July 2, 1940. P. ROBINSON 2,206,050

ELECTROLYTIC DEVICE

Original Filed March 21, 1934

Fig. 1.

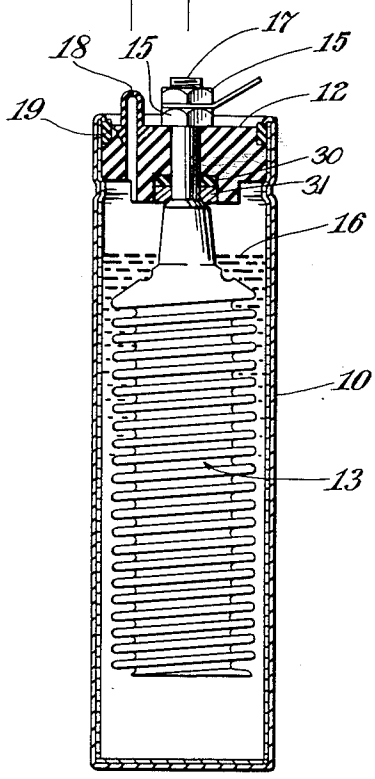


Fig. 2.

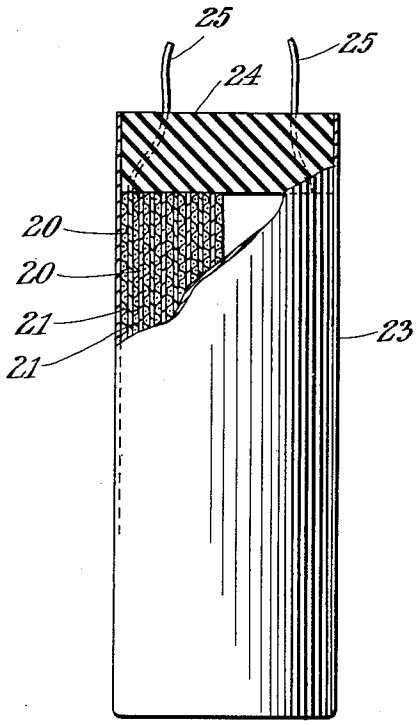
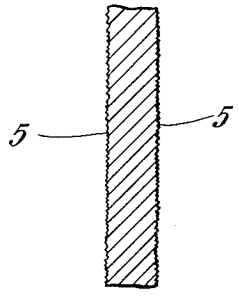


Fig. 3.



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2,206,050

ELECTROLYTIC DEVICE

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Original application March 21, 1934, Serial No. 716,714. Divided and this application June 12, 1935, Serial No. 26,291

11 Claims. (Cl. 175—315)

This invention relates to a novel process of manufacture of electrolytic devices and more particularly to the manufacture of electrolytic condensers.

The present invention is a divisional application of my copending application Serial No. 716,714 filed March 21, 1934.

Electrolytic condensers in their usual form comprise two electrodes, at least one of which is of so-called filming metal, for instance, of aluminum, tantalum, zirconium, etc. The condenser is provided with a suitable electrolyte, which may be highly fluid, as in the case in the so-called "wet" electrolytic condensers, or may be more or less viscous, as is the case in the so-called "dry" electrolytic condensers. My invention applies to both wet and dry types of electrolytic condensers and irrespective of whether one or both of the electrodes of the condenser are filmed.

In electrolytic condensers the capacity effect is due mainly to the dielectric properties of the film formed on the filmed electrode or electrodes. This film consists as a rule of an electrolytically-formed, partly hydrated oxide of the metal of the filming electrode.

As is known, the capacity of any type of condenser is proportionate with the effective area of the electrode and inversely proportionate with the thickness of the dielectric layer.

In the electrolytic condensers the thickness of the film depends to a considerable extent upon the forming voltage, respectively operating voltage of the condenser, this thickness increasing and the capacity of the condenser decreasing with increasing voltages. Under substantially identical conditions a square inch of filmed electrode area, at a given voltage, will thus produce in the condenser a capacity of a substantial fixed value. For instance, in the "wet" electrolytic condensers now widely used, having electrolytes consisting of boric acid and a salt of boric acid dissolved in water, at room temperature and low frequencies, one square inch of superficial filmed electrode area at 450 volts gives about .1 mfd.

