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ELECTROLYTIC DEVICE

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Fig. 2.

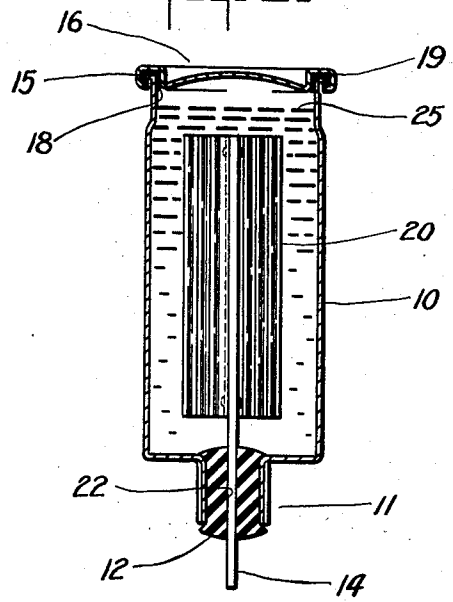
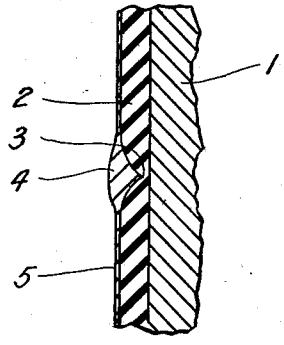


Fig. 1.



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ELECTROLYTIC DEVICE

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11 Claims. (Cl. 175—315)

Our invention relates to electrolytic devices having filmed electrodes, such as electrolytic condensers, rectifiers and the like, and more particularly to the film formation of such devices.

While we shall describe our invention in connection with so-called "wet" electrolytic condensers, the invention is also applicable to so-called "dry" electrolytic condensers, as well as to other electrolytic devices having filmed electrodes.

The general principle on which is based, the condenser, or valve action of such electrolytic cells, is well understood and no detailed description thereof is deemed necessary.

Aluminum, tantalum, zirconium, etc. are suitable filming metals for such use, of which metals, aluminum, because of its good all around properties and low price, is the most widely used. We shall describe our invention in connection with aluminum electrodes, although our invention also applies to the formation of other filming metals.

The formation of the filming electrode (or electrodes) of the condenser usually takes place before the assembly of the condenser, the electrodes being electrolytically formed in a suitable forming electrolyte. The filmed electrodes are then assembled with other parts and in known manner into condensers. Such condensers may be of the wet type, in which case they have a fluid electrolyte or the dry type in which case they have a viscous electrolyte, which is usually carried by a spacer.

They may be used for circuits in which a D. C. component prevails, in which case, as a rule, only the anode is filmed, or they may be used in A. C. circuits, in which case, as a rule, both electrodes are filmed.

The electrolyte used in the condenser has, as a rule, a lower pH than is the pH of the forming electrolyte for reasons fully described in our Patent No. 1,916,586.

As a rule the formation of the electrodes takes place in a single forming step, which as stated takes place prior to the assembly of the condenser. Frequently, in addition, a second formation of the electrode takes place in the final electrolyte, after the condenser has been assembled. In fact such after formation may take place under the usual operating conditions of the condenser.

In some instances, it has been found advantageous to form the electrodes in two steps prior to the assembly of the condenser, whereby as a rule two films of somewhat different properties are deposited one underneath the other.

In one of its aspects, the present invention relates to a double formation process, which process however is of novel and quite unique character. The process of our invention is usually, but not necessarily carried out in two formation steps, prior to the assembly of the condenser. Thereby, the film formed in the first step is a very dense film which covers practically the entire exposed electrode surface, whereas the film of the second forming step, is a less dense, fibroid and elastic film, which merely complements the first film to cover unfilmed voids remaining after the first formation.

As will be more fully explained, the aluminum oxide film formed by the first forming step is of unusual denseness, denser in fact than the aluminum it covers and because of this fissures, voids or at least weak spots are difficult to avoid, especially if the electrode is corrugated or etched.

The second forming step takes care of this, by forming a less dense and elastic film, which would not be good as a basic film, but is exceedingly well-suited for repair.

Alternately, this second forming step can take place after the assembly or even in the operation of the condenser, but to obtain the best results, it is preferable to give the second forming electrolyte a somewhat different character as has the final electrolyte and therefore to apply the second formation as a separate step, prior to the assembly of the condenser.

