

UNITED STATES PATENT OFFICE

2,224,835

STORING AND HANDLING HYDROGEN
PEROXIDE SOLUTIONS

Joseph S. Reichert and Wilbie S. Hinegardner,
Niagara Falls, N. Y., assignors to E. I. du Pont
de Nemours & Company, Wilmington, Del., a
corporation of Delaware

No Drawing. Application April 14, 1938,
Serial No. 202,045

2 Claims. (Cl. 23—240)

This invention relates to the storing and handling of hydrogen peroxide solutions in containers of aluminum or aluminum alloys and more particularly to the inhibiting of corrosion of such containers by hydrogen peroxide solutions.

Hydrogen peroxide solutions have long been stored and shipped in containers made of glass or other ceramic materials. More recently, vessels made of aluminum or its alloys have been used to a considerable extent. Containers made of metals, including aluminum and its alloys, are generally attacked to some extent by commercial hydrogen peroxide solutions with the result that dissolved metal impurities are introduced into the solution. These metallic impurities act catalytically to decompose the hydrogen peroxide and for this reason metal containers were long considered impracticable for use in storing and handling hydrogen peroxide solutions.

In the comparatively recent use of vessels made of aluminum, one method of preventing attack of the vessel by hydrogen peroxide solutions has been to coat the inner surface of the container with an inert material such as asphalt. This method has not been very satisfactory since the protective coating tends to scale off in time, leaving unprotected surfaces exposed and introducing undesirable solid particles into the solution. A superior method of inhibiting corrosion of aluminum containers by hydrogen peroxide solutions and of enhancing the stability of the solutions in such containers which has proven very satisfactory is described in the Reichert Patent 2,008,726, issued July 23, 1935. According to the method of this patent, corrosion of the aluminum is effectively inhibited by the addition to the hydrogen peroxide solution of a soluble nitrate, e. g., ammonium nitrate. Preferably, the aluminum is previously rendered passive by treatment with nitric acid solution and the acidity of the hydrogen peroxide solution is adjusted to a pH of about 3.5 to 6, since the catalytic effect of dissolved aluminum is at a minimum in this range of acidity.

Commercial hydrogen peroxide solutions attack aluminum and its alloys in two ways which may be designated as "uniform solution" and "pitting." In the "uniform solution" attack, the metal is dissolved at a substantially equal rate at all points on the surface in contact with the solution and the metal is not greatly changed in appearance. "Pitting" is a localized attack wherein the metal is dissolved at a number of definite points resulting in the formation of cavities or "pits." Severe pitting due to accelerated local action removes considerable metal and leaves a rough, dull-colored surface. In general, "pitting" corrosion is much more of a problem than attack in the form of "uniform solution" and our present invention is particularly concerned

with the inhibition of pitting, although the invention which is described below is also effective to inhibit uniform solution.

It is an object of our invention to provide a method for effectively inhibiting corrosion, particularly pitting corrosion of aluminum and its alloys by acidic hydrogen peroxide solutions. A further object is to provide an improved method of storing and handling acidic hydrogen peroxide solutions in aluminum vessels, whereby corrosion of the surface of the vessel which is exposed to the solution or its vapors may be inhibited to a practical extent without the necessity for having special compounds present in the hydrogen peroxide solutions. A further object is to provide containers for such hydrogen peroxide solutions which are highly resistant to corrosion. These and still further objects will be apparent from the ensuing description of our invention.

The above objects are accomplished in accordance with our invention by providing the inner surface of a container made of aluminum or its alloys with a firmly adherent resistant oxide coating. This oxide coating may be conveniently formed in place upon the aluminum surface by subjecting the inner surface of the aluminum vessel to an anodic oxidizing treatment. We have discovered that an oxide coating on aluminum, when formed by anodic oxidation, is not only hard and highly resistant to abrasion but is also remarkably resistant to attack by acidic hydrogen peroxide solutions, e. g. solutions whose hydrogen ion concentration is not greater than that corresponding to a pH of about 1.5. Furthermore, such an oxide coating is firmly adherent to the aluminum surface upon which it is formed and does not scale off in the presence of hydrogen peroxide solutions, even upon bending of the underlying aluminum. A still further highly important characteristic of the oxide coating is that it is highly absorbent to substances such as paraffin, petroleum oils and other paraffin like substances, e. g., waxes and the like, which substances are chemically inert to hydrogen peroxide solutions. Because of this property the resistance to corrosion of aluminum containers whose inner surface has been coated with such an oxide coating may be appreciably enhanced by having adsorbed on the relatively porous coating, for example, paraffin, petroleum oil or other paraffin like substances or mixtures thereof.

