METHOD OF PASSIVATING METAL SURFACES

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ABSTRACT OF THE DISCLOSURE

The water and steam containing portions of a steam generator are cleaned and passivated by cleaning with an acid cleaning solution followed by neutralization and then filling the portions with a passivating solution containing 25—1000 p.p.m. hydrogen peroxide or in excess of 500 p.p.m. hydrogen peroxide at a pH in excess of 7.0. The passivating solution is drained from the portions and the metal surfaces exposed to the atmosphere.

This invention relates to the prevention of corrosion and more particularly to the passivation of metal surfaces to reduce the possibility of corrosion.

The present invention is principally concerned with the passivation of oxide-free metal surfaces prior to exposure to the atmosphere to prevent oxidation upon such exposure. The invention will be described with particular reference to the cleaning and passivation of the water-side heat transfer surfaces in steam generating units.

The importance of maintaining clean heat transfer surfaces in boilers has been recognized for many years. Tube cleanliness becomes increasingly more important as higher and higher pressures are maintained in such boilers. Because of the size of modern utility boilers and the large number of long inaccessible circuits, mechanical cleaning of an entire unit is virtually impossible. For this reason, the practice of chemically cleaning boilers has progressed in recent years to the point of becoming a routine maintenance procedure. Chemical techniques are used for both pre-operative and post-operative cleaning. The pre-operative cleaning is utilized to remove mill scale and oxidation products which have been formed as a result of heat treatment, hot working and welding as well as ordinary atmospheric rusting. Post-operative cleaning is utilized to remove deposits which have accumulated during operation of the boiler such as iron, copper, nickel, zinc, calcium and magnesium. The copper and iron are the most prevalent and troublesome deposits in utility boilers.

Chemical cleaning is normally accomplished with an acid solution. Freshly cleaned surfaces are free of protective films and thus quite active and more susceptible to oxidation than scaled surfaces. This active metal surface rusts rapidly in the presence of moisture and oxygen thereby causing corrosion problems particularly if the unit is to be out of service for a period of time. If the unit is to be kept in wet storage, i.e., filled with water, an inhibitor is normally placed in the water so as to inhibit corrosion. On the other hand, if the unit must be drained so as to expose the metal surfaces to the atmosphere, it is quite important that the surfaces be passivated prior to draining. Pre-operative passivation to which this invention is directed. The atmospheric rusting of ferritic materials proceeds rapidly in the presence of oxygen and moisture and it is difficult or impossible to keep and a drained unit free from moisture. The pits formed during storage seldom penetrate the tube surface but these discontinuities represent sites for future operational corrosion. Likewise, the oxides formed are objectionable and they may become loose and move to critical areas of the boiler.

Passivation has been carried out in the past by the use of buffered sodium nitrite solutions as well as with other soluble salts. These passivating solutions may contain on the order of 10,000 p.p.m. of dissolved solids. Such solutions, although they have proved to be effective, all present one significant problem. This is the fact that some of the dissolved solids invariably remain behind in the boiler and may cause problems when the boiler is eventually put back into service.

An object of the present invention is, therefore, to provide a novel technique for passivating metal surfaces to prevent oxidation and corrosion.

A specific object of the present invention is to provide a technique for chemically cleaning a steam generating unit and passivating the cleaned metal surfaces to reduce corrosion upon exposure to the atmosphere.

Another object of the invention is to provide a passivating technique utilizing materials which contain no dissolved solids.

Other objects and advantages will become apparent from the description of the invention which follows.

Chemical cleaning procedures generally involve four steps which are: (1) pre-boiling with alkaline materials, (2) contacting of the surfaces with an acidic solvent or a solvent containing a chelate, (3) neutralizing and post-boiling with a strong alkaline solution, and (4) passivating the freshly cleaned surfaces if an extended lay-down period is anticipated. The alkaline pre-boil is not a necessary procedure and is usually only carried out in pre-operative cleaning to remove organics. A suitable material for this pre-boil would be a solution of Na₂CO₃ and Na₃PO₄. The conventional material utilized for the acid cleaning step is a solution of inhibited hydrochloric acid, usually a 5 percent by weight solution. It is imperative that the acid be inhibited so that once the mill scale and deposits have been removed, the acid attack on the base metal will be minimized. Many inhibitors are commercially available and they vary depending upon the acid with which they are to be used. Polyamines are used in many of these products. Dow Chemical Co., for example, has an inhibitor for hydrochloric acid designated as "A-120." This solution is admitted to the boiler and the temperature of the solvent and metal is maintained at about 150—180° F. Other suitable acid cleaning materials include organic solvents such as citric acid, formic acid, hydroxy-acetic acid and ethylenediamine tetraacetic acid. Hydrochloric acid is a much more rapid cleaning agent than the organic solvents and the organics are, therefore, used for applications where the chloride ion is objectionable such as with austenitic stainless steels. At the conclusion of the acid cleaning period, the acid solution is drained from the boiler under a positive pressure of nitrogen. The boiler is then rinsed with demineralized water to remove any residual acid and filled with a neutralizing solution consisting of 0.5 percent by weight soda ash.

