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TREATMENT OF ALUMINUM SURFACES

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This invention relates to the treatment of aluminum surfaces which are to be contacted with hydrogen peroxide. More particularly, it relates to containers or equipment for storing or handling hydrogen peroxide and to the treatment of aluminum surfaces thereof to improve the resistance of such surfaces to attack by hydrogen peroxide.

Aluminum and aluminum alloy containers and equipment are used extensively for storing, shipping and handling hydrogen peroxide. However, hydrogen peroxide solutions tend to corrode or pit aluminum, particularly when the hydrogen peroxide solution contains small or even trace concentrations of chlorides or heavy metal compounds. Heavy metal impurities in the aluminum surface also enhance attack by the solution. Moreover, solution of the aluminum as a result of such attack and impurities introduced from the aluminum surfaces decrease the stability of the peroxide solution.

Aluminum and aluminum alloys can be made more resistant to attack by hydrogen peroxide solutions by pretreating the surfaces thereof with nitric acid, as heretofore proposed. Such a pretreatment has a passivating effect on the aluminum and leaves on the surfaces a protective aluminum oxide coating. Other acids such as phosphoric, sulfuric and hydrochloric acids have also been proposed for pretreatment of aluminum containers for hydrogen peroxide. In all such methods, the aluminum surfaces to be treated should be thoroughly clean and, when necessary, it is common practice to degrease the aluminum with a solvent such as trichloro-ethylene, and/or to wash the aluminum with a solution of an alkali before treating the aluminum with the acid.

While previously proposed nitric acid treatments are beneficial, the oxide coatings formed thereby are not as resistant to attack by hydrogen peroxide as is desired. Moreover, such oxide coatings are quite porous and adsorptive, which is objectionable since they tend to adsorb and retain impurities including those which catalyze peroxide decomposition.

It is an object of the invention to provide aluminum and aluminum alloy surfaces having improved protective oxide coatings thereon which increase the resistance of such surfaces to attack by hydrogen peroxide solutions. A further object is to provide a method for producing such protective oxide coatings on aluminum and aluminum alloys. Another object is to provide an improved method of packaging hydrogen peroxide, and also improved hydrogen peroxide packages. Still other objects will be apparent from the following description.

The objects of the invention are accomplished by treating the surfaces of aluminum or aluminum alloys which are to be contacted with hydrogen peroxide with nitric acid to form an aluminum oxide coating on such surfaces, and then subjecting the oxide coating on such surface

to the action of hot water or steam whereby the oxide coating is rendered non-porous and non-adsorptive. Preferably, the resulting coating is then passivated by contacting it with an aqueous hydrogen peroxide solution of 20% or greater strength for about 0.5 hr. or longer. In a preferred embodiment, the above method is applied to a vessel having an interior aluminum surface to provide a non-porous non-adsorptive protective oxide coating on said surface having improved resistance to attack by hydrogen peroxide.

The invention and its advantages are illustrated by the following examples in which all percentages are by weight.

EXAMPLE 1

Test strips 2 in. wide and 3 in. long of aluminum (2S grade containing 99.6% aluminum) were cleaned with a 2% NaOH solution for 2 minutes at room temperature, washed, immersed in 50% nitric acid solution at 20 to 30° C. for 20 minutes, thoroughly washed with water, then divided into Groups A and B. At this point, the strips of both groups had a uniform oxide coating resulting from the nitric acid treatment.

The test strips of group A were then subjected to an accelerated corrosion test which involved immersing them at room temperature in a water solution containing 5% NaCl and 0.4% H_2O_2. Within 10 to 15 minutes, numerous gas bubbles had formed on the strips, the strips had darkened considerably, and a flocculent precipitate of aluminum hydroxide had formed in the solution. These results show that the strips were attacked by the solution.

The strips of group B were submerged in boiling water for 10 minutes, after which they were cooled and subjected to the above accelerated corrosion test under the same conditions. There was no visible evidence of attack after 4 hours in the solution.

EXAMPLE 2

A number of aluminum test strips were cleaned, treated with nitric acid and washed as described in Example 1, then divided into groups A, B, C and D.

The strips of group A were immersed in a 1% solution of an anthraquinone sky blue dye at 25 to 30° C. for 24 hours. The strips adsorbed dye and the adsorbed dye was not removed by washing, and only with difficulty by scrubbing with pumice.

The strips of group B were submerged in boiling water for 15 to 60 minutes, removed, cooled, and then treated with a dye solution as described for the strips of group A. The strips of group B did not adsorb dye from the solution.

The strips of group C were immersed for several hours in a 1% solution of ferric ammonium sulfate, then thoroughly washed. Application of a 1% solution of potassium ferrocyanide to surfaces of the treated strips developed numerous blue areas. Similar application of a 1% solution of ammonium thiocyanate developed red areas. These results show that the oxide coating formed by the nitric acid treatment readily adsorbed iron compounds from the ferric ammonium sulfate solution.

