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REMOVAL OF CORROSION PRODUCTS FROM METAL SURFACES

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ABSTRACT OF THE DISCLOSURE

Corrosion products are removed from metal surfaces by contacting the surface with hydrogen chloride gas and allowing the hydrogen chloride gas to react with the surface to produce a soluble reaction product and then applying a solvent for the reaction product to the surface in an amount sufficient to dissolve and remove substantially all of the reaction product.

The present invention relates to a process for removing corrosion products from metal surfaces. More particularly, the present invention relates to a process for removing the corrosion products and other types of scale from metal surfaces by means of gaseous reactants.

Many methods for removing corrosion products from the surfaces of ferrous metals have been proposed over the years. In general, the bulk of these methods have comprised the use of aqueous solutions of acids, usually sulfuric acid, to dissolve corrosion products such as iron oxide. A major disadvantage of such methods has been the reaction of dissolved ferric iron in the cleaning solution with the iron in the metal surface to be cleaned. This reaction results in oxidation of the iron in the metal surface by the ferric ions in solution with the consequent sacrifice of some metal from the cleaned surface.

In addition, the art has continually attempted to develop processes for removal of corrosion products, scale and the like which will decrease the time required to complete removal of corrosion products, which will result in the uniform scale removal, which do not require high energy inputs in the form of heat, electricity or the like and which will effectively penetrate crevices, pits, etc. which often make complete cleaning quite difficult.

The process of the present invention which comprises the use of a gaseous reactant processes all of these advantages and others which will be apparent to those skilled in the art.

It is an object of the present invention to provide a process for the removal of corrosion products from metal surfaces in which a gas is used as the reactant.

It is a further object of the present invention to provide a process for the removal of corrosion products from metal surfaces in which anhydrous hydrogen chloride gas is used as the reactant.

It is a further object of the present invention to provide a process for the removal of corrosion products from metal surfaces in which a gas is used as the reactant and in which an inert gas is combined with the gaseous reactant.

Other objects and advantages of the present invention, it is believed, will be apparent from the following detailed description of specific embodiments thereof.

Briefly, the present invention comprises removing corrosion products and other scale from metal surfaces by contacting the metal surfaces with a gaseous reactant which

will convert the corrosion products and other scale to a more readily soluble reaction product. Thus, the present invention comprehends the use of hydrogen chloride gas to remove iron oxide corrosion products or other scale from metal surfaces including ferrous metal surfaces. In a preferred embodiment of the present invention, an inert gas is combined with the gaseous reactant to provide control over the reaction rate between the gaseous reactant and the corrosion products which are to be removed and to improve the overall efficiency of the corrosion removal process. As used in the present specification and claims, the "inert gas" which may be combined with the gaseous reactant is any gas which while present at the reaction site does not react in any way with the gaseous reactant or the corrosion products and does not react with the metallic surface being treated. For example, when hydrogen chloride gas is used to remove corrosion products from ferrous metal surfaces, gases such as nitrogen, carbon dioxide and, in some circumstances, air, may be used as the inert gas.

The present invention is particularly useful for the removal of industrial scales resulting from corrosion which conventionally occurs on the surfaces of boilers, heat exchangers, pipelines, etc. Such corrosion products generally consist primarily, if not entirely, of oxides of iron. An example of one type of reaction which occurs when such corrosion products are contacted with hydrogen chloride gas is believed to be as follows:

$$Fe_2O_3+6HCl\rightarrow 2FeCl_3+3H_2O$$

In practice, the vessel, pipeline or other surface to be treated is purged of air by the introduction of hydrogen chloride gas and excess hydrogen chloride gas is added to maintain a slight positive pressure throughout the sysytem. Progress of the reaction is observed by measurement of the quantity of gas consumed by the reaction, keeping the pressure constant. At the conclusion of the reaction, or at some selected time prior to conclusion of the reaction, the residual hydrogen chloride gas is displaced with a solvent suitable for the reacted scale or corrosion product such as a weak aqueous acid solution or water. Preferably, the metal surface is then subjected to conventional metal passivation and acid neutralization procedures.

It will be immediately apparent to those skilled in the art that the undesirable corrosive attack on cleaned metal surfaces which occurs in conventional cleaning processes where aqueous acid solutions are used as the cleaning agent are minimized by the use of a gaseous reactant to convert the corrosion or scale material to an easily removable reaction product. In addition, it has been found that the reaction between ferric ions and the cleaned metallic iron surface which occurs in conventional cleaning methods is very substantially reduced by practice of the present invention.

Since the presence of water slows the rate of reaction between the gaseous reactant and the corrosion products or scales, it is preferred that the surfaces to be treated be dried before treatment. In this regard, it should be pointed out that any water present will be converted to hydrochloric acid on contact with hydrogen chloride gas and that such acid may be expected to be highly corrosive on most metal surfaces.

It is highly desirable that the water formed during the reaction of hydrogen chloride and iron oxide scale be removed as vapor phase water. Condensed water will rapidly be converted to hydrochloric acid by the hydrogen chloride gas present and this will create the danger

of corrosion on the cleaned metal surfaces. In addition, as noted above, the presence of liquid water will decrease the rate of reaction between the gaseous reactant and the corrosion product and thus will decrease the efficiency of corrosion product removal. In some cases, the heat of reaction between the gaseous reactant and the corrosion product will cause the water formed by this reaction to be generated as harmless vapor. To assure that this water of reaction will be removed in the vapor state, it has been found desirable to admix the gaseous reactant with an inert gas. It has been found that the inert gas-reactant ratio may be adjusted to cause all of the water of reaction to be removed in the vapor state.