As aluminum is the most commonly used film-forming metal, in the further description I shall assume aluminum as the film-forming metal. It should, however, be well understood that certain aspects of my invention apply also to condensers having electrodes made of other film-forming metals, for instance, tantalum, zirconium, etc.

In present-day electrolytic condensers the aluminum electrode subjected to film formation is usually a foil or thin sheet having a microscopically smooth surface. While it has been realized long since that by roughening or etching the surface of the aluminum, its effective area could be increased, and thus with a given aluminum electrode a condenser of a larger capacity obtained, past endeavors in this direction have generally been unsuccessful and did not result in satisfactory condensers.

In the copending application of Preston Robinson and Joseph L. Collins, Serial No. 526,118, filed March 28, 1931, now U. S. Patent No. 2,067,703, issued January 12, 1937 a treatment of the aluminum foil has been described, by means of which the effective area of a filmed electrode can be substantially increased, whereby a considerable saving in aluminum is obtained without affecting the quality of the condensers. More specifically, in said application, there is described a method of treating an aluminum electrode, prior to film formation, in a strong alkaline solution in the presence of a proper inhibiting agent. By means of this treatment the aluminum surface is evenly etched and the effective area of the electrode and the specific capacity of the condenser considerably increased.

I have found that the successful etching of the film-forming electrode, for instance, of aluminum, to obtain thereby an increased capacity for a given electrode area, depends primarily upon the grain structure of the aluminum.

The grain structure of aluminum not only depends on its purity but also on the character and amount of the impurities contained therein, and I have found that the finer grained and the denser the structure of the aluminum, the better results can be obtained by etching the aluminum surface prior to film formation, and the larger thereby the gain in the capacity of the condenser for a given aluminum electrode.

In present day practice a commercially available, high-purity aluminum is used for the filming electrode. Such aluminum may comprise about 99.6%–99.8% of aluminum, the balance being made up of various impurities, as iron, silicon, with traces of copper and manganese.

I have found that such high-purity aluminum is not the best material to be subjected to such etching (and to thereby obtain a large increase in capacity), and this not only because of the deleterious influence of the remaining impurities upon its grain structure, but because even if these impurities are entirely removed, the

grain structure of the pure aluminum itself is of considerable coarseness.

I have found that by adding to the aluminum, whether having a purity of 99.6%–99.8%, or even less, certain ingredients, hereafter referred to as modifiers, a much finer and denser grain structure of aluminum can be obtained. A particularly good modifier is, for instance, sodium, either as a metal, or in the form of an easily reducible salt, for instance a sodium halide. Other alkaline or earth metals and salts thereof, as potassium, lithium, calcium and the halides thereof, can be successfully used as such modifiers.

The reduction of grain structure of a silicon-aluminum alloy by similar modifiers has already been described by Pacz in U. S. Patent No. 1,387,990. But the fact that such modifiers also favorably influence the grain structure of high-purity aluminum, and especially that the aluminum so modified gives far better results than high-purity aluminum as a material for an etched electrode of electrolytic condensers, is a most surprising result.

The advantage in this use of an aluminum having a very fine grain structure, seems to be due to the following:

In present-day condensers, using commercial high-purity aluminum electrodes, the film is formed on a smooth aluminum surface, for instance, on rolled aluminum foils. In the rolling operation the aluminum crystals on the surface of the foil are compressed. When forming the film on such a smooth surfaced aluminum electrode, it is immaterial whether the grain structure below the surface is finer or coarser.

However, when an aluminum electrode is subjected to etching, the character of the etched surface and its adaptability to film formation greatly depends upon the grain structure of the aluminum. This is partly due to the fact that the area and character of the resulting etched surface is to a great extent dependent on the grain structure of the aluminum, whereby a finer grain structure permits a greater increase of the effective area through etching than does a coarser grain structure, and partly because of the oxide film formed on the electrode having a very fine structure, a better film coverage and a better adhering film can be obtained on a fine-grained aluminum surface than on a coarse-grained surface.

