United States Patent Office 2,890,974 Patented June 16, 1959

2,890,974

PASSIVATION OF STAINLESS STEEL ALLOYS

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No Drawing. Application December 2, 1957
Serial No. 699,912

9 Claims. (Cl. 148—6.14)

This invention relates to a method of passivating stainless steel alloys to render them non-reactive to hydrogen peroxide.

While stainless steel alloys by their very nature are considered to be resistant to corrosion and other decomposition in the presence of most materials, it has been found that under certain conditions stainless steels possess a certain reactivity which is detrimental either to the stainless steel itself or to materials coming in contact with the stainless steel. A prominent example of this is where hydrogen peroxide solutions are brought in contact with stainless steel. The hydrogen peroxide is relatively unstable and is decomposed, giving rise to oxygen bubbles in the solution. This is detrimental not only for the reason that the strength of the hydrogen peroxide solution is lessened, but also, the bubbles which are formed interfere in certain operations. Examples of such operations are where the rate of fluid flow of a hydrogen peroxide solution is measured in a flowmeter.

The flowmeter conventionally employed for measuring the rate of fluid flow of a hydrogen peroxide solution consists of a transparent tube mounted vertically, and gradually tapering from a small inside diameter at the bottom of the tube to a larger inside diameter at the top. The fluid flows vertically upward through the tube, causing a float to rise in the tube in accordance with the rate of flow of the fluid. The distance traveled by the float is directly proportional to the rate of flow and is determined by a scale on the tube.

The floats and other parts conventionally employed in flowmeters used in measuring the rate of flow of hydrogen peroxide solutions are fabricated of a stainless steel alloy. The body of the flowmeter may also be of the same material. If the hydrogen peroxide flowing past the float or other stainless steel parts is decomposed, gas bubbles will adhere to the float causing it to read incorrectly. In addition, any gas bubbles formed by decomposition of the hydrogen peroxide caused by contact with stainless steel prior to its reaching the flowmeter will also cause a source of reading error. In addition to the errors caused by the gas bubbles formed, the loss of oxygen represented thereby significantly decreases the strength of the hydrogen peroxide solution. These factors are of utmost importance in the field of hydrogen peroxide power plants and it thus becomes desirable to passivate the stainless steel parts employed in such power plants to render them inert to hydrogen peroxide.

Several methods are currently employed in passivating stainless steel alloys. In general, they comprise the steps of immersing the stainless steel in a pickling solution and then immersing it in a solution of hydrogen peroxide until all bubbling ceases. While a process of this nature is of some benefit, it is found that the passivation thus obtained is not of satisfactory duration, and that after a short period of time the stainless steel again becomes reactive to hydrogen peroxide. With some stainless steels, such as Type 303, the prior art methods are completely unsatisfactory.

It has now been found that by heating the stainless steel alloy in an oxidizing atmosphere after the pickling step, but prior to the contacting thereof with hydrogen peroxide, a more complete passivation of the alloy is obtained which will last for a much longer period of time than the passivation obtained according to prior art practices. This step is of particular benefit with stainless steel alloys having a relatively low content of chromium and nickel, such as that commonly designated Type 303 according to American Iron and Steel Institute type numbers established in June 1939. Various other stainless steels, however, are also benefited by treating them according to the process of this invention. The passivation obtained with the Type 303 stainless steel according to the method of this invention may possibly be of a permanent nature, no failures having been obtained at this time.

As an indication of the types of stainless steel which are benefited according to this invention, reference is made to the Chemical Engineers' Handbook by John H. Perry, The McGraw-Hill Book Company, Inc., 1941, pages 2119–2121 and 2141–2142. The stainless steels there listed are identified by type numbers assigned by the American Iron and Steel Institute. Type 303 stainless steel contains 0.20% maximum carbon content, 17.5–20.0% chromium, 8.00–10.00% nickel, sulphur or selenium 0.07% minimum or molybdenum 0.60% maximum.