In addition, the use of inert gas in combination with the gaseous reactant permits control over the rate of reaction between the gaseous reactant and the corrosion products by controlling the proportion of inert gas to reactant. Control of the rate of reaction makes it possible to control the rate of heat evolution during the reaction. Control of heat evolution is essential in many pressure vessels, e.g., high pressure, high temperature steam generators, in order to avoid excessive heat differentials which would lead to undesirable stresses within the pressure vessel being cleaned.

The present invention is further illustrated by the following examples.

EXAMPLE 1

A section of line pipe having a diameter of two inches and a length of eight inches and having on its surface a scale identified primarily as ferric oxide was stoppered at both ends and a stream of anhydrous hydrogen chloride gas was passed through the pipe. An immediate exothermic reaction was initiated by the hydrogen chloride gas. After 15 minutes, the reaction, as indicated by the temperature of the pipes, had terminated. Inspection of the inner surface of the pipe made it apparent that the scale had reacted with the hydrogen chloride gas and that some water had been formed during the reaction. The pipe was then immersed in a beaker of water and the major portion of the reacted ferric oxide scale was observed to dissolve as ferric chloride.

EXAMPLE 2

A sample of ferric oxide was placed in a glass tube and was reacted for 15 minutes with a stream of anhydrous hydrogen chloride gas. The pressure was maintained at eight inches of water during the reaction. After completion of the reaction, the tube was flushed with distilled water and an iron determination was made on the water after passing it twice through the tube. This iron determination indicated that 88.2% of the original sample was reacted with the hydrogen chloride gas.

EXAMPLE 3

A sample of magnetic iron oxide (Fe_3O_4) was placed in a glass tube and was reacted for 30 minutes with a stream of hydrogen chloride gas under a pressure of eight inches of water. An extremely rapid and highly exothermic reaction was observed, the rate of which reaction was decreased by increasing quantities of water of reaction. After completion of reaction, the sample was back flushed with 1% acetic acid and an iron determination performed on the flush water after filtration. It was found that 81.2% of the sample was dissolved.

EXAMPLE 4

Coupons having dimensions of one inch by 4.25 inches were cut from a section of six-inch steel pipe having a mill scale coating thereon. These coupons were then contacted with anhydrous hydrogen chloride gas and, after washing, weight loss was determined. It was found that from 0.30 to 0.39 gram per coupon were removed by the hydrogen chloride gas treatment. Inspection of the treated coupons established that a highly effective removal of mill scale occurred.

The process of the present invention may be successfully applied to virtually any metallic oxide removal operation such as iron oxides, copper oxides and aluminum oxides. It has been found that the present invention substantially reduces the time required for removing corrosion products or scale as compared with conventional liquid treatment procedures. In addition, the gaseous reactant of the present invention is present at the same concentration at all reaction surfaces thereby eliminating the possibility of uneven scale removal which often occurs when liquid treatments are used because the concentration of reactants at the reaction surface may be influenced by the mixing procedure or the flow conditions of the liquid cleaning agent at the reaction surface. In addition, the gaseous reactant of the present invention does not require heating in order for the reaction to take place at a practicable rate and this gaseous reactant will more readily penetrate crevices, pits, etc. which liquid reactants would be likely to miss. Since moisture is generally considered to be undesirable in the practice of the present invention, it is preferred to use an anhydrous gas such as anhydrous hydrogen chloride as the corrosion product or scale removal agent. Similarly, if inert gases are combined with the gaseous reactants, they will also preferably be anhydrous.

The proportion of inert gas to gaseous reactant may be varied according to the nature of the corrosion product or scale being removed, the nature of the metal surface being treated, the nature of the article having the metal surface, the efficiency of cleaning required, etc. Thus, these proportions may be substantially equal or the gaseous reactant or the inert gas may be substantially predominant. Furthermore, the relative proportions of gaseous cleaning agent and inert gas may be varied during the course of a single corrosion product or scale removal operation. In general, the inert gas will be present in proper amount to cause the water of reaction to be maintained in the vapor phase. Although the present invention is not to be limited to any particular theory, it would appear that the function of the inert gas in this regard is based on equilibrium considerations. Thus, liquid water may be prevented from forming if the reaction rate, or temperature, or concentration of inert gas is such as to keep all of the water of reaction in the vapor phase.

Having fully described the present invention, it is to be understood that it is not to be limited to the specific details set forth, but is of the full scope of the appended claims.

I claim:

1. A process for removing iron oxide-containing corrosion products, scale and the like from a ferrous metal surface comprising the steps of contacting said surface with anhydrous hydrogen chloride gas, allowing said gas to react with said iron oxide to produce a soluble chloride reaction product, said reaction product occurring at a temperature below that at which said chloride product vaporizes, and applying a solvent for said chloride reaction product to said surface in sufficient amount to dissolve and remove substantially all of said chloride reaction product.

2. A process for removing iron oxide-containing corrosion products, scale and the like from a ferrous metal surface comprising the steps of contacting said surface with an admixture comprising anhydrous hydrogen chloride gas and an inert gas, allowing said anhydrous hydrogen chloride gas to react with said iron oxide to produce a soluble chloride reaction product, said reaction occurring at a temperature which is substantially uniform along said surface and below that at which said chloride product vaporizes, said inert gas being present in sufficient amount to cause the water of reaction resulting from said reaction to be generated in the vapor phase, and applying a solvent for said chloride reaction product to

said surface in sufficient amount to dissolve and remove substantially all of said chloride reaction product.

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