iron, such as hydrochloric or sulfuric acid, may be employed. The metal surface may be chemically or electrolytically pickled or etched.

The treatment prior to exposure to hydrogen perioxide will also involve roughening of the surface of the metal; this may be accomplished by oxidation and reduction of the surface of

the metal, by pickling or etching the metal at the surface, or by other means such as mechanical abrasion. Oxidation may be achieved by exposure of the metal to an atmosphere containing gaseous oxygen such as air at a temperature and for a time sufficient to oxidize the metal; heating of the metal will reduce the time required. The oxidized surface may be reduced by treating it in a reducing atmosphere such as hydrogen for a time and temperature sufficient to reduce it to metal; the times and temperatures indicated above for hydrogen occlusion are suitable. Pickling or etching solutions and processes for ferrous metals which are well known in the art may be employed, as indicated above.

The treatment of the surface of the metal prior to exposure to the hydrogen peroxide may be accomplished in separate steps of recrystallization, roughening and hydrogen occlusion in any suitable order. For example, such steps may be a suitable combination of the steps indicated above.

However, it is not necessary that separate steps be employed; indeed, it is advantageous in carrying out the process of the present invention to effect the treatment of the metal at the surface to be passivated prior to exposure to the hydrogen peroxide by a sequence of steps each of which may provide more than one result. For example, it has been found that satisfactory pretreatment is obtained if the metal at the surface is heated in an atmosphere containing hydrogen to a temperature above the recrystallization temperature of the metal; this causes both hydrogen occlusion and recrystallization. This treatment can be followed by an exposure of the metal to an acid pickling or etching solution which will cause roughening of the surface of the metal and further hydrogen occlusion.

As another example the metal at the surface prior to exposure to the hydrogen peroxide may be heated in the presence of gaseous oxygen, as in air, to a temperature above the recrystallization temperature of the metal. The oxidized metal may then be pickled or etched in a suitable solution which will remove the oxide. The initial heating of the metal above the recrystallization temperature will cause recrystallization of the metal and oxidation of its surface, while the subsequent pickling or etching step will not only remove the oxide but cause roughening of the surface and occlusion of hydrogen into the metal.

As another alternative method, the metal surface prior to exposure to hydrogen peroxide may be heated in the presence of gaseous oxygen as in air to oxidize the metal, and then may be heated in the presence of gaseous hydrogen to reduce the oxide to metal. Either or both of the heating steps should be above the recrystallization temperature of the metal to cause recrystallization of the metal. The oxidation and reduction treatment will cause roughening of the metal, the reduction in hydrogen will cause occlusion of hydrogen to the metal, and the heating above the recrystallization temperature will cause recrystallization of the metal.

As another alternative method, the metal surface to be passivated is, prior to exposure to hydrogen peroxide, oxidized by suitable means, then reduced by suitable means, and thereafter pickled or etched in an acidic solution. Either the oxidation or reduction or both should involve heating of the metal to temperature above the recrystallization temperature of the metal

to cause recrystallization of the metal; the oxidation, reduction and pickling steps cause roughening of the metal, while the pickling step also causes hydrogen occlusion. If the reduction is carried out in the presence of hydrogen, this step also causes hydrogen occlusion.

As is apparent, the treatment of the metal prior to the exposure to hydrogen peroxide may be carried out in these or other suitable manners. It is only necessary that the metal prior to exposure to the hydrogen peroxide be chemically clean, recrystallized, roughened and contain occluded hydrogen.

The hydrogen peroxide to which the surface of the metal in this condition is next exposed in the process of the invention is in substantial concentration. Particularly advantageous results in passivating the metal are provided when the hydrogen peroxide is in a concentration in solution of at least five per cent by weight, since lower concentrations tend to promote rather than inhibit rusting. Satisfactory results have been obtained with aqueous solutions containing hydrogen peroxide in concentrations of from five per cent by weight of the solution to about thirty per cent by weight of solution, the latter concentration being the highest commercially available. The hydrogen peroxide advantageously is in aqueous solution since this is the most economical and most readily available form of hydrogen peroxide, but it may be employed in solution in other liquids.

