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ALUMINUM ELECTRODE AND METHOD OF PREPARING

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Fig. 1.

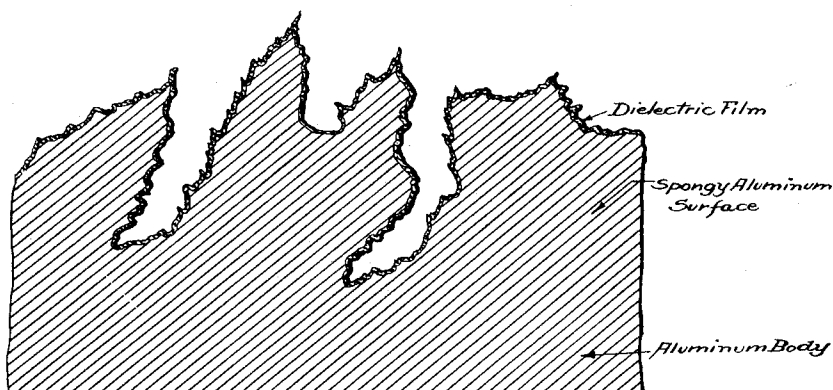
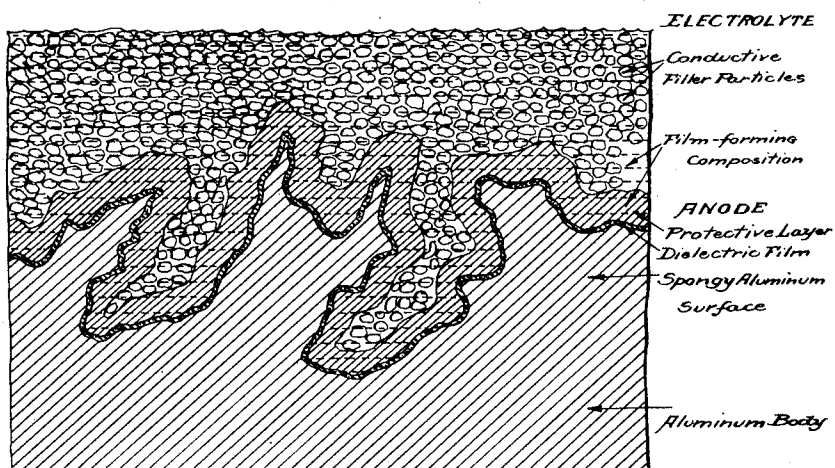


Fig. 2.



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UNITED STATES PATENT OFFICE

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ALUMINUM ELECTRODE AND METHOD OF PREPARING

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30 Claims. (Cl. 175—315)

My invention aims to provide a method of treating aluminum bodies to produce a spongy surface structure or coating thereon so as to increase the effective surface area. The invention particularly relates to the preparation of aluminum electrodes, such as anodes for use in electrolytic condensers and the like.

This application is in part a continuation of my copending application Ser. No. 560,141, filed August 29, 1931, which is in part a continuation of my application Ser. No. 462,251, filed June 19, 1930, and copending therewith.

As applied to the preparation of an electrolytic condenser anode of aluminum, an object of the invention is to provide a treatment for the aluminum, prior to the formation of a dielectric film thereon, which will permit of obtaining a much greater capacitance due to the increase of effective surface area made available for film formation by the treatment. The invention thus makes possible the production of electrolytic condensers having a greater capacitance per unit of weight and volume than present types. In this connection, a feature of the invention is the simplicity and low cost of the treatment, making possible the production of condensers of given capacitance at less expense than would otherwise be possible.

A further object of the invention is to provide, in combination with the treatment producing a spongy surface structure, a treatment which produces a porous hydratable protective layer coating the spongy surface, making possible an efficient formation of a dielectric film of high quality and great endurance. Advantages of this combined treatment and of resulting electrodes will be described in more detail hereafter.

Still another object of the invention is to provide a new and useful combination of anode and electrolyte for employment in electrolytic condensers.

Other objects and features of my invention will be made evident as the description progresses.