The strips of group D were submerged in boiling water for 15 to 60 minutes and then subjected to the tests described for the strips of group C. Results showed that the strips of group D did not adsorb iron compounds.

The results of the above example show that the boiling water treatment converts the oxide coating resulting from the nitric acid treatment to a non-adsorptive coating. Such a coating is highly desirable for the interior of aluminum containers such as drums in which hydrogen

peroxide is stored and shipped. Between fillings with hydrogen peroxide the interior surfaces of such containers are frequently subjected to contact with solutions containing impurities. These are readily adsorbed by oxide coatings which have not been rendered non-adsorptive by the hot-water treatment.

EXAMPLE 3

A number of aluminum strips were cleaned, treated with nitric acid, washed and divided into groups A and B as described in Example 1. Those of group A were then submerged in boiling water for 15 to 30 minutes. The weights of the oxide coatings on the strips of both groups were then determined by weighing the washed and dried strips both before and after removing the oxide coating by treatment with an aqueous solution containing 5.3% H_3PO_4 and 10% Cr_2O_3. The results showed that the coating on the strips of group A was about 50% heavier per unit area than the coating on the strips of group B. Thus, a substantially heavier coating resulted when the nitric acid treatment was supplemented by a subsequent boiling water treatment.

EXAMPLE 4

Strips of aluminum were treated with nitric acid and boiling water as described in Example 1. Portions of the surfaces of the strips were then covered with 35% aqueous hydrogen peroxide containing about 130 mg. per liter each of sodium stannate and sodium pyrophosphate. Examination of the covered areas at 10 to 50 diameters magnification showed that bubbles formed on the surface due to decomposition of the peroxide. After several applications of such a peroxide solution to the same areas, no further decomposition of the peroxide was indicated. The same results were obtained in similar tests using hydrogen peroxide solutions of 50% and 70% strength. In each instance, gasing at the area covered by the solution decreased with each additional application of the solution until after about 2–5 applications substantially no gasing occurred.

The interior surfaces of aluminum drums which had been treated with nitric acid and then with hot water showed a similar behavior. Thus, the stability of peroxide solutions stored in such treated drums improves sharply after first being passivated by contact with peroxide solution.

EXAMPLE 5

A set of drums (A) fabricated of 2S grade (99.6%) aluminum were cleaned then filled with 50% nitric acid and let stand at room temperature 3 to 5 hrs. After washing thoroughly, the drums were filled with live steam for 0.5 hr.

A second set of drums (B) fabricated of a 52S grade of aluminum (aluminum containing 2.5% magnesium and 0.25% chromium) was treated in the same way as set A. Still a third set of drums (C) fabricated of the same grade of aluminum as set A was treated the same way except that the steaming treatment was omitted.

All three sets of drums were then filled with aqueous hydrogen peroxide solution. The pH and H_2O_2 content of the solution in each drum were determined at the beginning of the test and again after an 8 week storage period. Accelerated decomposition or stability tests were also determined for the solution in each drum initially and after 8 weeks. These tests involved heating samples of the solutions at 100° C. for 15 hrs., and determining at the beginning and at the end of the test period the amount of hydrogen peroxide present. The difference, representing hydrogen peroxide lost by decomposition, was calculated as percent hydrogen peroxide lost, based upon the amount present at the beginning of the test. The results below show that the steaming treatment following the treatment with nitric acid decreases substantially the amount peroxide lost during storage and increases substantially the stability of the peroxide.

Average solution tests results

	At Beginning	After 8 Weeks	Change
Drum Set A:			
pH of Solution	3.6	3.5	0.1
H_2O_2 Conc., Percent	35.04	34.91	0.13
Stability Test (100° C.), Percent	0.50	0.57	0.07
Drum Set B:			
pH of Solution	3.6	3.5	0.1
H_2O_2 Conc., Percent	34.98	34.86	0.12
Stability Test (100° C.), Percent	0.32	0.38	0.06
Drum Set C:			
pH of Solution	3.7	3.6	0.1
H_2O_2 Conc., Percent	35.00	34.77	0.23
Stability Test (100° C.), Percent	0.57	0.82	0.25

Nitric acid of 40 to about 55% strength is preferred for use in forming the initial oxide coating, although solutions of strength ranging from about 25 to 75% are generally useful. The treating time should be at least about 10 minutes but may be several hours if desired. If the aluminum surface is badly contaminated, two or more successive treatments with nitric acid may be desirable. In addition to forming an oxide coating, the acid treatment also serves to dissolve and remove from the aluminum surface occlusions of heavy metals (usually chiefly iron) and other impurities adventitiously present. Generally, it is desirable to repeat the nitric acid treatments until tests show the effluent acid to be substantially free of iron.