The hydrogen ion concentration of the aqueous solution of hydrogen peroxide employed is not highly important since beneficial results may be obtained with acidic, neutral or even alkaline solutions of hydrogen peroxide; in general, however, best results are obtained when the solution is somewhat acidic since such a solution is more stable. Advantageous stability of the hydrogen peroxide solution is obtained when the pH of the solution is between 1 and 2.

In carrying out the process of the invention, the metal surface which was treated as indicated above to cause it to be in the chemically clean, recrystallized and roughened state and to contain occluded hydrogen, is exposed to, as by immersion in, the hydrogen peroxide solution. To prevent dilution of the hydrogen peroxide at the surface of the metal with a consequent possibility of rusting of the metal, it is advantageous to insure that the metal prior to immersion in the hydrogen peroxide solution is dry or that if the metal is wet it is introduced into the solution under conditions such that relative agitation between the liquid of the solution and the surface of the metal is provided. Such agitation will prevent localized dilution of the hydrogen peroxide and diminish the possibility of rusting.

It is also advantageous that at the time of initial exposure of the surface of the metal to the hydrogen peroxide both the metal and the solution be at a relatively low temperature to prevent initial rusting. However, after the metal is immersed in the hydrogen peroxide solution, it is advantageous to heat the solution, since the passivation reaction is hastened. For example, passivation proceeds much more rapidly at higher temperatures and approaches completion in fifteen to twenty minutes at the boiling point of the liquid solution, whereas the reaction is much slower at room temperature and the protection due to passivation may still be

poor after one hundred hours exposure to hydrogen peroxide.

In some cases it may be advantageous to remove rapidly the water from the surface of the passivated metal if the metal surface has been exposed to an aqueous solution of hydrogen peroxide. This may be accomplished by immersing the treated surface in alcohol for a few minutes and then allowing the surface to drain dry. However, in most cases, drying of the treated metal surface in air is satisfactory.

The following examples illustrate several processes embodying the present invention which have been found satisfactory:

Example 1

A low carbon steel part was degreased by the use of trichlorethylene and then heated in gaseous hydrogen at about 925° C. for about fifteen minutes. The part was then immersed for about one minute in a hydrochloric acid solution containing about fifty per cent hydrochloric acid by weight, removed, and washed in cold running tap water for about two minutes. The excess water was shaken off and the part was immediately immersed with agitation in ten per cent by weight hydrogen peroxide solution at room temperature. The solution was heated to its boiling point and maintained at that temperature for fifteen minutes. The part was cooled for thirty minutes in the hydrogen peroxide solution, removed, and then transferred directly to a bath of methyl alcohol. After about two minutes it was removed from the bath, given a final rinse in fresh alcohol for about three minutes, and drained dry. This was found to be a preferable treatment because of its simplicity.

Example 2

A part formed of Armco iron, which is commercially pure iron, was degreased in trichlorethylene, washed in tap water, and then heated in an air oven at about 550° C. for about five minutes to cause oxidation of the surface of the part. The oxide covered part was then immersed for about a minute in a fifty per cent hydrochloric acid solution at room temperature to remove the oxide coating. The pickled part was washed for about five minutes in cold water, and then immersed with agitation in a twenty per cent aqueous solution of hydrogen peroxide at room temperature. The hydrogen peroxide solution was then heated to boiling temperature at which it was maintained for ten minutes, after which the part was cooled in the solution for about thirty minutes. The part was then removed, rinsed in alcohol, and dried.