The step of heating the stainless steel alloy in an oxidizing atmosphere is very important to the process of the present invention. The oxidizing atmosphere which is preferably employed is air, but any other suitable oxidizing atmosphere may be employed.

It has been found that heating the alloy to a temperature of about 750° F. for about two hours provides the desired effect where an object having a size similar to that of the float used in the flowmeter is being treated. The temperature may vary somewhat from the 750° F. level. Temperatures within the range of about 700° F. to about 800° F. have been found to provide good results. In addition, the heating time employed in the process of this invention may vary, depending upon the size of the object being heated. Objects which are smaller than the float may require somewhat less time for a complete passivation, while a large and dense stainless steel object may require considerably more time than two hours. In any event, the time and temperature required for a given stainless steel article may be readily determined by simple experimentation. In general, heating times from thirty minutes to several hours will be employed.

The following example further illustrates the process of this invention.

Example 1

A flowmeter float made from Type 303 stainless steel alloy was immersed in a solution of 20% caustic soda for thirty minutes at room temperature. It was then rinsed and immersed in a solution of 50% nitric acid for twenty-four hours at room temperature.

The float was then pickled in a 10% chromic acid solution at room temperature for about one hour, rinsed, and then pickled in a sodium picrate solution at its boiling point for one hour. The sodium picrate solution contained 245 grams of sodium hydroxide and 20 grams of picric acid in 735 ml. of water.

After the pickling process, the float was rinsed, heated to 750° F. for two hours in air, air cooled, and immersed in a solution of 30% hydrogen peroxide until all reaction ceased.

If desired, the float may be immersed in a 90% hydrogen peroxide solution after pickling and before the heat treatment step to determine the passivity of the alloy

at that stage. This is not an essential process step, however.

After passivating the stainless steel float in this manner, it was employed in a flowmeter to determine the rate of flow of a hydrogen peroxide solution. Each of the other stainless steel parts of the flowmeter had been passivated in the same manner. No interfering bubbles were formed on the float or in the hydrogen peroxide solution itself. This made accurate determination of the rate of flow possible and prevented any deterioration in the strength of the hydrogen peroxide solution passing through the flowmeter. Furthermore, the passivation obtained in this manner is of a much more permanent nature than the passivation obtained by prior art techniques.

It is understood that the passivation process referred to throughout the specification is applied to and is effective only on the surface of the stainless steel alloy. If the alloy is machined after passivation, the entire process must be repeated in order to provide a properly passivated alloy.

While the process of this invention has been described with reference to a particular type of stainless steel, and to a small float and other parts of a flowmeter, it should be understood that the process is applicable to other types of stainless steel, and in different forms.

I claim:

1. In the process of passivating a stainless steel alloy including the steps of immersing the alloy in a pickling bath and thereafter exposing the alloy to a solution of hydrogen peroxide until all reaction ceases, the improvement comprising the inclusion of the step of heating the alloy in an oxidizing atmosphere after exposure of the alloy to the pickling bath and before reacting the alloy with hydrogen peroxide.

2. In the process of passivating a stainless steel alloy including the steps of immersing the alloy in a pickling bath and thereafter exposing the alloy to a solution of hydrogen peroxide until all reaction ceases, the improvement comprising the inclusion of the step of heating the alloy in an oxidizing atmosphere at a temperature of from about 700° F. to about 800° F. after exposure of the alloy to the pickling bath and before reacting the alloy with hydrogen peroxide.

3. In the process of passivating a stainless steel alloy including the steps of immersing the alloy in a pickling bath and thereafter exposing the alloy to a solution of hydrogen peroxide until all reaction ceases, the improvement comprising the inclusion of the step of heating the alloy in an oxidizing atmosphere at a temperature of from about 700° F. to about 800° F. for from one-half hour to several hours, the time of heating depending upon the mass of the alloy and the heating step taking place after exposure of the alloy to the pickling bath and before reacting the alloy with hydrogen peroxide.

