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CORROSION RESISTANCE APPARATUS FOR USE WITH ACID CHLORITE SOLUTIONS

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The present invention relates to improvements in apparatus used in contact with acid chlorite solutions, such as, for example, acid chlorite bleaching solutions.

It is known that acid chlorine dioxide solutions, such as, for example, are obtained upon acidification of alkali metal and alkaline earth metal chlorites, are rather aggressive and corrode most materials normally employed in most bleaching apparatus. Consequently, considerable difficulties are encountered in bleaching textiles, fibrous materials and the like with acid chlorite solutions. The usual materials which are considered corrosion resistant, such as, for example, nickel or chromium alloyed steels, are attacked by acid chlorite solutions. Consequently, it has been proposed to employ titanium or its alloys, or certain synthetic plastics, for the construction or coating of apparatus employed with acid chlorite solutions. However, in general, bleaching with acid chlorite bleaching solutions is usually carried out in wooden or ceramic apparatus.

It has also been proposed to add nitrates to the chlorites to be used for bleaching or to add nitric acid or nitrates to the acid chlorite bleaching solutions. However, these proposals did not lead to really satisfactory protection of the apparatus.

While it is known that aluminum is stable against a number of oxidizing substances, it is strongly attacked by acid chlorite solutions. Also, the thin natural oxide layer which normally forms on aluminum surfaces does not prevent attack by acid chlorite solutions.

It is also known that a very dense and firmly adhering artificial aluminum oxide coating can be achieved on aluminum by chemical or electrolyte treatment, such as, for example, anodic oxidation. Aluminum provided with anodic oxide coatings is very corrosion resistant in many instances, but is attacked by acid chlorate.

According to the invention, it was unexpectedly discovered that aluminum provided with artificial aluminum oxide coatings obtained by chemical treatment or preferably by anodizing and, if desired, sealed, are corrosion resistant to acid chlorite solutions when care is taken that such solutions are devoid of nitrate and phosphate ions. It was furthermore found that in addition to artificially oxide coated pure aluminum, also artificially coated aluminum containing insignificant quantities of alloying components could be employed. Furthermore, it was unexpectedly found that the presence of chlorate ions in the acid chlorite solutions was not detrimental and that under certain circumstances increases the corrosion resistance of the anodized aluminum to the acid chlorite solutions.

The artificially oxide coated aluminum and particularly the anodized aluminum according to the invention is excellently suited as a construction material for bleaching apparatus for use with acid chlorite bleaching solutions devoid of nitrate and phosphate ions, for example, for bleaching cellulosic materials. The artificially oxide coated aluminum not only can be employed for the

bleaching vats, but also parts of the bleaching apparatus, such as pumps, pump parts, spindles for cross-reel bleaching and the like, which are either in contact with the acid chlorite bleaching solution or are located in the gas space above the bleaching solution. It is, of course, not necessary that the entire apparatus be constructed of the artificially oxide coated aluminum, as naturally the oxide coated aluminum can be employed as cladding on those parts which are subject to corrosion during the bleach operation, it merely being necessary that an artificially oxidized aluminum surface on the aluminum be presented to the corrosive influences.

The following table illustrates the exceptionally good corrosion resistance of anodized aluminum to acid chlorite solutions in the absence of nitrate and phosphate ions.

In the tests, chlorite solutions containing 1 g. per liter of sodium chlorite were employed and the tests were carried out at 70° C. In such tests, anodized aluminum strips were immersed in the chlorite solution so that ⅘ of the length thereof was below the surface of the solution and ⅕ above. The chlorite solutions employed were acidified to a pH of 3.8 with the acid indicated in the table.