Following the treatment with nitric acid, the resulting surface is thoroughly washed with water. It is important that water of good purity be used for this purpose since the oxide coating at this stage is porous and adsorptive. Distilled water or water deionized by ion-exchange methods is generally satisfactory.

The initial porous, adsorptive oxide coating is rendered non-porous and non-adsorptive by subjecting it to the action of water, either as liquid or vapor, at a temperature of at least 80° C. A treatment time of about 10 minutes or more generally is required but much longer times may be used. The aluminum surface with its oxide coating, can in some cases be simply immersed in boiling water for about 10 minutes or longer. When the interior surfaces of vessels such as drums are being treated, the vessel can be filled with water kept at about the boiling point for the desired time. When the interior surfaces of drums, pipe lines, etc. are being treated, it often will be most convenient to subject such surfaces to the action of live steam, e.g. at temperatures up to about 150° C. Any water or steam used for such purpose should be of good purity.

In treating the interior surface of a vessel for shipping and storing peroxide, it is generally preferred that the nitric and the hot water treatments be followed by a passivating treatment with a hydrogen peroxide solution of at least 20%, preferably 35 to 70% strength. A single treatment for a few minutes, e.g. 5 to 10 minutes, is beneficial, but a contact time of 30 minutes or longer is preferred. It is also preferred that the passivating solution be of good stability and to insure this, it is most preferred that it contain a small amount of a peroxide stabilizer, such as sodium stannate or a combination thereof with sodium pyrophosphate. Other commonly used peroxide stabilizers may also be used.

Should it be necessary or desirable to degrease, clean or polish the original aluminum surfaces to remove grease, dirt, occlusions or roughness, such degreasing, cleaning or polishing treatments should precede the acid treatment in which the oxide coating is formed.

The method of the invention has been found to increase substantially the resistance of aluminum and aluminum alloys (containing a predominant amount of aluminum but not more than about 0.5% of heavy metal components which catalyze the decomposition of peroxide)

to attack by hydrogen peroxide, particularly non-alkaline hydrogen peroxide solutions. Such solutions when stored in aluminum vessels treated in accordance with the invention are significantly more stable than when stored in similar aluminum vessels which have not been so treated and little or no attack of the aluminum by the peroxide occurs.

I claim:

1. In a method for treating an aluminum surface which is to be contacted with hydrogen peroxide, which method includes the treatment of such surface with nitric acid to form an oxide coating thereon, the improvement comprising subjecting said oxide coating on said aluminum surface to the action of water at a temperature of at least 80° C. whereby said oxide coating is rendered non-porous, non-adsorptive and more resistant to attack by hydrogen peroxide.

2. In a method of preparing a container for storing and handling hydrogen peroxide, which container has an interior surface of aluminum, in which method said interior surface is treated with nitric acid to provide an oxide coating on said interior surface, the improvement comprising subjecting the oxide coating on said interior surface to the action of water at a temperature of at least 80° C. for a time of at least 10 minutes.

3. In a method of preparing a container for storing and handling hydrogen peroxide, which container has an interior surface of aluminum, in which method the interior surface is treated with nitric acid of 25 to 75% strength to provide an oxide coating on said interior surface, the improvement comprising subjecting said oxide coating on said interior surface to the action of water at a temperature of at least 80° C. for at least 10 minutes.

4. The method of packaging hydrogen peroxide comprising subjecting the interior aluminum surface of a vessel to the action of a nitric acid solution of a strength in the range 25 to 75% whereby to form an oxide coating on said interior surface, subjecting said oxide coating on said interior surface to the action of water at a temperature of at least 80° C., and thereafter placing hydrogen peroxide in said vessel.

5. The method of packaging hydrogen peroxide comprising subjecting the interior aluminum surface of a vessel to the action of a nitric acid solution of a strength ranging from 25 to 75% whereby to form an oxide coating on said surface, subjecting said oxide coating on said surface to the action of water at a temperature of at least 80° C. for at least 10 minutes, passivating the resulting coating on said surface by contacting it with aqueous hydrogen peroxide of at least 20% strength for at least 30 minutes, and thereafter placing hydrogen peroxide in said vessel.

6. A package comprising a container having an interior aluminum surface coated with a non-porous, non-adsorptive oxide coating, and containing a hydrogen peroxide solution in contact with said coating, said oxide coating having been formed upon said aluminum surface by the treatment of said aluminum surface with nitric acid, and having been rendered non-porous and non-adsorptive by a subsequent treatment with water at a temperature of at least 80° C.

7. A package comprising a container having an interior aluminum surface coated with a non-porous, non-adsorptive oxide coating and containing an aqueous hydrogen peroxide solution in contact with said oxide coating, said oxide coating having been formed upon said aluminum surface by the action of a nitric acid solution of a strength in the range 25 to 75%, and having been rendered non-porous and non-absorptive by a subsequent treatment thereof with water at a temperature of at least 80° C.

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