4. A method of passivating a stainless steel alloy which comprises immersing the alloy in a pickling solution, rinsing, heating the alloy at a temperature of from about 700° F. to about 800° F. in an oxidizing atmosphere, cooling the alloy and reacting the alloy with hydrogen peroxide until all reaction ceases.

5. A method of passivating a stainless steel alloy which comprises immersing the alloy in a strong alkali, rinsing, immersing the alloy in a strong acid solution, rinsing, immersing the alloy in a solution of sodium picrate, rinsing, heating the stainless steel in an oxidizing atmosphere at a temperature of from about 700° F. to about 800° F. for from one-half hour to several hours depending upon the mass of the alloy, cooling in air, and immersing the alloy in a solution of hydrogen peroxide until reaction ceases.

6. A method of passivating a stainless steel alloy to render it substantially non-reactive to hydrogen peroxide solutions comprising immersing the alloy in a 20% caustic soda solution at room temperature for about thirty minutes, rinsing the alloy, immersing the alloy in a solution of 50% nitric acid at room temperature for about twenty-four hours, rinsing the alloy, immersing the alloy in a 10% chromic acid solution at room temperature for one hour, rinsing, immersing the alloy in a freshly prepared sodium picrate solution of about 2% concentration at the boiling point thereof for one hour, rinsing the alloy, heating the alloy to about 750° F. for about two hours in air, air cooling and immersing the alloy in a 30% solution of hydrogen peroxide until all reaction ceases.

7. A method of passivating AISI Type 303 stainless steel alloy having no more than 0.20% carbon, from 17.5 to 20% chromium, from 8 to 10% nickel, a minimum of 0.07% sulphur and molybdenum, at a maximum level of 0.60% to render it substantially non-reactive to hydrogen peroxide solutions comprising immersing the alloy in a 20% caustic soda solution at room temperature for about thirty minutes, rinsing the alloy, immersing the alloy in a solution of 50% nitric acid at room temperature for about twenty-four hours, rinsing the alloy, immersing the alloy in 10% chromic acid solution at room temperature for one hour, rinsing the alloy, immersing it in a freshly prepared sodium picrate solution containing about 2% of picric acid and an excess of sodium hydroxide at the boiling point of said solution for one hour, rinsing the alloy, heating the alloy to about 750° F. for about two hours in an oxidizing atmosphere, cooling, and immersing the alloy in a 30% solution of hydrogen peroxide until all reaction ceases.

8. A method of passivating the surface of AISI Type 303 stainless steel alloy including no more than 0.15% carbon, from 17.5 to 19% chrominum, from 8 to 10% nickel, at least 0.15% sulphur, and molybdenum at a maximum level of 0.60%, to render it substantially non-reactive to hydrogen peroxide solutions comprising immersing the alloy in a 20% caustic soda solution at room temperature for about thirty minutes, rinsing the alloy, immersing the alloy in a 50% solution of nitric acid at room temperature for about twenty-four hours, rinsing the alloy, immersing the alloy in a 10% chromic acid solution at room temperature for about one hour, rinsing, immersing the alloy in a freshly prepared sodium picrate solution containing about 2% by weight of picric acid and about 25% by weight of sodium hydroxide at the boiling point thereof for about one hour, rinsing the alloy, heating the alloy to about 750° F. for about two hours in an oxidizing atmosphere, cooling, and immersing the alloy in a concentrated solution of hydrogen peroxide until all reaction ceases.

9. In the process of passivating a stainless steel alloy including the steps of immersing the alloy in acid and alkali pickling solutions to remove non-metallic impurities and thereafter exposing the alloy to a solution of hydrogen peroxide until all reaction ceases, the improvement comprising the inclusion of the steps of contacting the alloy with a solution of sodium picrate containing an excess of sodium hydroxide and thereafter heating the alloy in an oxidizing atmosphere at a temperature of from about 700° F. to about 800° F., said steps being employed after the exposure of the alloy to the pickling solutions and before reacting the alloy with hydrogen peroxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,172,428	Wulff et al.	Sept. 12, 1939
2,473,456	Thurber	June 14, 1949