After the acid cleaning and neutralization, the passivating technique of the present invention is carried out. This technique, as has been pointed out, is directed to the use of passivating materials which will effectively prepare a boiler for exposure to the atmosphere and which will be volatile and leave behind no solids. The invention is particularly directed to the use of hydrazine and hydrogen peroxide as passivating materials.

Hydrazine has been employed in the past in low concentrations as an oxygen scavenger to remove dissolved oxygen from boiler water during wet storage. The present invention, however, is directed to the use of this material in greater concentrations prior to the draining of the cleaning and rinse solutions from the boiler and then passivating the metal surface. To be effective as a passivator hydrazine should be present in solution at concentrations in excess of 300 p.p.m., although slightly lower concentrations will
provide some degree of passivation. The upper limit to the concentration of hydrazine in the passivating solution will be determined by economic factors since at a certain level the cost of adding more hydrazine to the solution could not be justified by the small increase in passivating capacity. A solution of perhaps 1 percent hydrazine would be a practical upper limit. A desirable pH for the hydrazine passivating solution is in the range of 9.5 or 10. The pH is adjusted to the desirable value with ammonia or some other amine which will itself add no solids to the system such as morpholine or cyclohexylamine. Test specimens passivated with hydrazine have, upon exposure, retained their luster for periods of at least two months under various adverse atmospheric conditions.

The hydrogen peroxide passivating solution of the present invention has a hydrogen peroxide concentration of preferably less than 1000 p.p.m. and perhaps down to 50 or 25 p.p.m., although such low concentrations would not be very effective. The pH of the hydrogen peroxide solution is also adjusted with ammonia or other amines to a value somewhere around 10. Although this pH adjustment is not necessary, the fastest and best passivation can be obtained if the pH is elevated to a value in excess of 7.0.

The upper concentration limit of 1000 p.p.m. was selected since an increase in the concentration would greatly increase the effectiveness and higher concentrations might be slightly hazardous in the presence of oxidizable materials, such as organics. The products of the hydrogen peroxide passivation of pickled steel are the unobjectionable materials of water and oxygen. The by-products of the use of hydrazine as a passivator are also unobjectionable, consisting of nitrogen, hydrogen, ammonia and hydrogen peroxide which, in turn, produces water and oxygen. It can be seen that these materials will leave behind no harmful deposits as would the passivators employing dissolved solids.

Although the mechanism of the passivation of the metal surfaces by the hydrazine is not known, it is thought that the passivation by both the hydrazine and the hydrogen peroxide are related. In studies of the decomposition of dilute aqueous solutions of hydrazine, hydrogen peroxide has been identified as one of the by-products. The amount of hydrogen peroxide formed is inversely proportional to the rate of oxidation of the hydrazine. It is thought that this formation of hydrogen peroxide oxidizes the metal and forms a protective film to render the surface passive to corrosion. The invention, however, is not to be limited by any particular theory with respect to either the hydrazine or the hydrogen peroxide.

The amount of time that it is necessary to subject the metal surfaces to the passivating solution will, of course, vary depending upon many factors. Some of these factors include the concentration of the passivating material in the solution, the pH of the solution, the temperature and particular metal being treated. The amount of time required is also dependent upon the degree of passivation desired. The longer the treatment period, the more complete will be the passivation up to a certain point beyond which no further action will take place. A period of perhaps 24 hours would yield at least some significant passivation. One factor involved in determining the period necessary will be the amount of time the metal is to be exposed to the atmosphere; the longer the expected exposure, the longer should be the passivation treatment.

While the invention has been described with reference to a particular application and with reference to particular materials and procedures, it will be understood that this description is illustrative only and that changes may be made within the scope of the claim without departing from the invention.

I claim:

1. A method of cleaning and passivating the metal surfaces of the water and steam containing portions of a steam generator comprising the steps of filling said portions with an acid cleaning solution, draining said acid cleaning solution from said portions, filling said portions with a neutralizing solution, draining said neutralizing solution, from said portions, filling said portions with a passivating solution having a pH in excess of 7.0 and comprising at least in part a compound selected from the group consisting of hydrogen peroxide and hydrazine wherein the concentration of said hydrogen peroxide is from 25 to 1000 p.p.m. and the concentration of said hydrazine is in excess of 300 p.p.m. and then draining said passivating solution from said portions and exposing said metal surfaces to the atmosphere.

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