This can be explained as follows: When aluminum is attacked by etching reagents, one crystal dissolves at a time. With large crystals in the aluminum, the dissolution of a given amount of aluminum results in a surface deeply pitted where large crystals have dissolved out. With the fine grain aluminum, such as is the modified aluminum used according to my invention, the dissolution of an equal amount of aluminum will result in a microscopically smooth surface, which, however, under the microscope reveals that a great number of small crystals have dissolved out. In consequence the surface area left on the modified aluminum is much greater than on the unmodified aluminum.

The better film characteristics and easier formation are due primarily to the smoother contours of the surface of the etched modified aluminum, as compared with the etched unmodified aluminum. The film on the aluminum, in contradistinction to the parent metal itself, is hard and brittle. Consequently when in case of large aluminum crystals, it is stretched over a sharply angled surface, it may fracture, which will result in a poorly formed film or at least necessitate the reformation of the film at such points.

Such treatment of the aluminum with the modifying agent takes place preferably while the aluminum is in a molten state. The aluminum so treated, upon fracture, shows a silky appearance due to the aluminum crystals' being broken through by the fracturing process.

From this, by analogy, it seems not unlikely that when etching modified aluminum the solution of the aluminum does not take place preferentially, i. e., crystal by crystal, but takes place uniformly over the exposed surface. This assumption seems to be warranted by the fact that the beneficial results obtained with the modified aluminum are even greater than could be expected merely because of the fine crystalline structure of such aluminum. Or in other words, the smoothness of the contour of the etched modified aluminum may be greater than if it were merely due to the smallness of the crystals.

Irrespective of what the reason may be, the aluminum treated with a modifying agent provides for a larger increase in the effective area through etching and for a better film than does commercial high-purity aluminum. Furthermore, the modified aluminum is easier to etch, can be etched in a shorter time with less etching solution, or in a less strong etching agent.

The amount of sodium or of other modifying agent to be added to the aluminum need not be large and about .1 to .2% usually suffices. During the casting of the aluminum a great portion of this sodium evaporates after the agent has performed its action in modifying the grain structure. The remaining sodium after the casting of the aluminum may be as small as .01%.

But even if sodium or another alkaline or earth metal forming the modifying agent remains in larger quantities in the aluminum, its presence does not deleteriously influence the properties of the aluminum in the film formation or its action as a filmed electrode of the condenser, as I have found that in the etching process practically all of the sodium disappears from the aluminum surface.

In this regard these modifying agents behave quite differently from other impurities normally present in aluminum, as iron, silicon, etc. The latter impurities in the etching solution are electro-negative with respect to the aluminum, and therefore do not dissolve during the etching in preference to aluminum. Sodium and the alkaline metals and some alkali earth metals, as calcium, are, however, electro-positive with respect to aluminum, and dissolve in the etching solution in preference to aluminum. Thus these modifying agents disappear from the surface of the aluminum during the etching, leaving a pure and fine-grained aluminum surface for film formation.

While a so modified aluminum gives much better results when subjected to etching and subsequent film formation, than does commercial high-purity aluminum, nevertheless the electrodes so etched may still exhibit some drawbacks usually present in the case of etched aluminum electrodes.

These drawbacks involve difficulties in film formation and corrosion in the operation of the condenser.

I have found that these difficulties have a common cause and can be overcome simultaneously, as will be shown hereafter.

In the electrolytic formation of the film on an aluminum surface, the best results are obtained when the aluminum is freely suspended in the electrolyte; those portions of the aluminum electrode which contact with foreign material and which contact with adjacent portions of the electrode, are difficult to form and in the operation of the condenser, corrosion is likely to occur at such portions.

In the past it has been assumed that poor film formation and corrosion of such portions was because the proper access of the electrolyte to such portions was prevented.

I have found that such difficulties are not only present in case of direct contact between such portions, but exist as long as the distance between adjacent portions of the filmed electrode is below certain limits, the values of which depend primarily on the voltage applied to the filmed electrode.

I believe that this is due to high-speed positive ions being emitted from the filmed electrode—which constitutes the anode in formation as well as in operation of the condenser—and which ions impinge upon and damage the film of closely-spaced adjacent electrode portions.

For instance, in condensers formed or operated at 450 volts, these difficulties will exist to a more or less marked extent, unless the mean free distance between adjacent portions of the filmed electrode is at least .02 to .03 inch.

In etched electrodes adjacent portions of the filmed electrodes are necessarily quite close to each other, and this causes difficulties in film-formation and corrosion in operation.