Table

Aluminum base	Acid and other additions	Change in weight, g./m.²/day		
		After 5 days	After 10 days	After 15 days
Al, 99.99%	HCOOH	+0.030	−0.048	−0.060
Al, 99.99%	CH_3COOH	+0.046	+0.015	+0.023
Al, 99.99%	HCOOH+$NAClO_3$	+0.050	±0.000	±0.000
Al, 99.99%	HNO_3	+0.119	+0.059	−0.719
Al, 99.99%	H_3PO_4	−0.059	−0.100	−0.105
Al, 99.99%	HCOOH+$Na_4P_2O_7$	−0.882	−0.778	−0.756
Al, 99.99%	HCOOH+$NaNO_3$	−2.060	−1.485	−0.988
Al, 99+% (25)	HCOOH	−0.050	−0.015	−0.012
Al, 99+% (25)	CH_3COOH	+0.038	+0.025	+0.020
Al, 99+% (25)	HCOOH+$NaClO_3$	+0.030	±0.000	+0.010
Al, 99+% (25)	HNO_3	−0.086	−0.032	−0.023
Al, 99+% (25)	H_3PO_4	−0.050	−0.096	−0.131
Al, 99+% (25)	HCOOH+$Na_4P_2O_7$	−0.856	−1.052	−1.115
99.5% Al+0.5% Mg	CH_3COOH	+0.025	+0.018	+0.030
99.5% Al+0.5% Mg	H_3PO_4	−0.210	−0.185	−0.158
99.5% Al+0.5% Mg	HCOOH+$Na_4P_2O_7$	−1.042	−0.850	−0.762

The anodic oxide coating on the aluminum was produced as follows:

A degreased aluminum strip (99%) is thoroughly purified by a short immersion into a solution containing about 20% of sodium hydroxide at a temperature of 90° C. whereby the bath is vehemently foaming. The aluminum strip is then rinsed with water and pickled with a cold 3% nitric acid whereupon a second rinsing with water follows. After this purification process the aluminum is further treated in accordance with the examples:

(1) *Electrolytic oxidation.*—Into a bath of cold chemically pure 20% sulfuric acid a cathode of graphite or aluminum is suspended whilst the working piece to be oxidized is suspended as anode. After applying a voltage of about 15 volts or more a current density of about 0.3 to 1.5 amp./dm.² is obtained. After a period of ½ to 2 hours the electrolysis is switched off, the working piece removed and thoroughly rinsed for half an hour.

To harden the oxide film the oxidized aluminum is treated with boiling water or a diluted solution of sodium silicate for a period of ½ to 2 hours.

Instead of sulfuric acid (20%) a 10% oxalic acid, combined with chromic acid (for instance, 0.1% CrO_2), if desired; or pure chromic acid 3 to 10%, may be employed accordingly.

(2) *Chemical oxidation.*—For a period of 12 to 20 minutes an aluminum strip is immersed in a solution containing 50 grs./liter of soda and 15 grs./liter of sodium

chromate at a temperature of 90 to 100° C. After removal from this solution the strip is thoroughly rinsed with water and the oxide film is subsequently hardened by a treatment with a diluted (for instance 5%) solution of sodium silicate. The following examples show some practical tests with the thus oxidized aluminum:

(3) 2000 kgs. of grey cotton cloth are treated in a circulation bleaching apparatus made of the thus coated aluminum in a bleaching bath consisting of 9 m.³ of water and 30 kgs. of sodium chlorite 80% (the chlorite must be free of nitrates which are sometimes added as protective agents against corrosion; in general, the chlorites with such an addition of nitrate, however, have only a content of $NaClO_2$ of 50%); pH value adjusted to 3.9 to 4.1 by means of acetic acid. The treatment is carried out during a period of 4 to 5 hours and at a temperature of 60 to 100° C.

(4) To the bleaching bath as described in the foregoing example 10 to 20 kgs. of sodium or potassium chlorate are added. Adjustment of the pH value (3.7 to 3.8) may be carried out with formic acid or acetic acid either; in the latter case, however, the pH value should be 3.9 to 4.1.

A careful subsequent examination of the bleaching apparatus used in the aforementioned tests revealed no corrosion leading to a destruction of the apparatus and no trouble in the bleaching process.

I claim:

1. A method of bleaching cellulosic materials which comprises bleaching such cellulosic materials with acid chlorite bleaching solutions devoid of nitrate and phosphate ions in an apparatus in which at least a portion of the surfaces in contact with the bleaching solution and the gas space above the bleaching solution are anodically oxidized aluminum surfaces.

2. An acid chlorite bleaching solution confined in a container in which at least a portion of the surfaces in contact with such bleaching solution and the gas space above such bleaching solution are constructed of anodically oxide coated aluminum, said bleaching solution being devoid of nitrate and phosphate ions.

3. An acid chlorite bleaching solution confined in a container in which at least a portion of the surfaces in contact with such bleaching solution and the gas space above such bleaching solution are constructed of anodically oxide coated aluminum, said bleaching solution containing chlorate ions but being devoid of nitrate and phosphate ions.

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