The electrode prior to its formation is preferably cleaned in an alkaline solution, for example, as described in our copending application, Ser. No. 526,118, filed March 28, 1931, now Patent No. 2,067,703, or may be etched in a dilute acid, or again may be anodically cleaned in a dilute acid solution at low voltage according to known processes used in finishing aluminum to increase its wearing properties.

Our novel forming process has several important advantages; among others it requires but a very small amount of electrical energy for formation, and a very short forming time. Furthermore, the resulting film has remarkable stability, and does not deteriorate even in long periods of idleness.

Our process also has various other advantageous features, which will appear as the specification progresses.

According to a preferred embodiment of our invention the formation of the filming electrodes takes place in two separate forming steps, of which at least the first step is a "rapid" formation process as described in the copending ap-

plications of Preston Robinson, Ser. No. 548,270, filed July 1, 1931, and Ser. No. 741,493 now Patents Nos. 2,057,314 and 2,057,315 respectively.

The process described in said Robinson applications, consists in an almost instantaneous formation of the film, obtained by progressively forming successive unfilmed portions of the electrode. A high voltage, as a rule the maximum operating voltage, is applied directly to the electrode, and successive electrodes portions are formed at extremely high current densities substantially as they enter into the electrolyte. Due to the rapid formation and the high electrostatic pressure prevailing, a dense and unhydrated oxide film is formed on the electrode.

According to our invention in the first forming step an alkaline forming electrolyte is used, comprising as a rule an alkaline salt of a weak acid, for instance, borax, tri-sodium phosphate, sodium-oxalate or the like. The electrodes, which are preferably supported from a common rack, are immersed gradually in the electrolyte, with the immediate application of the maximum forming voltage, as described in detail in said application Ser. No. 741,493.

While it has already been attempted to form films in alkaline solutions, such formation has been abandoned in modern practise, as such formation involves a secondary reaction, namely, the chemical attack by the alkaline electrolyte of the film already formed on the electrode.

The phenomenon which thereby takes place can be described briefly as follows: As the film forms on the filming electrode, for instance in our example the aluminum oxide on the aluminum, part of this aluminum oxide is again attacked by the alkaline electrolyte, which results in a continuous partial dissolution and disintegration of the film while it forms. Not only does this phenomenon effect an important loss of energy, which may amount to 50% or more of the input energy used in formation, but the formed film is not uniform, this non-uniformity not only involves different film portions but also manifests itself in different depths of a given film portion. This results in an erratic and unstable behaviour of the condensers.

In view of the above in present day formation more or less acidic or at least neutral forming electrolytes are used. However, in acidic and even neutral electrolytes—thus in all electrolytes which are not pronouncedly alkaline—another type of secondary chemical reaction takes place. This consists in the production of hetero-poly acids as a result of the reaction between the aluminum oxide of the film and the acidic constituents of the electrolyte. These hetero-poly acids are largely insoluble in the electrolyte, and part of the film structure in fact instead of consisting of aluminum hydroxide, consists of such hetero-poly acids, for instance in the case of boric acid consists of highly complex compounds of boric acid, aluminum oxide and water, of types analogous to those described in "Anorganische Chemie", Ephraim, 4th edition, pp. 414–423, incl., published by Steinkopff, 1929. Such hetero-poly acids permeate throughout the oxide film and deleteriously affect its overall properties. Besides that a thicker film is formed and also losses in the forming energy take place.

Thus a film formed in a non-alkaline electrolyte, because of its consisting partly of such compounds instead of pure aluminum oxide does not give the best results.

Our novel process has the unique characteristic that notwithstanding the use of an alkaline solution no secondary chemical reaction takes place and except for some unimportant liberation of oxygen, the only chemical reaction which takes place at the anode is film formation. For instance, if borax is used as the forming electrolyte, several thousands of anodes can be formed in the same electrolyte, without finding therein even traces of solid aluminum hydroxide or of aluminum or boric acid in solution in the electrolyte.

The absence of such secondary chemical reaction seems to be closely related with the "rapid" formation employed in this forming step. It results in an unhydrated and very dense oxide film having superior properties than the film formed in acidic or neutral electrolytes.

The final electrolyte in which these electrodes are used in the condenser, however is preferably acidic or at least neutral, because an alkaline electrolyte would eventually cause the above referred to, undesired secondary reactions whereas the above acidic reactions, once the film is provided on the electrode do not greatly influence the property of the film.