In the accompanying drawing, wherein the application of the invention is illustrated,

Fig. 1 shows diagrammatically a greatly magnified cross-section of an aluminum body provided with a spongy surface structure having a dielectric film thereon, and suitable for use as an anode in an electrolytic condenser; and

Fig. 2 shows diagrammatically a greatly mag-

nified cross-section of an anode in the region of its juncture with an electrolyte, the latter being shown in elevation, illustrating a preferred type of anode employed in combination with a preferred type of electrolyte.

Preparation of spongy aluminum surface

The aluminum to be treated, in the form of a thin sheet or foil, for example, is exposed to the action of hydrochloric acid, as by being dipped or immersed therein. The acid employed is of such concentration and temperature as to cause a violent, and in many cases an almost explosive, surface reaction on the aluminum, producing an extremely high local temperature.

As a result of this treatment, the surface of the aluminum becomes dark or blackish gray in color; and has the appearance of a more or less velvety coating upon the underlying metal body when the aluminum is of high purity, depending upon the particular treatment procedure used. Under a magnifying glass or low power microscope, a granular or spongy structure is plainly visible, holes or interstices of substantially microscopic size being clearly observed. When the treatment has been carried only to the point of producing a thin streaked coating, the aluminum body will appear to the naked eye to be covered with an adherent coating of gray metallic dust.

The hydrochloric acid employed for the treatment will, as a result of the reaction, be found to contain black finely divided particles of aluminum which have been driven off from the aluminum surface.

While the coating or surface structure produced on the aluminum is closely adherent and is integral with the underlying body, it is possible to rub off some of the material in the form of a fine black powder similar to that found in the acid used, particularly if the treatment has been continued for some time.

By analogy to the well known spongy platinum and platinum black, which consist of finely divided platinum, the surface of the treated aluminum may aptly be referred to as "spongy aluminum". The particles which become detached or are driven off may likewise be aptly termed "aluminum black".

While the spongy aluminum structure consists

essentially of aluminum, it is probably oxidized on the exposed surfaces, and this, together with the finely divided state of the structure, causes the dark or blackish gray color.

As a result of treating an aluminum body so as to produce a spongy aluminum surface or coating thereon, the effective surface area is greatly increased. Hence when the treated aluminum is subjected to any of the usual film-forming operations, for example by being electrolyzed as an anode in a solution of boric acid or the like, and is then employed in an electrolytic condenser, a considerably greater capacitance is obtained that would result if the hydrochloric acid treatment had been omitted. This increase of capacitance may amount to 100% or even more, depending upon the particular treatment procedure followed.

Fig. 1 illustrates in diagrammatic manner the general character of an aluminum body which has been treated in hydrochloric acid according to my invention. This drawing shows a greatly magnified cross-section of the surface region and indicates schematically the spongy nature of the aluminum surface and the great increase of effective surface area resulting therefrom. When provided with a dielectric film, as shown, it is thus evident that a greater capacitance per unit area of the aluminum body results than if the body had not been treated and possessed only the usual substantially smooth surface.

Prior to the hydrochloric acid treatment, the aluminum may be cleaned in any of several ways, for example, by washing with soap and water, in a 10% borax solution, or in a hot solution of potassium hydroxide. I prefer to clean the aluminum with a solution of 18N sulfuric acid containing 50 grams of potassium dichromate per liter. Following cleaning, the metal is rinsed in water and is then ready for the hydrochloric acid treatment. This preliminary cleaning is not essential and may be omitted, particularly when new aluminum foil or sheets having clear surfaces are used.

The hydrochloric acid employed for treating aluminum in accordance with my invention, to produce the surface structure previously described, may be dilute, moderately concentrated, or highly concentrated. It is essential that the temperature be sufficiently high to cause the violent reaction characteristic of my method, or to cause this type of reaction to become initiated, as otherwise a mere etching only will occur and the spongy surface structure will not be produced.

The actual minimum acid temperature necessary for any given acid concentration depends to a considerable extent upon the conditions and technique of treatment employed.