Example 3

A steel part was heated in air at about 550° C. for five minutes to cause an oxide coating to form thereon. The oxidized part was then heated in hydrogen to a temperature of about 925° C. for fifteen minutes and cooled in a non-oxidizing atmosphere. The oxidized and reduced part, the surface of which was in the roughened, recrystallized state, and contained occluded hydrogen, was next immersed in a thirty per cent solution of hydrogen peroxide at room temperature. The solution was then heated to its boiling point and the part maintained therein at that temperature for five minutes. The part was then cooled in the solution for about one-half hour, after which it was dried in air.

Example 4

The steel part, after being degreased and water washed, was heated in air at about 550° C. for about five minutes so that its surface became oxidized; the oxidized part was then heated in hydrogen at a temperature of about 925° C. for about fifteen minutes so that the oxide was reduced to metal, and cooled in a non-oxidizing atmosphere. The reduced part was then immersed in a fifty per cent hydrochloric acid solution for about one minute and washed in cold water. The washed part was immediately immersed with agitation in a fifteen per cent hydrogen peroxide solution at room temperature. The solution with the part therein was heated to its boiling point for about ten minutes and then cooled for about one-half hour. The part was removed, rinsed in alcohol and dried in air.

The iron or steel part produced by the process of each of the above examples had a passive surface which completely resisted rusting for long periods of time. It was found that such a part displayed no sign of rusting even after being exposed to an atmosphere periodically contaminated with acid fumes for a period of two months. Accelerated corrosion tests involving exposing the part to hot aerated water caused no sign of rusting of the part even after it had been exposed for two months to such conditions. Iron and steel parts having no passivation treatment, or treatment involving only immersion in hot concentrated hydrogen peroxide were badly corroded if not entirely destroyed after being exposed to such conditions for such a period.

Surfaces of ferrous metals such as iron and steel, ordinarily having pronounced tendencies to rust, after treatment according to the process of the present invention apparently are coated with a highly adherent continuous film of a highly stable oxide which is so thin as to be invisible and which, particularly when the surface of the metal is originally free of defects such as deep scars, cracks, pits or segregated impurities, very effectively and completely prevents rusting of the metal for long periods of time. In the effectiveness and duration of their resistance to rusting, ferrous metal surfaces treated according to the process of the present invention are believed to be superior to most, if not all, passivated surfaces produced by other processes.

In the process of the present invention the pretreatment of the surface of the metal to cause it to be in the chemically clean, roughened, recrystallized, hydrogen occluded state, prior to treatment with hydrogen peroxide is highly important in producing the highly effective long existing passivation of the surface by the hydrogen peroxide. It was found, for example, that if the metal was not so treated prior to exposure to the hydrogen peroxide, the passivation which was obtained was incomplete and of short duration. The reasons for the beneficial effects of the pretreatment are not definitely known, but it is believed that cleanliness of the surface promotes the formation of the passivating film, that recrystallization causes the metal of the surface to be in a more active crystalline form, that the roughening of the surface permits better adherence of the passivating oxide film and removes surface and subsurface contaminants, and that the occlusion of hydrogen provides temporary inhibition prior to the passivation by hydrogen peroxide and promotes the formation of con-

tinuous oxide film having a passivating action which may exist for long periods of time.

Various modifications may be made in the steps and processes indicated above as embodying the invention. For example, processing steps and combinations thereof for the treatment of the metal surface prior to the exposure to the hydrogen peroxide different from those indicated above may be employed; temperatures different from those indicated above for recrystallization, hydrogen occlusion, oxidation and reduction may be employed; and procedures for treating the metal with hydrogen peroxide different from those indicated above may be followed.

The process of the present invention finds wide application in improving the rust resistance of surfaces of ferrous metals having a tendency to rust. It has been found to be of particular usefulness in providing rust resistant surfaces on iron and steel parts, such as electrodes, employed in electron discharge devices in which rust is highly detrimental to operation.

It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty reside in the invention.