In one modification of our invention, a preformed aluminum vessel is filled with a suitable electrolyte, e. g., a sulfuric acid solution. Electric current is then passed through the electrolyte between a cathode immersed therein and the aluminum container, the latter functioning as the anode. This treatment is continued until a suitable oxide coating is formed. Any suitable metal, e. g. aluminum, tin, lead or the like, may be made

the cathode. A coating thus produced is hard and highly resistant to corrosion by acidic hydrogen peroxide solutions having an acidity corresponding to a pH not less than about 1.5 and preferably within the range 3.5 to 6. Furthermore, such a coating adheres firmly to the underlying aluminum even upon bending.

The adsorbent property of the coating is dependent to a certain extent upon the concentration of sulfuric acid in the electrolyte and also upon the thickness of the coating. The thickness of the coating will depend upon the current employed in the oxidation treatment and the duration of the treatment. A current of about 5 to 6 amperes applied for about 10 to 30 minutes produces a coating of sufficient thickness to be highly adsorptive, providing a suitable electrolyte has also been employed. With an electrolyte containing 5 to 20% by weight of sulfuric acid, hard, resistant coatings are obtained but they are relatively non-adsorbent. With an electrolyte containing 20 to 75% of sulfuric acid, the coatings are hard and also highly adsorbent, being capable of adsorbing effective amounts of paraffin like material. Regardless of whether an adsorptive coating is desired, we prefer generally to use an electrolyte containing 20 to 75% by weight of sulfuric acid. In order to prevent local pitting of the surface during the anodic oxidation, smooth but vigorous agitation during the passage of the current is desirable.

Another modification of our invention comprises forming on the inner surface of an aluminum container an adsorptive anodically oxidized coating as described above and adsorbing thereon an inert paraffin like substance. Coatings so treated are highly resistant to attack by acidic hydrogen peroxide solutions, being somewhat more effective than are coatings upon which no protective material has been adsorbed. The materials which may be adsorbed for this purpose are substances such as paraffin, petroleum oils or other paraffin like substances such as waxes. These substances are chemically inert to hydrogen peroxide and apparently fill the pores of the coating so that hydrogen peroxide solution is maintained out of actual contact with the aluminum itself.

Adsorption may be effected simply by applying the material to be adsorbed in the form of a liquid to the anodically oxidized surface and then removing the excess liquid. If the material is not a liquid at ordinary temperatures, as in the case of ordinary paraffin, it may be applied at a temperature above its melting point or in the form of a solution in an inert solvent such as petroleum ether. However, the use of a solution is generally not necessary and is not recommended. A simple method is to place some of the liquid or melted material in the aluminum vessel whose inner surface has been previously anodically oxidized and rotate the container so as to wet the entire inner surface thereof with the liquid. The treated surface may then be freed of all excess liquid, e. g., by wiping, draining or by solution methods. If desired, the material to be adsorbed may be sprayed or brushed onto the oxidized coating. Excess material should be removed so that it will not contaminate the hydrogen peroxide solution.