A reaction will occur even at temperatures too low to immediately cause the characteristic violent reaction which produces a finely divided or spongy surface, and as this reaction is exothermic the heat generated may ultimately cause a sufficient increase of temperature in the reaction zone to initiate the necessary violent type of reaction. Thus the distinction must be borne in mind between the actual reaction zone temperature which is needed, and the temperature of the body of acid which is necessary to produce, directly or indirectly, the requisite reaction zone temperature. The more nearly the acid temperature (by which is meant the temperature of the body of acid) approaches the required reaction zone temperature, the quicker the initiation of

the desired violent type of reaction. On the other hand, if the acid temperature is too low, the rate of heat generation compared with the rate at which the heat becomes dissipated, as by conduction away, will be too low to cause the necessary reaction zone temperature to build up within a reasonable length of time, or before an excessive amount of metal has become lost by dissolving in the acid. Moreover, if the acid is of too low concentration, equilibrium may occur before a sufficiently high reaction zone temperature is reached, in which case the desired violent reaction will not be initiated irrespective of the length of treatment.

Since the rate of heat dissipation from the reaction zone is a factor in determining the rate of increase of the reaction zone temperature, it follows that the technique of treatment will influence the minimum acid temperature that can be successfully used with any given concentration. It will be found, for example, that a higher acid temperature is required when the aluminum is continuously immersed in an acid bath than when it is repeatedly dipped, and raised into the air between dippings. In the latter case, sufficient acid will cling to the metal and react therewith during the intervals when it is raised out of the bath, and during these periods less heat will be conducted away by the air than by the acid bath during immersion, thus speeding up the reaction by producing a higher reaction zone temperature.

Due to the differences in heat dissipation it will also be found that a thin sheet or foil of aluminum can be treated successfully in acid of lower temperature than is the case with a thick body of aluminum. Circulation or stirring of the medium in contact with the aluminum during treatment will increase the rate of heat dissipation and thus slow down the reaction and make a higher acid temperature necessary.

Accordingly, it is impractical to set forth any formula or definite figures to indicate the exact minimum acid temperature required under various conditions of treatment. Moreover, as a practical matter, the necessary temperature can readily be determined by trial in any given case.

In order to secure uniformity of results when the treatment is employed commercially, it is advisable to conduct the treatment by immersing the aluminum continuously in the hydrochloric acid for a period of one to three minutes, the concentration and temperature of the acid being adjusted so as to secure a good coating or spongy surface structure within this period.

From the practical standpoint it is undesirable to employ an acid temperature which requires more than five minutes of immersion of the aluminum to produce a satisfactory spongy aluminum surface, since not only would there be an undue loss of metal but, in general, a relatively poor surface structure would be obtained. Accordingly, the minimum temperature, for various acid concentrations, to produce a good formation of a spongy aluminum surface within five minutes, will be of significant interest.

The following table gives a minimum acid temperature which will produce an excellent spongy aluminum surface with five minutes immersion of a thin aluminum sheet or foil, for hydrochloric acid baths of various concentrations. The acid concentrations are given both in terms of the hydrogen chloride (HCl) percentages, and in terms of the normalities of the acid solutions (by

which is meant the number of molecular weights of HCl per liter of water).

Hydrochloric acid concentration		Minimum acid temperature (° C.)
Normality	Percent HCl	
12	37	45
10	31	35
8	26	25
6	20	45
5	17	60
4	14	70
3	10	75
1.5	5	95

The above temperature figures should not be regarded as exact minimum values, but as indicating the approximate lower limits for satisfactory treatment by continuous immersion of the aluminum. It will be understood that higher temperatures should be used when the treatment is to be completed in less than five minutes, as can readily be determined by trial.

With any given combination of acid temperature and concentration capable of producing a good uniform spongy surface, an optimum length of treatment exists beyond which no additional increase of capacity will result when the surface is later formed with a dielectric film, and the capacity may even be less than when the optimum time is employed if the treatment is continued unduly long.