What is claimed is:

1. The method of improving the rust resistance of a surface of a ferrous metal object which has a tendency to rust and which is free from deep scars, cracks, pits or segregated impurities, said method comprising heating said object in an atmosphere of hydrogen at a temperature of about 925° C. for about 15 minutes, cooling said object and immersing it in an aqueous solution of hydrochloric acid containing about 50 per cent by weight of hydrochloric acid for about one minute, washing said object, immersing it with agitation in an aqueous solution of hydrogen peroxide at room temperature, said solution of hydrogen peroxide containing about 10 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having said object immersed therein to approximately its boiling point, maintaining the solution at that temperature for about 15 minutes, allowing said object to cool to substantially room temperature while in contact with said solution, and subsequently removing said object from said solution.

2. The method of improving the rust resistance of a surface of a ferrous metal object which has a tendency to rust comprising subjecting said object to a preliminary treatment comprising at least two of the operations of heating said object in the presence of oxygen until an oxide coating is formed on the surface, heating said object in an atmosphere of hydrogen at a temperature sufficient to cause occlusion of hydrogen at the surface of said object and to reduce any oxide coating present on the surface, and contacting said object with an aqueous solution of a non-oxidizing acid of sufficient strength and for a sufficient time to roughen the surface of said object by etching and to remove any oxide coating which may be present, said operation of heating in the presence of oxygen being followed by one of the other of said operations, at least one of said heating operations being carried out at a recrystallizing temperature for said metal until recrystallization of the metal at the surface of said object occurs, the surface after said preliminary treatment being free from deep scars, cracks, pits or segregated impurities, and subsequent to said preliminary treatment immersing said object with agitation, in an aqueous solution of hydrogen peroxide at a temperature in the vicinity of room temperature, said solution of hydrogen peroxide containing at least 5 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having said object immersed therein to a temperature in the vicinity of its boiling point, maintaining the solution at that temperature for at least about 5 minutes and allowing said object to cool while in contact with said solution.

3. The method of improving the rust resistance of a surface of a ferrous metal object having a tendency to rust comprising subjecting said object to a preliminary treatment comprising heating said surface in the presence of hydrogen at a recrystallizing temperature for the metal until recrystallization of the metal at said surface occurs and roughening said surface by etching with a non-oxidizing etching solution, and subsequent to said preliminary treatment immersing said object with agitation in an aqueous solution of hydrogen peroxide at a temperature in the vicinity of room temperature, said solution of hydrogen peroxide containing at least 5 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having said object immersed therein to a temperature in the vicinity of its boiling point, maintaining the solution at that temperature for at least about 5 minutes and allowing said object to cool while in contact with said solution.

4. The method described in claim 3 wherein the heating in hydrogen is conducted at a temperature between about 850° C. and about 950° C.

5. The method of improving the rust resistance of a surface of a ferrous metal object having a tendency to rust comprising subjecting said object to a preliminary treatment comprising heating said surface in the presence of oxygen until said surface becomes oxidized and heating said oxidized surface in the presence of hydrogen at a temperature above about 300° C., but below that at which the metal is damaged, until said oxidized surface is reduced, at least one of said heating operations being conducted at a recrystallizing temperature for said metal until recrystallization of the metal at said surface occurs, and subsequent to said preliminary treatment immersing said object with agitation, in an aqueous solution of hydrogen peroxide at a temperature in the vicinity of room temperature, said solution of hydrogen peroxide containing at least 5 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having said object immersed therein to a temperature in the vicinity of its boiling point, maintaining the solution at that temperature for at least about 5 minutes and allowing said object to cool while in contact with said solution.