The second forming step takes place in an acidic electrolyte, for instance in a boric acid solution, or a solution of another weak acid as phosphoric, citric, tartaric acid to which a salt of a weak acid may be added. This formation has a double purpose, i. e., it preconditions the electrode for its use in the final electrolyte, and improves the general character of the film.

The film formed by the rapid forming process in the alkaline forming electrolyte is, as has been stated, a very high density, unhydrated aluminum oxide film. This film is denser than the aluminum which it covers and is less flexible than the usual partly hydrated oxide film formed by the previously known slow-forming processes. Such a dense film has the tendency, especially in case of corrugated or etched electrodes, of showing weak spots, fissures, and even voids, and one of the main functions of the second forming step is to form on such weak spots, fissures, and voids, a complementary or mending film of a fibroid, elastic character.

This second forming step usually requires a forming time of the order of 10 to 30 minutes, the exact time not being critical.

In the drawing forming part of the specification:

Figure 1 illustrates schematically and on an enlarged scale, an electrode portion, filmed in accordance with our novel process.

Figure 2 is a vertical sectional view of a condenser embodying our invention.

The aluminum used for the electrodes is preferably a high-purity aluminum of about 99.8% purity.

The electrodes are cleaned or etched in accordance with one of the previously referred to treatments.

The exact composition of the electrolytes used depends upon various factors, especially the final electrolyte used, and the voltage of the condenser.

A suitable forming electrolyte for a 500-volt wet condenser is, for instance, one comprising a dilute aqueous solution comprising 1 oz. of borax to 3 gallons of water.

Preferably a plurality of electrodes, supported on a common rack are immersed simultaneously and gradually into the electrolyte, with the immediate application of the full forming voltage of 500 volts between the electrodes and the electrolyte, whereby, as described in said above re-

ferred to application, Ser. No. 741,493, of Preston Robinson, the successive electrode portions are filmed at an extremely high current density and practically at their entrance into the electrolyte.

The temperature of the first forming electrolyte should preferably not exceed 50° C.

The electrodes so formed are then subjected to the second forming step in an acid electrolyte which may contain a weak acid with the possible addition of a salt of a weak acid, suitable acids being boric acid, phosphoric acid, citric acid, tartaric acid, etc., and salts of such acids can be added.

For the 500-volt condensers under consideration, a suitable electrolyte for the second forming step is one comprising 3 oz. of borax, 3 lbs. of boric acid, and 3 gals. of water. The temperature of this second forming electrolyte should be higher than that of the first forming electrolyte, and is preferably 80° C. or more.

The reason that in the first forming step the temperature should be kept low and in the second forming step kept high, is that in the first step a secondary chemical reaction is to be avoided, whereas in the second step a chemical reaction is desired, and an elevated temperature accelerates the rate of the chemical reaction.

The forming voltage in the second step is preferably the same as in the first forming step, although it may be slightly higher or in some specific cases even slightly lower. This formation does not need to take place by gradually immersing the electrodes as the electrodes are already formed. However, we prefer also in this case to immediately apply the full forming voltage. The duration of formation is of the order of 15 to 30 minutes, the exact time being not critical.

We prefer to add to the second forming electrolyte a substance which is of the same constituency as the film, this substance in the case of aluminum electrodes is aluminum hydroxide, with which we preferably saturate the second forming electrolyte. Such addition greatly speeds up the second forming step.

The so formed electrodes are then assembled into condensers the electrolytes of which have preferably a lower pH than has one of the two forming electrolytes, and preferably a lower pH than has the first forming electroly

We also prefer to add to the final electrolyte a substance of the same constituency as the film. The addition of such a substance and the advantages so obtained, are fully described in the copending application Ser. No. 468,466 filed July 16, 1930, of Preston Robinson.

Very good results are obtained if the pH of the electrolyte of the first forming step is about 9 to 10; of the second electrolyte about 4 to 6.8; and of the third electrolyte less than 6.8.

When the electrodes so formed are used for dry condensers, the pH of the final electrolyte is usually considerably lower and may be as low as 3 or even less.

An electrolytic condenser of the so-called wet type using an anode formed in accordance with our invention, is shown in Fig. 2.

The container 10 is preferably of metal and constitutes the cathode of the condenser. It may be either of filming or non-filming metal and is preferably a chromium-plated aluminum can. The container is provided with a reduced tubular extension 11.

A liquid electrolyte 25 is provided in the container, for instance, an aqueous solution of a weak acid, as boric acid, phosphoric acid, citric acid, etc., and preferably also containing the salt of a weak acid, for instance an alkali-metal or ammonium salt.