I have found that such difficulties can be overcome, or at least can be greatly reduced, both in the case of smooth surfaced aluminum electrodes having closely spaced portion (for instance closely pleated aluminum foils) as well as in the case of etched electrodes, by the additions to the electrolyte of certain substances which I shall refer to as film protective agents.

Such agents are, for instance, certain carbohydrates, which have the property of forming insoluble compounds with the aluminum oxide film. Thus the high-speed positive ions which are emitted from the film, instead of impinging on adjacent portions of the film, are caught or absorbed in the carbohydrate compound layer protecting the film.

A suitable carbohydrate for this purpose is, for instance sucrose, and similarly levulose, lactose, maltose, etc.

I have also found that besides carbohydrates other chemicals may be used as such film protecting agents. For instance, monobasic acids of the long chain type, as palmitic, stearic, oleic, abietic acids, can be used for this purpose, since they form compounds with the film, which compounds are insoluble in the electrolyte.

Carbohydrates are soluble in both aqueous solutions and polyhydric alcohol solutions of the usual electrolytes, for instance of electrolytes comprising boric acid, phosphoric acid and citric acid, and/or the salts of such weak acids, and can therefore be added directly to the electrolyte.

In the case of monobasic, fatty, long-chain acids, as above enumerated, which are not soluble in the electrolyte usually employed, these acids are preferably emulsified in the electrolyte by the addition of salts of these insoluble acids, for example of sodium or ammonium salts of such acids, and by mechanically agitating the electrolyte.

I have found that a very small amount of such a protective agent, for instance, 1% of sucrose, has a very marked effect on the film formation and prevention of corrosion on such critical points. The amount added, however, depends on the agent, on the specific properties of the electrolyte, on the thickness of the aluminum, and on the voltage for which the condenser is designed.

The amount to be added is usually smaller in the case of wet condensers than in the case of dry condensers.

In the case of wet condensers I may add about .5% to 5% of the agent, and in the case of dry condensers I may add about 5 to 40%, although more or less this amount may be used at discretion.

The addition of such agents does not injure the electrolyte as long as it is otherwise free of impurities.

I shall describe more fully some embodiments of my invention in connection with the attached drawing, in which:

Figure 1 is a partly sectionized side view of a "wet" electrolytic condenser embodying my invention.

Fig. 2 is a partly sectionized side view of a "dry" electrolytic condenser embodying my invention.

Fig. 3 is an enlarged schematic section through an etched aluminum electrode made in accordance with my invention.

In the manufacture of condensers, according to my invention, aluminum of high purity, preferably of 99.6–99.8% purity, is molten and cast together with the modifying agent. As far as the etching results are concerned, the purity of the aluminum is not critical. However, the film-forming properties of the aluminum are improved with higher purity, and therefore I prefer to use high-purity aluminum as above stated.

The modifying agent is preferably an alkaline metal either in metallic form, or in the form of an easily reducible salt, for instance, a halide of an alkaline metal. Alkaline earth metals which are electropositive with regard to aluminium, for instance calcium, can also be used. I prefer to use sodium and add about .1 to .2% sodium to the aluminum before casting it.

During the casting, most of the sodium evaporates, the remaining sodium being of the order of about .01%.

The above treatment gives an aluminum of fine-grained crystalline and high-density structure.

The aluminum is then subjected to the mechanical operations to bring it in proper shape, for instace, to rolling to obtain aluminum sheets or foils, and to corrugation or pleating, etc. The so-formed aluminum is then subjected to etching.

As to the exact schedule of the etching process I have found in general any of the methods used in preparing aluminum for electro-plating such as are described in "The Aluminum Industry" by Edwards, Frary and Jeffries, McGraw-Hill, New York 1930, page 492, et seq., may be used. For example, the metal may be first cleaned with an alkaline cleaner or with a solvent such as kerosene. The surface of the metal may then be made uniformly active by a dip of from five to thirty seconds in a solution of one part 50% hydrofluoric acid to nine parts of water, or in a solution containing one part 50% hydrofluoric acid and three parts of nitric acid. The main

etching action may then be carried out in a dilute solution of hydrochloric acid to which, however, other reagents such as sodium chloride, ferrous chloride, nickelous chloride or manganous chloride may be added.

