

UNITED STATES PATENT OFFICE

2,067,703

ELECTROLYTIC DEVICE

Preston Robinson and Joseph L. Collins, North
Adams, Mass., assignors to Sprague Specialties
Co., Quincy, Mass., a corporation of Massa-
chusetts

No Drawing. Application March 28, 1931,
Serial No. 526,118

2 Claims. (Cl. 175—315)

Our invention relates to electrolytic devices, such as electrolytic condensers, rectifiers, or the like, comprising film-forming electrodes.

In such devices use is made of the film-forming effect exhibited by certain metals, for instance aluminum which, when placed in suitable electrolytes, upon application of the proper voltage are covered with a film. Such films consist of partially hydrated aluminum oxide and have a uni-directional character.

We shall describe our invention in its application to electrolytic condensers, using aluminum electrodes, although it should be well understood that our invention is not limited to such devices or electrode material.

We have found that the oxide layer which forms on aluminum, when exposed to the action of acids or to air, while chemically similar to the substance of the film built up in the electrolytic forming process, substantially differs therefrom in its insulating and dielectric properties. We have also found that if an aluminum electrode, before it is subjected to electrolytic formation, is covered by such an oxide layer, such layer disadvantageously influences film formation, respectively, the properties of the films obtained. More specifically we have found that condensers having electrodes, which were thus oxidized prior to their formation have higher power factor and smaller effective capacity than condensers—otherwise identical—in which electrodes are used on which oxidization before film formation has been prevented.

It is, therefore, one object of our invention to provide films of improved qualities by preventing oxidization of the electrode surface prior to the formation of the film.

Other objects of our invention will appear as the specification progresses.

As in the manufacture and handling of the electrodes impurities such as filings, grease, etc., are deposited on and adhere to the electrode surface, the deleterious influences of which are well recognized, it is practice to clean the electrodes before subjecting them to the film-forming process.

In the past, such cleaning was effected by subjecting the aluminum electrodes to an aqueous acidic bath and subsequently rinsing them in water. However, the acid while removing the impurities from the surface of the aluminum, also dissolves the outer layer of aluminum, and—due to the water present—forms an oxide layer on the electrode. This oxide layer is not removed through rinsing and its presence, as stated above,

deleteriously affects the quality of the dielectric film.

We have found that by immersing the aluminum in a properly prepared alkaline solution, we can remove the impurities just as effectively as with an acidic cleanser without forming an oxide layer on the aluminum.

Attempts to use alkaline cleansers for such purpose, have been unsuccessful so far, because an excessive amount of alkaline was required to properly clean the electrode. In addition, the alkaline attacked and pitted the aluminum to such an extent, particularly around metal impurities in the surface, that it was unfeasible to form a good quality film on the electrodes so cleaned, particularly in the neighborhood of the exposed impurities.

To prevent pitting of the aluminum, it has been suggested to treat the anodes in a weakly alkaline solution, such as borax or trisodium phosphate which will attack aluminum oxide or hydroxide, but which will not strongly attack aluminum. However, in order to obtain complete cleaning with such reagents, it would be necessary to operate at very high temperatures and for long continued times, which is objectionable and uneconomical.

We have found that the pitting action of a strongly alkaline solvent can be overcome, respectively changed in character, by adding to such solvent—which for instance may be caustic soda—a suitable inhibiting agent, such as sodium phosphate, sodium meta-silicate, sodium fluoride, etc. The strong local action of the alkali is hereby transformed into an evenly distributed moderate action and the aluminum, instead of being pitted and damaged in spots, is evenly etched over its whole surface. At the same time, only a small amount of caustic reagent is required.

Thus by using a caustic cleanser in the presence of proper inhibiting agents, objectionable oxidization of the electrode is prevented, and at the same time through evenly distributed etching of the aluminum surface, the effective area of the electrode is considerably increased.

After their cleaning in a caustic solvent, the electrodes are preferably subjected to rinsing.

However, we have found that objectionable oxidization of the electrode before it is formed is not fully prevented even by alkaline cleaning because, as above stated, the cleaned electrode when left exposed to air, oxidizes on its surface and this oxide layer is just as objectionable as the oxide film formed in an acidic cleaner.