A seal provided in the extension 11 may consist of a plug 12 of rubber or other resilient material through the central bore 22, of which protrudes an extension 14 of the anode 20. The extension 11 is crimped around the rubber plug 12 to form a liquid- and gas-tight seal therewith.

The anode 20 consists of an aluminum foil folded back and forth upon itself in the manner of accordion pleating, the extension 14 being secured thereto, for example, by riveting.

At its free end the container is provided with a rim 15 around which is spun the edge 19 of the cap 16 with the interposition of a gasket vent 18, of a material sufficiently porous to permit the escape of gases liberated in operation, but at the same time providing for a good liquid-tight seal.

The above electrode and condenser constructions are given merely as an illustration and any suitable construction of either wet or dry condensers may be used.

When the above novel forming process is used for condensers formed at 350 volts or less, a quite unusual phenomenon takes place, namely, the condensers do not show the regular spark discharge at a voltage exceeding their maximum forming voltage, but have at such critical voltage merely an increased leakage current. The specific application of our invention to such lower voltage condensers, and the condensers obtained thereby are fully described in our copending application, Ser. No. 743,469 filed September 10, 1934.

As appears from the drawing, the aluminum electrode 1 is covered by a dense unhydrated pure aluminum oxide film 2. This film because of its high density and comparatively small elasticity may show weak spots as indicated at 3. In the second forming step an elastic film forms over this spot at 4. While a thin layer 5 of this film may also form on the good portion of film 2, this layer 5 is exceedingly thin and its influence is practically negligible.

While we have described our invention in connection with specific examples, we do not wish to be limited thereto, but desire the appended claims to be construed as broadly as permissible in view of the prior art.

What we claim is:

1. In the manufacture of electrolytic condensers, the process which comprises, electrolytically forming an operating dielectric film on a filming electrode in an alkaline solution having a pH between 8 and 10, and subjecting the electrode to a second formation in a non-alkaline electrolyte.

2. In the manufacture of electrolytic condensers for voltages of several hundred volts, the process which comprises immersing successive portions of a filming electrode into an alkaline solution having a pH less than 10 and applying immediately the maximum forming voltage to the electrode.

3. In the manufacture of electrolytic condensers, the process which comprises, forming in an alkaline solution a filming electrode at such a rate that no secondary chemical reaction occurs at said electrode.

4. In the manufacture of electrolytic condensers, the process which comprises, electrolytically forming in an alkaline solution having a pH between 8 and 10 an operating dielectric film on a filming electrode and subsequently forming said electrode in a non-alkaline forming electrolyte.

5. In the manufacture of electrolytic condensers, the process which comprises, immersing successive portions of a filming electrode into an alkaline solution having a pH less than 10, applying immediately the maximum voltage of several hundred volts to said electrode, and subjecting said filmed electrode to a second formation in an acidic electrolyte.

6. In the manufacture of electrolytic condensers, the process which comprises, forming on an electrode of filming material a dense and unhydrated oxide film which is free of heteropoly acids, and subsequently subjecting said filmed electrode to a second formation to mend the weak spots of said first film, by covering same with a less dense and elastic film.

7. In the manufacture of electrolytic condensers, the steps which comprise forming a filmed electrode in an electrolyte having a pH higher than 7, subsequently forming said filmed electrode in an electrolyte having a pH less than 7, and assemblying said electrode into a condenser having a final electrolyte having a pH less than 7.

8. In the manufacture of electrolytic condensers, the process which comprises forming a filming electrode in an alkaline solution at a temperature less than 50° C., and subsequently forming said filmed electrode in an acidic electrolyte at a temperature of more than 80° C.

9. An electrolytic condenser comprising a filming electrode, said electrode being provided with a high density and unhydrated oxide film free of heteropoly acids, the weak spots of said film being covered by a less dense and elastic mending film.

10. An electrolytic condenser comprising an aluminum electrode, a high-density and unhydrated oxide film adhering to said electrode, and a complementary elastic film of less density, covering as a thin layer said first-mentioned film and forming a heavy layer on the weak spots of said first film.

11. In the manufacture of electrolytic condensers, the steps which comprise, forming a filmed electrode in an electrolyte having a pH of about 9 to 10, subsequently forming said filmed electrode in an electrolyte having a pH of about 4 to 6.8, and assembling said electrode in a condenser having a final electrolyte having a pH less than 6.8.

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