By way of example to illustrate a preferred treatment method to secure a good spongy surface structure upon aluminum foils, it may be mentioned that excellent results will be obtained by using 6.0-6.5 normal acid having a temperature of 55° C., the period of immersion being about 120 seconds.

As previously indicated, the reaction can be hastened by dipping the aluminum in the acid and exposing it to the air between dips, although it is hard to secure highly uniform results due to the difficulty of exactly duplicating the treatment. To illustrate this mode of carrying out the treatment, it will be found that two to four dips of 2-3 seconds' duration each, in 6 normal hydrochloric acid having a temperature of 85-90° C., produces an excellent treatment, resulting in a dark gray fine-grained surface layer of spongy aluminum which adheres firmly to the underlying metal as a thin integral coating.

It is also feasible in some cases to heat the aluminum before contacting it with the acid, thus making possible the use of lower acid temperatures. However, when a thin sheet or foil of aluminum is to be treated, as is normally the case when electrolytic condenser anodes are being prepared, the metal will almost immediately assume the temperature of the acid bath after immersion without substantially affecting the temperature of the latter; so that heating of the aluminum before immersion in such case will not ordinarily permit of satisfactory using lower acid temperatures than otherwise required.

I am aware that etching or pickling of aluminum by use of hydrochloric acid has been employed in the past for the purpose of cleaning the surface, or as a step in cleaning methods. The purpose of such pickling is to clean the surface and not to produce a surface structure of different type. Pickling is conducted with dilute hydrochloric acid, such as acid of 5-10% strength, at room or only moderately elevated tempera-

tures, and is usually followed by treatment in nitric acid to produce a bright surface. Such treatment does not cause the extremely violent surface reaction characteristic of my method and hence does not produce a spongy aluminum surface. A filmed anode which has merely been pickled prior to film forming will not have the high capacity characteristic of a filmed anode which has been treated according to my process prior to film forming.

Following treatment of the aluminum with hydrochloric acid to produce a spongy surface structure as heretofore described, the aluminum is next washed to remove all traces of hydrochloric acid and chlorine ions, as the presence of chlorine ions will prevent proper film formation. This may be accomplished by washing the surface in a film-forming acid solution, as for example an aqueous solution of boric acid. A hot or boiling solution permits of a shorter washing period and a more complete removal of the hydrochloric acid from the spongy surface of the aluminum.

Washing in hot water as in an alkaline solution is ordinarily not used because it affects the properties of the dielectric film and makes for a higher leak and power factor.

The treated and washed aluminum is next subjected to film-forming treatment to produce a dielectric film upon the surface, if the preparation of an anode for use in electrolytic condensers is the objective. This may be done in any manner suitable for forming untreated aluminum, many such methods being known to those skilled in the art. For example, the aluminum may be electrolyzed as an anode in a solution of boric acid containing a small amount of borax or ammonium borate. This procedure results in an anode of the type illustrated in Fig. 1, as previously described.

Production of protective layer

In the preparation of filmed anodes, I have found that very advantageous results follow from providing a treatment to produce a permeable hydrated protective layer upon the spongy aluminum surface prior to the formation of a dielectric film thereon. Not only does the presence of such a protective layer facilitate the formation of the dielectric film, but the dielectric film is of better quality than would otherwise be the case. Moreover, the protective layer mechanically strengthens the spongy aluminum surface structure. In addition, the filmed electrode will possess a protective layer over the dielectric film which mechanically protects it and which makes possible the use of the electrode in electrolytic condensers of the type having an electrolyte containing conductive filler particles, as described and claimed in my Patent No. 1,986,779, issued January 1, 1935, and in my copending application Ser. No. 560,141, filed August 29, 1931.

A protective layer of this type may be formed upon the aluminum surface by electrolyzing the metal, as an anode, in a solution of oxalic, sulfuric, or phosphoric acid, for example. When superposed over an active dielectric film, as results when the aluminum is subsequently formed to produce an aluminum oxide film on the surface of the aluminum beneath the protective layer, this protective layer is relatively conductive, even at low voltages, in the presence of hydroxyl ions and does not function as a dielectric layer. Only when dry, and hence non-hydrated, is the outer protective layer highly insulating. This type of

layer is comprised of a highly hydratable aluminum compound and when in the hydrated condition it operates as a porous or permeable conductive coating which permits a film-forming electrolyte to film the underlying metal to produce or maintain a dielectric film.