6. The method of improving the rust resistance of a surface of a ferrous metal object having a tendency to rust comprising subjecting said object to a preliminary treatment comprising heating said surface in the presence of oxygen at a recrystallizing temperature for said metal until recrystallization of the metal at the surface occurs and until an oxide coating is formed on said surface and exposing said surface having an oxide coating to the action of a non-oxidizing pickling solution of sufficient strength and for sufficient time to remove said oxide coating, said pickling solution being one which is capable of etching the surface of said metal and thereby causing hydrogen to be occluded at said surface, and subsequent to said preliminary treatment im-

mersing said object with agitation, in an aqueous solution of hydrogen peroxide at a temperature in the vicinity of room temperature, said solution of hydrogen peroxide containing at least 5 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having said object immersed therein to a temperature in the vicinity of its boiling point, maintaining the solution at that temperature for at least about 5 minutes and allowing said object to cool while in contact with said solution.

7. The method of improving the rust resistance of a surface of a ferrous metal object which has a tendency to rust and which is free from deep scars, cracks, pits or segregated impurities, said method comprising heating said object in an atmosphere of hydrogen at a temperature in the vicinity of 925° C. until recrystallization of the metal at the surface of the said object occurs, cooling said object and immersing it in an aqueous solution of a non-oxidizing acid for a sufficient time to roughen the surface of said object by etching, immersing said object in an aqueous solution of hydrogen peroxide at a temperature in the vicinity of room temperature, said solution of hydrogen peroxide containing at least 5 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having the object immersed therein to a temperature in the vicinity of its boiling point, maintaining the solution at that temperature for at least about 5 minutes, and allowing said object to cool while in contact with said solution.

8. The method of improving the rust resistance of a surface of a ferrous metal object having a tendency to rust comprising subjecting said object to a preliminary treatment comprising heating said surface in the presence of hydrogen at a recrystallizing temperature for the metal until recrystallization of the metal at said surface occurs, and roughening said surface by etching with a non-oxidizing etching solution, and subsequent to said preliminary treatment drying the surface of said object and immersing said object while dry in an aqueous solution of hydrogen peroxide at a temperature in the vicinity of room temperature, said solution of hydrogen peroxide containing at least 5 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having said object immersed therein to a temperature in the vicinity of its boiling point, maintaining the solution at that temperature for at least about 5 minutes, and allowing said object to cool while in contact with said solution.

9. The method of improving the rust resistance of a surface of a ferrous metal object having a tendency to rust comprising subjecting said object to a preliminary treatment comprising heating said surface in the presence of oxygen until said surface becomes oxidized and heating said oxidized surface in the presence of hydrogen at a temperature above about 300° C., but below that at which the metal is damaged, until said oxidized surface is reduced, at least one of said heating operations being conducted at a recrystallizing temperature for said metal until recrystallization of the metal at said surface occurs, and subsequent to said preliminary treatment drying the surface of said object and immersing said object while dry in an aqueous solution of hydrogen peroxide at a temperature in the vicinity of room temperature, said solution of hydrogen peroxide containing at least 5 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having said object immersed therein to a temperature in the vicinity of its boiling point, maintaining the solution at that temperature for at least about 5 minutes and allowing said object to cool while in contact with said solution.

10. The method of improving the rust resistance of a surface of a ferrous metal object having a tendency to rust comprising subjecting said object to a preliminary treatment comprising heating said surface in the presence of oxygen at a recrystallizing temperature for said metal until recrystallization of the metal at the surface occurs and until an oxide coating is formed on said surface and exposing said surface having an oxide coating to the action of a non-oxidizing pickling solution of sufficient strength and for a sufficient time to remove said oxide coating, said pickling solution being one which is capable of etching the surface of said metal and thereby causing hydrogen to be occluded at said surface, and subsequent to said preliminary treatment drying the surface of said object and immersing said object while dry in an aqueous solution of hydrogen peroxide at a temperature in the vicinity of room temperature, said solution of hydrogen peroxide containing at least 5 per cent by weight of hydrogen peroxide, raising the temperature of the hydrogen peroxide solution having said object immersed therein to a temperature in the vicinity of its boiling point, maintaining the solution at that temperature for at least about 5 minutes and allowing said object to cool while in contact with said solution.

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