The main difference between the technique developed for preparing aluminum for electroplating and preparing it for film formation so as to bring about a high capacity, is that in general a longer schedule of operations is necessary. For example, where for electro-plating, hydrochloric acid with or without the addition of other chlorides need only be applied for times of the order of one or more minutes, for the purpose of the present application a schedule of the order of magnitude of one or more hours yields better results.

Also, other processes for etching aluminum well known in the art may be adjusted to apply to the present object of increasing the surface area of the aluminum.

As an example of the comparative effects, I have treated so-called commercially pure aluminum and modified aluminum plates according to the following schedule:

Dipped in hydrofluoric acid and nitric acid mixture as described above for five seconds, immersed in 5% hydrochloric acid for one hour. The commercially pure aluminum (99.8%) has approximately the following impurities: iron .12%; silicon .07%; copper .01% or less; manganese .01% or less. The modified aluminum had substantially the same composition except that it had been modified with sodium and contained a remnant of .01% or less sodium. Plates so treated were rinsed in alkali and in boric acid solution and were then formed in an electrolyte of borax and boric acid to 450 volts and the following was found: The capacity of the commercial aluminum was 0.13 mfd. per square inch; the capacity of the modified aluminum was 0.2 mfd. per square inch.

Ordinary aluminum of the same composition, but not subjected to etching, will upon similar film formation give a capacity of about 0.1 mfd. per square inch.

Other schedules of etching than the example cited will produce different capacities on the aluminum plate, rating as high for the modified aluminum as 0.5 mfd. per square inch, and, somewhat erratically, even higher.

Modified aluminum has the further advantage of requiring much shorter etching or less strong solutions than does commercial aluminum.

During the etching, as has been stated, the remaining sodium or other modifying agent, dissolves in the etching solution, which leaves a clean and pure aluminum surface.

The etching greatly increases the aluminum surface compared to a smooth surface, a two or threefold increase being obtained as a rule, although under certain conditions a five-fold and even higher increase may be obtained.

The etched aluminum, after suitable rinsing is, in known manner, subjected to film-formation which may take place with the application of a suitable voltage, which for present-day condensers is normally 30 to 600 volts depending on the use of the condenser. The electrolyte used in the formation process contains as a rule an aqueous solution of an acid, for instance, boric acid, phosphoric acid, citric acid, etc., and preferably also contains a salt of a weak acid, for instance, a sodium or ammonium salt of boric acid, phosphoric acid, citric acid, etc., whereby the salt of the acid does not need to be the acid used in the electrolyte.

To improve the film formation, in overcoming the difficulties caused by the closeness of adjacent portions of the etched electrodes, I preferably add to the forming electrolyte a film-protective agent in the form of a carbohydrate soluble in the electrolyte, for instance, sucrose, lactose, etc., or a monobasic fatty, long-chain acid, as palmitic, stearic, oleic and abietic acids. Such acids as a rule are insoluble in the electrolyte and I emulsify these acids in the electrolyte by adding to the electrolyte salts of these acids, for example, their sodium or ammonium salts, and by mechanically agitating the electrolyte.

The addition of such film-protective agents, of which I normally use .5 to 5%, obviates the difficulties encountered in the filming of etched electrodes.

The filmed electrodes are then assembled into condensers, for instance, into wet condensers of the type as shown in Figure 1. This figure illustrates a wet condenser as used in filter circuits; it has a corrugated aluminum electrode 13 which has been modified, etched and filmed according to the above-described method and has a capacity several times as large as has a corrugated electrode of exactly the same dimensions, but having a smooth surface. The container 10 forms the other electrode of the condenser and is preferably a chromium-plated aluminum can, the advantages of which are described in my Patent No. 1,938,464.

The container 10 is closed by a cover 12 of insulating material, through which projects a threaded extension 17 of the electrode 13, said extension being provided with nuts 15—15 to form one of the outside terminals of the condenser, the container 10 forming the other terminal. The cover is provided with a vent 18 and a gasket 19, around which is crimped the free end of the container 10. Preferably sealing means for example a gasket 30 and a resilient washer 31 are also provided between the protruding end of the electrode 13 and the cover 12.

The mechanical construction of the condenser is given merely as an illustration and various other known constructions may be used.