Fig. 2 illustrates in diagrammatic fashion the surface strata on the aluminum following the combined treatment. The aluminum body still possesses a spongy surface structure and this is covered with the dielectric film which in turn is coated with the protective layer.

The protective layer, formed by electrolytic action as described above, may be made to any desired thickness, since a characteristic of this type of layer or film, in contradistinction to an active dielectric film, is that its thickness is not limited by the applied voltage, but can be regulated, and is dependent upon the concentration and temperature of the forming electrolyte, the current density, and duration of treatment. Preferably, the protective layer is formed to a thickness of no more than 1/1000 mm. and should not be made so heavy as to destroy the fine structure of the spongy aluminum surface.

In preparing electrodes according to this method, the aluminum is thoroughly washed following the treatment in hydrochloric acid to produce the spongy surface. Washing in hot water, or in water to which an alkali has been added, will itself produce a protective coating of aluminum hydroxide or hydrated aluminum oxide; and in some cases it may be desirable to follow this procedure whether or not a further protective coating or layer is formed by electrolytic action as previously described.

However, I ordinarily avoid this mode of washing because it will result in the subsequently formed dielectric film having a higher power factor and leakage, and in a less uniform protective layer formed electrolytically. Instead, I prefer to wash with an acidulated bath, as for example a hot or boiling solution of boric acid or other dielectric film-forming acid, or a weak solution of the acid used to form the protective layer may be employed. Generally, I wash with a hot or boiling boric acid solution and then rinse with the latter acid, in order to avoid diluting the bath used for forming the protective layer.

The aluminum is then electrolyzed as an anode in a suitable solution to form the protective layer. By way of example, a proper formation can be effected in $\frac{1}{2}$ normal phosphoric acid at a current density of 16 milliamperes per square inch of the effective surface area of the immersed aluminum body, the duration of forming being 45 minutes. This means a current density of about 30 ma/in² with respect to the original surface area, or the surface area as measured with a ruler.

The aluminum is then removed from the electrolytic bath and thoroughly washed to remove all traces of the acid, preferably in a hot or boiling solution of boric acid or other dielectric film-forming acid of this type. Hot water may be used, although not preferred, with less disadvantage than when the protective layer is not present; but alkaline washes are generally harmful.

The aluminum is then formed to produce a dielectric film as heretofore described.

It has been found that when a dielectric film is formed on a spongy aluminum surface directly, following treatment of the aluminum in hydrochloric acid, the formation of the dielectric film takes longer and the final leak is higher than is

the case when plain aluminum is filmed; and that condensers made up with anodes prepared in this manner possess a higher power factor. In some cases this will not be so important and will be more than compensated for, from the practical standpoint, by the great increase of capacitance.

I have discovered that these disadvantages can, however, be avoided by forming the above-mentioned protective layer upon the spongy aluminum surface (following washing with boric or other acid as described) prior to forming the dielectric film. Hence the combined treatment in hydrochloric acid and subsequent formation of a protective layer makes possible the production of electrolytic condenser anodes having the same advantages attendant upon employing untreated aluminum, and which at the same time possess a much higher capacitance than if the hydrochloric acid treatment were omitted. Thus the increased capacitance can be obtained without sacrifice of quality.

Electrolytic condenser anodes prepared in this manner can be employed in conjunction with any type of electrolyte customarily used, since the protective layer is permeable and will not interfere with the desired relation between electrolyte and dielectric film, and accordingly are of general application.

Special anode-electrolyte combination

An electrolytic condenser anode prepared in the manner just described, having a protective layer covering the dielectric film on the spongy aluminum surface, as shown in Fig. 2, may be used to advantage with electrolytes containing finely divided particles of conductive or non-conductive nature, to avoid contact of such particles with the dielectric film on the anode. This advantageous characteristic of anodes provided with a permeable protective layer is described and broadly claimed in my copending application, Ser. No. 560,141, filed August 29, 1931.