Even relatively short exposures to air of the

cleaned electrodes cause a marked increase in power factor and decrease in capacity, and such deleterious effects increase with the duration of such exposure; and we found that the lowest power factors and maximum capacities are obtained when the electrodes, after their cleansing and rinsing are immediately submerged in the forming electrolyte and subjected to formation therein.

For instance, taking two electrodes of identical construction and cleaned by the same process and leaving one before its formation for half an hour exposed to air, while subjecting the other to the forming process immediately after its cleaning, we have found the following:

The capacity of the condenser using the first electrode was 6.2 MFD and its power factor 24%, while of the condenser using the second electrode, the capacity was 7.1 MFD and the power factor 15%.

In practice, therefore, after we have cleaned the electrodes in a proper alkaline solution and subsequently rinsed them preferably in a very weak alkaline solution—as a diluted solution of borax—we transfer the electrodes from the bath immediately into the forming tank and subject them therein immediately to formation, whereby the electrolyte used in the formation process is preferably slightly acidic.

Instead of using the above described method, we have found that undesirable oxidization of the electrode can be prevented by a second method as follows:

The electrodes, instead of being subjected to a preliminary chemical cleaning, undergo a preliminary forming process, which consists of placing the electrodes in a slightly acidic electrolyte, for instance, borax and boric acid in which the electrodes are subjected to a short formation. As a result of this formation, a thin oxide film covers the electrode, which film also includes the surface contaminations of the aluminum.

After such preliminary formation, the electrodes are submerged in an alkaline solution, for instance, borax, sodium phosphate, etc., which attacks and removes the preliminary film without oxidizing or attacking the aluminum. Thereafter, the electrodes are subjected to the regular forming process, preferably in a slightly acidic electrolyte.

In using this method, it is sometimes found advisable to have the alkaline solution only dissolve such outer portion of the preliminary film which actually contains the impurities, and to leave the inner portion of the film adhering to the electrode.

A third method of obtaining the same or similar results is the following:

The electrode, without preliminary cleaning, is placed in the forming tank which contains an alkaline electrolyte, for instance, borax. Current is now applied, whereby a film is formed on the electrode but partly attacked by the borax. Thereafter the electrolyte is made slightly acidic

by addition of boric acid and the electrode subjected to the regular formation process.

A fourth method is similar to the third and consists in placing the electrode without preliminary cleaning in the forming tank, which again comprises an alkaline solution as caustic soda, but instead of applying a forming current, the caustic soda is left chemically to clean the aluminum—preferably in the presence of inhibitive agents—as described in connection with the first method. After a short period of alkaline cleaning of the electrode, the electrolyte is made acidic, for instance, by addition of boric acid and the forming process undertaken in the regular way.

We have also found that while the highest quality commercially available aluminum, the so-called grade "A" aluminum, having 99.6% to 99.7% aluminum is subjected to corrosion in air, an aluminum of 99.9% or higher purity, does not corrode in air. Electrodes made of this material can be cleaned from adherent contaminations by means of an organic solvent and no further special precaution is required to prevent the electrode from corroding in air before it is subjected to formation.

In the foregoing we have described various methods to prevent objectionable oxidation of aluminum electrodes during or subsequent to their cleaning and to obtain higher quality oxide films. While we have illustrated our invention in connection with electrolytic condensers, using aluminum electrodes, and described specific methods, we do not wish to be limited to such devices, material or methods, but desire the appended claims to be construed as broad as permissible in view of the prior art.

Since claims relating to the second and third method hereinabove described are made in our Patent #2,035,022, of March 24, 1936, which issued on an application, Ser. No. 1,432, filed January 11, 1935, as a division of the present application, claims to said second and third methods are not made herein.

What we, therefore, claim and desire to secure by Letters Patent is:

1. In the manufacture of aluminum electrodes for electrolytic devices, the process which comprises immersing an electrode in an alkaline solution chemically to remove the impurities and the oxide from the surface of the electrode, adding thereafter, while maintaining the electrode in the solution, an excess of a weak acid to the solution and subjecting the electrode to film formation in said acidic solution.

2. In the manufacture of electrolytic devices, the process which comprises subjecting an electrode to chemical cleaning in a borax solution, adding thereafter, while maintaining the electrode in the solution, boric acid to the solution and subjecting the electrode to film formation in the solution of borax and boric acid.

PRESTON ROBINSON.
JOSEPH L. COLLINS.