The paraffin like substances which may be adsorbed on the oxide coating in accordance with our invention are not to be confused with ordinary coatings of these substances upon surfaces in general. We have found that an oxide coating

such as is formed by anodic oxidation in 20 to 75% sulfuric acid solution strongly adsorbs these substances so that their removal from the coating is exceedingly difficult. Thorough wiping of the surfaces after treatment thereof with the paraffin like substances does not accomplish removal of the adsorbed material, nor is it removed by usual washing methods with solvents which would accomplish the complete removal of coatings of such substances from ordinary surfaces. Apparently the paraffin like substance is distributed throughout and is strongly held within the porous structure of the oxide coating so as to fill completely all of the pores thereof. Thus an impervious protective barrier is provided between the hydrogen peroxide solution and the walls of the aluminum container. On the other hand, coatings of the same materials upon ordinary surfaces, including ordinary aluminum surfaces, are far more weakly held and are much more readily removed. Thus, paraffin coatings on ordinary aluminum tend to crack or become dislodged in time therefrom, particularly in cold weather if the underlying aluminum is bent, with the result that unprotected surfaces become exposed and the hydrogen peroxide solution is contaminated by the dislodged materials. Such cracking or dislodgment of the paraffin does not occur when it is adsorbed on the anodically formed oxide coating in accordance with our invention.

The effectiveness of oxide coatings anodically formed on the aluminum, and of such coatings having adsorbed thereon paraffin like substances, to inhibit the corrosion of aluminum by acidic hydrogen peroxide solutions and to improve the stability of such solutions in the presence of aluminum is demonstrated by the results presented in the example below. In the example, the concentrations of hydrogen peroxide solutions are expressed in terms of the volume of available oxygen in a unit volume of solution. Thus, one unit volume of a "100 volume" solution, measured at 20° C., when completely decomposed to oxygen and water yields 100 unit volumes of oxygen gas, measured at 0° C. and 760 mm. pressure. Similarly, one unit volume of a "90 volume" solution yields 90 unit volumes of oxygen gas and one unit volume of a "50 volume" solution yields 50 unit volumes of oxygen gas.

Example

In this example clean aluminum test strips one inch wide and three inches in length were utilized. Some of the strips were anodically oxidized in a 10% sulfuric acid solution for 30 minutes, employing a current of 6 amps. at 25 volts. Aluminum strips were used as cathode during the treatment. Only the lower two-thirds of the strips were immersed in the electrolyte so that the upper one-third of each strip was not oxidized. The oxidized portion was hard and very resistant to scratching by sharp objects. It was also somewhat adsorbent since it was dyed by dipping in a 10% ferrous sulfate solution followed by dipping in a 10% potassium ferricyanide solution. In contrast, the upper unoxidized portion of each strip was readily scratched and was nonadsorbent. Others of the cleaned strips were anodically oxidized in a similar manner using an electrolyte containing 65% by weight of sulfuric acid. Five amperes of current at 25 volts were impressed upon the cell for 25 minutes. Here again only the lower two-thirds of each strip was oxidized. The oxide coating

formed was hard and very adsorbent. Some of these strips were then dipped completely in melted paraffin after which they were thoroughly wiped at a temperature above the melting point of the paraffin to remove excess paraffin therefrom.

The above anodically oxidized strips were then immersed to the halfway point in samples of a hydrogen peroxide solution contained in "Pyrex" flasks fitted with paraffin coated stoppers provided with capillary vents. It should be noted that only the bottom half of each strip was immersed. Since the bottom two-thirds were anodically oxidized, the portion of each strip above the solution was partly oxidized and partly unoxidized, whereas the portion in the solution was all oxidized. Similar test flasks were set up using hydrogen peroxide solution from the same stock sample, but employing aluminum strips which had been cleaned but had not been anodically oxidized. The hydrogen peroxide used in the tests contained no added special agents other than the usual stabilizers and had an acidity corresponding to a pH of about 4 to 4.5. The solutions were analyzed and the strips observed at various intervals during a storage period of 6½ months at a constant temperature of 32° C. The following table presents the data obtained in the tests.

Flask*	Volume concentration of solution			Final appearance of solution	Final appearance of Al strips
	At start	After 3 months	After 6½ months		
A.....	100.91	103.16	105.2	Clear.....	
A.....	100.91	103.96	106.3	do.....	
B.....	100.91	93.76	79.1	Clear.....	Slightly pitted above soln.
B.....	100.91	98.76	91.3	do.....	Do.
C.....	100.91	97.76	83.3	Clear.....	Slightly pitted above soln.
C.....	100.91	103.26	93.9	do.....	Do.
D.....	100.91	105.76	108.5	Clear.....	No corrosion.
D.....	100.91	102.36	100.7	do.....	Slightly pitted above soln.
E.....	100.91	28.66	0.1	White ppt..	Badly corroded and pitted.
E.....	100.91	47.56	0.4	do.....	Do.