I have discovered that the spongy surface type of anode having a protective layer may also be used with an electrolyte possessing an extremely high specific resistance film-forming composition component and a lamp black conductive filler. The general combination of anode and electrolyte of this type is described and claimed in my Patent No. 1,986,779, issued January 1, 1935, in which however the combination is specifically illustrated in connection with anodes which have not been provided with a spongy surface.

The interstices between the finely divided aluminum particles of the spongy surface are quite small and are of substantial depth, and the anode surface interstices are rendered even smaller by the formation of the protective layer. It was therefore not expected that lamp black particles contained in an electrolyte in contact with the anode would be able to adequately penetrate or fill the interstices so as to permit the electrolyte in toto to contact the whole outer surface of the protective layer. This would mean that when the electrolyte contained a film-forming composition of a high order of specific resistance, for example of 100,000 ohms/cm³ or more, that the high resistance of the electrolyte within the interstices would cause the condenser to have a large power factor.

I have found, however, that lamp black particles are not so coarse, relative to the size of the interstices, as to produce this undesirable result, and that on the contrary the power factor remains acceptable notwithstanding that the alu-

minum has been provided with a spongy surface. The same result will of course be obtained when other conductive particles of sufficiently small size to penetrate the interstices of the anode surface are used.

This holds true even when the electrolyte is of a highly viscous or plastic consistency and thus makes possible the use, in combination, of an anode prepared according to my invention, herein described, with the special forms of electrolytes described in my aforesaid patent.

Fig. 2 illustrates in diagrammatic fashion this and similar combinations of my present anode with electrolytes containing finely divided particles, such as conductive filler particles of lamp black. In the combination, as shown, the protective layer maintains the particles in the electrolyte spaced away from the dielectric film, while permitting healing or forming of the film, and yet the electrolyte as a whole, including the particles, is enabled to penetrate thoroughly into the surface interstices and hence is not unduly separated from the dielectric film as a whole.

Having described and illustrated my invention, what I claim is as follows:

1. A method of preparing a filmed aluminum electrode suitable for use in electrolytic condensers and the like, comprising treating an aluminum body with hydrochloric acid having a sufficient temperature with respect to its concentration to cause a violent surface reaction producing a spongy aluminum surface thereon, and subsequently forming on the aluminum a dielectric film having a substantially greater area than is obtainable without the presence of said spongy surface.

2. A method of preparing a filmed aluminum electrode suitable for use in electrolytic condensers and the like, comprising reacting the surface of an aluminum body with hydrochloric acid under suitable elevated temperature conditions to produce a finely divided surface structure and greatly increased effective surface area, substantially as described, and forming a dielectric film thereon by electrolyzing the aluminum as an anode in a film-forming electrolyte.

3. A method of preparing a filmed aluminum electrode suitable for use in electrolytic condensers and the like, comprising cleaning an aluminum body with a hot alkali solution, treating the aluminum with hydrochloric acid of at least 5% strength and having a temperature sufficient to cause a violent surface reaction producing dark colored finely divided aluminum particles and a spongy surface on said body, washing and forming a dielectric film on the aluminum by electrolyzing the aluminum as an anode in a film-forming electrolyte.

4. A method of preparing a filmed aluminum electrode for use in electrolytic condensers and the like, comprising immersing an aluminum body in hydrochloric acid of suitable concentration and temperature to cause a violent surface reaction and the production within five minutes of a dark colored spongy surface structure, and forming a dielectric film on the aluminum by electrolyzing the aluminum as an anode in a film-forming electrolyte.

5. A method of preparing a filmed aluminum electrode for use in electrolytic condensers and the like, comprising immersing a sheet of aluminum in hydrochloric acid for a sufficient period to produce a spongy surface structure, the temperature of the acid being not less than about

that indicated below in relation to the acid strength:

37%—45° C.
31%—35° C.
26%—25° C.
20%—45° C.
17%—60° C.
14%—70° C.
10%—75° C.
5%—95° C.

and forming a dielectric film on the aluminum by electrolyzing the aluminum as an anode in a film-forming electrolyte.

6. A method of preparing a filmed aluminum electrode for use in electrolytic condensers and the like, comprising immersing an aluminum body in hydrochloric acid of suitable concentration and temperature to cause a violent surface reaction and the production in one to three minutes of a dark colored spongy surface structure, thereafter removing the aluminum from the acid and thoroughly washing the spongy surface, and forming a dielectric film on the aluminum.

7. A method of preparing a filmed aluminum electrode for use in electrolytic condensers and the like, comprising immersing an aluminum sheet for two minutes in a bath of hydrochloric acid having a normality of about 6.0–6.5 and a temperature of about 55° C., removing the aluminum from the acid and washing, and forming a dielectric film on the aluminum.

8. A method of preparing a filmed aluminum electrode suitable for use in electrolytic condensers and the like, comprising dipping a thin aluminum sheet or foil several times for several seconds each in about 6 normal hydrochloric acid having a temperature of about 85–90° C., washing, and forming a dielectric film on the aluminum.

9. A method of preparing a filmed aluminum electrode suitable for use in electrolytic condensers and the like, comprising treating an aluminum body with hydrochloric acid having a sufficient temperature with respect to its concentration to cause a violent surface reaction producing a spongy surface thereon, washing the surface in a non-alkaline solution to remove traces of hydrochloric acid and chlorine ions and render it suitable for film-formation, and forming a dielectric film on the aluminum.

10. A method of preparing a filmed aluminum electrode suitable for use in electrolytic condensers and the like, comprising cleaning the surface of an aluminum body with a hot alkali solution, treating the aluminum with hydrochloric acid at a suitable elevated temperature to produce a fine-grained granular surface structure, washing the surface with a hot acid solution to remove traces of hydrochloric acid and chlorine ions and render it suitable for film-formation, and forming a dielectric film by electrolyzing the aluminum as an anode in a film-forming electrolyte.

11. A method of preparing a filmed aluminum electrode suitable for use in electrolytic condensers and the like, comprising treating an aluminum body with hydrochloric acid at a suitable elevated temperature to produce a fine-grained granular surface structure, washing the surface with a hot acid solution to remove traces of hydrochloric acid and chlorine ions and render it suitable for film-formation, and forming a di-

electric film by electrolyzing the aluminum as an anode in a film-forming electrolyte.

12. A method of preparing a filmed aluminum electrode suitable for use in electrolytic condensers and the like, comprising reacting the surface of an aluminum body with hydrochloric acid under conditions adapted to produce a dark colored spongy surface layer, washing in hot boric acid, and forming a dielectric film on the aluminum.

13. A method of preparing a filmed aluminum electrode, comprising treating an aluminum body with hydrochloric acid under conditions adapted to produce a spongy surface, treating the spongy surface so as to produce a thin protective layer of a hydrated aluminum compound thereon, and forming a dielectric film upon the aluminum and beneath said layer.

14. The method comprising treating an aluminum body with hydrochloric acid to produce a spongy surface, washing the surface with a non-alkaline solution, and electrolyzing the aluminum as an anode in a solution of an acid of the class consisting of oxalic, sulfuric and phosphoric acids.

15. The method comprising treating an aluminum body with hydrochloric acid to produce a spongy surface, washing the surface with a hot acid solution, and electrolyzing the aluminum as an anode in a solution of an acid of the class consisting of oxalic, sulfuric and phosphoric acids.

16. A method of preparing a filmed aluminum electrode, comprising treating an aluminum body with hydrochloric acid having a sufficient temperature and concentration to cause a violent surface reaction and produce a spongy surface structure, washing the surface with a hot acid solution, electrolyzing the aluminum as an anode in an acid having the character and action of phosphoric acid to produce a thin protective layer, and electrolyzing the aluminum as an anode in an electrolyte having the character and action of boric acid to form a dielectric film upon the aluminum beneath said layer.