*Flasks A contained no aluminum strips; flasks B contained strips oxidized in 10% sulfuric acid solution; flasks C contained strips oxidized in 65% sulfuric acid solution; flasks D contained strips oxidized in 65% sulfuric acid solution followed by paraffin treatment; and flasks E contained strips which were cleaned but not anodically oxidized.

NOTE.—The apparent increase in the hydrogen peroxide concentration in the more stable of the solutions was due to concentration by evaporation.

All of the strips which are stated in the above table to have been slightly pitted above the hydrogen peroxide solution were actually pitted on those portions of the strips that had not been anodically oxidized, or at the junction of such portions with the lower oxidized portions. This fact demonstrates that pitting corrosion by hydrogen peroxide vapors is effectively inhibited by the anodically formed oxide coating.

That the decomposition of hydrogen peroxide solution is accelerated by corrosion of the aluminum is evident from the results obtained with test samples E. In these samples, the aluminum strips, which incidentally had not been anodically oxidized, were badly pitted and a heavy white precipitate of an aluminum compound was formed in the solution. The solutions of hydrogen peroxide in these samples were practically completely decomposed.

The effectiveness of the anodically formed oxide coating to inhibit corrosion and thereby to improve the stability of hydrogen peroxide solution in contact with aluminum is evident from a comparison of the results obtained for samples B and C with those obtained for samples E. Furthermore, it should be noted that when the oxide coating contains adsorbed paraffin, the hydrogen peroxide solution in contact with the test strips is substantially as stable as the same solution when in contact only with high silica glass of the type sold commercially under the trade-mark "Pyrex".

The results presented in the above example illustrate the effectiveness of the present oxide coatings, or such coatings having adsorbed thereon a paraffin like substance, to inhibit or prevent pitting corrosion. Such coatings are also effective to inhibit uniform solution attack by acidic hydrogen peroxide solutions. However, the use of such coatings in accordance with our invention is not limited to hydrogen peroxide solutions which contain no added special corrosion inhibitors. It is generally desirable to have present in the hydrogen peroxide solution an effective stabilizer for the hydrogen peroxide, and all commercial solutions of hydrogen peroxide usually contain such stabilizing agents.

Since hydrogen peroxide vapors are corrosive to aluminum, the entire inner surface of the container should be treated in accordance with our invention to provide a protective coating thereon. If untreated surface is exposed to the vapors, corrosion eventually occurs on such surface. Furthermore, such corrosion results in the formation of aluminum compounds which in time find their way into and accelerate decomposition of the solution.

The term "paraffin like substance" is used in the appended claims to include paraffin, petroleum oils and other substances, e. g. waxes and the like, which are chemically inert to hydrogen peroxide solutions. The term "aluminum" is used to include besides relatively pure aluminum, aluminum alloys in which aluminum is the predominating constituent.

Various changes may be made in the details given herein as illustrative of our invention which will still come within the scope thereof. We have described herein the preferred embodiment of our invention and we do not desire to be restricted to various amounts, procedures, or other details given in the foregoing specification as merely illustrative of that preferred embodiment except as necessitated by the appended claims.

We claim:

1. A hydrogen peroxide package comprising an aluminum container and an acidic hydrogen peroxide solution having a pH of 1.5 to 6 within said container, the inner surface of said container being coated with an oxide coating formed on the aluminum by anodic oxidation.

2. A hydrogen peroxide package comprising an aluminum container and an acidic hydrogen peroxide solution having a pH of 1.5 to 6 within said container, the inner surface of said container being coated with an oxide coating having adsorbed thereon paraffin, said oxide coating being formed on the aluminum by anodic oxidation in a 20 to 75% sulfuric acid solution.

JOSEPH S. REICHERT.

WILBIE S. HINEGARDNER.