17. The method comprising treating an aluminum body with hydrochloric acid to produce a spongy surface, washing the surface with a hot acid solution, electrolyzing the aluminum as an anode in a solution of an acid of the class consisting of oxalic, sulfuric and phosphoric acids to produce a thin permeable coating on the surface, washing, and electrolyzing as an anode in a film-forming electrolyte to produce a dielectric film on the aluminum.

18. The method comprising washing the surface of an aluminum body with a hot alkali solution, treating the aluminum body with hydrochloric acid to produce a spongy surface thereon, washing the surface with a hot acid solution, electrolyzing the aluminum as an anode in a solution of an acid of the class consisting of oxalic, sulfuric and phosphoric acids to produce a thin permeable coating on the surface, washing with a hot solution of a film-forming acid, and electrolyzing as an anode in a film-forming electrolyte to produce a dielectric film on the aluminum.

19. A method of treating aluminum to obtain a greatly increased effective surface area, comprising subjecting an aluminum body to the action of hydrochloric acid having a sufficient temperature with respect to its concentration to cause

a violent surface reaction producing a spongy aluminum surface thereon.

20. The method which comprises treating an aluminum body with hydrochloric acid of at least 5% strength and having a temperature sufficient to cause a violent surface reaction producing dark colored finely divided aluminum particles and a spongy aluminum surface on said body.

21. A method of treating aluminum which comprises immersing an aluminum body in hydrochloric acid of suitable concentration and temperature to cause a violent surface reaction and the formation of a clearly observable spongy surface within five minutes treatment time, substantially as described.

22. A method of surface treating aluminum comprising immersing an aluminum sheet in hydrochloric acid for a sufficient period to produce a spongy surface structure, the temperature of the acid being not less than about that indicated below in relation to the acid strength:

37%—45° C.

31%—35° C.

26%—25° C.

20%—45° C.

17%—60° C.

14%—70° C.

10%—75° C.

5%—95° C.

23. A method of surface treating aluminum comprising immersing an aluminum sheet for two minutes in a bath of hydrochloric acid having a normality of about 6.0-6.5 and a temperature of about 55° C., to produce a spongy surface structure.

24. An aluminum body having a spongy aluminum surface and a thin protective layer thereover of a permeable hydratable aluminum compound.

25. An electrode suitable for use in electrolytic condensers and the like comprised of an aluminum body having a finely divided aluminum surface structure, a dielectric film in contact and integral therewith, and a protective layer thereover of a permeable hydratable aluminum compound.

26. In an electrolytic condenser or the like, the combination comprising an electrolyte containing finely divided filler particles, and an aluminum electrode having a spongy surface provided with a dielectric film and a superposed integral protective layer preventing contact between said particles and said dielectric film.

27. In an electrolytic condenser or the like, the combination comprising an aluminum electrode having a spongy surface provided with a dielectric film and a superposed integral protective layer of a hydrated aluminum compound having a thickness of the order of 1/1000 mm., and an electrolyte containing finely divided conductive filler particles of small enough size to penetrate into the interstices of the electrode face communicating with the electrolyte.

28. In an electrolytic condenser or the like, the combination with an electrolyte containing a filler of lamp black particles and a film-forming composition having a high order of specific resistance, of an electrode having a spongy aluminum surface structure provided with a dielectric film covered with a thin permeable protective layer of a hydratable aluminum compound, the

outer face of the electrode having minute interstices communicating with the electrolyte and of sufficient size to permit said lamp black particles to reach substantially the whole exterior surface of said protective layer.

29. A filmed electrode adapted for use in electrolytic condensers and the like comprising an aluminum body having a fine-grained spongy surface structure which has a granulated appearance when viewed under a magnifying glass

or low power microscope, and having a dielectric film on the aluminum surface.

30. In an electrolytic condenser, an anode comprised of an aluminum body having an integral gray surface layer of finely divided aluminum of the character resulting from treatment of the aluminum body with hydrochloric acid substantially as described, and having a dielectric film on said layer of aluminum.

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