The electrolyte 16 is preferably an aqueous solution of a weak acid, for instance of boric, phosphoric, citric acid, etc., to which may be added a salt of a weak acid, for instance, an ammonium or alkaline salt of a weak acid, whereby the salt added need not be that of the acid used in the electrolyte.

The electrolyte preferably also comprises a film-protective agent to prevent corrosion of the filmed electrode in the operation of the condenser, for the reasons previously set forth. One of the protective agents previously discussed in connection with the formation of the electrode, may be used, and preferably about .5 to 5% of such an agent is added to the electrolyte.

Fig. 2 illustrates my invention in a "dry" condenser. If this condenser is used for alternating current, as for example, for the starting of capacitor motors, both of the electrodes 20—20 are of film-forming metal, for instance of aluminum. The electrodes are treated as previously described and thus are of a fine-grained and dense modified aluminum and etched and filmed in accordance with the invention.

The filmed electrodes are assembled in rolls or stacks either with or without the interposition of

spacers. In case spacers 21—21 are used, as shown in the drawing, these consist preferably of a fabric, as gauze or of other absorbent material, for instance of Cellophane, paper, etc., and also serve as carrier for the electrolyte.

The electrolyte is more or less viscous and comprises preferably a weak acid, to which the salt of a weak acid may be added. These electrolytes have in general the same type of ionogens as enumerated in connection with the "wet" electrolytic condensers. However, the solvent of such dry condensers as a rule comprises a polyhydric alcohol, as glycerol, ethylene glycol, etc.; also a substance which increases the viscosity and/or conductivity of the electrolyte may be added.

Furthermore, to prevent corrosion of the condenser in operation, I prefer to add to the electrolyte a film-protective agent, as previously described, namely, a soluble carbohydrate or a monobasic, fatty, long-chain acid. The amount of such protective agent may greatly vary and may be between 5 and 40%. This agent may partly replace the polyhydric alcohol.

As stated above, the use of a protective agent of this type is also useful in the forming and/or final electrolyte of both wet and dry condensers, the electrodes of which are smooth, especially when the electrodes of such condensers have closely-spaced corrugations, or have electrodes in which closely adjacent portions may adversely influence each other.

In general, I prefer (both in the case of wet and dry condensers), to have a final electrolyte the pH of which is lower than the pH of the forming electrolyte, the advantage of this being fully described in the U. S. patent to Preston Robinson and Joseph L. Collins No. 1,916,586.

In the case of dry condensers, I prefer to use the forming processing methods described in my copending application Ser. No. 548,270, filed July 1, 1931, now U. S. Patent No. 2,057,314, issued October 13, 1936, and my Patent No. 1,935,860.

The novel articles obtained with the method of the present invention are claimed in my above application Ser. No. 716,714.

While I have described my invention on hand of specific embodiments and in specific applications, I do not wish to be limited to same, but desired the appended claims to be construed as broadly as permissible in view of the prior art.

What I now claim as new and desire to secure by Letters Patent is:

1. In the manufacture of electrolytic condensers, the process which comprises the steps, treating molten aluminum with a modifying agent which comprises a metal of the group of alkali and alkali earth metals which is electro-positive with regard to aluminum, casting said modified aluminum, and subjecting the aluminum so obtained to chemical etching to increase the effective surface of said aluminum, and removing by said etching the modifying agent from the aluminum surface.

2. In the manufacture of an electrolytic device, the process which comprises the steps, forming an etched electrode of filming material in an electrolyte comprising a weak acid which is soluble in water and a monobasic fatty, long-chain acid.

3. In the manufacture of electrolytic condensers, the process which comprises the steps, forming an electrode of filming material in an electrolyte comprising a weak acid which is soluble in water and a compound of a mono-basic fatty long-chain acid radical.

4. In the manufacture of electrolytic condensers, the process which comprises the steps, adding to an electrolyte comprising as a major constituent a weak acid which is soluble in water, salts of an insoluble monobasic fatty long-chain acid, emulsifying the long-chain acid in the electrolyte and forming an aluminum electrode therein.

5. In the manufacture of electrolytic condensers, the process of reducing the crystalline structure of the aluminum which comprises the steps, treating molten aluminum with a modifying agent of the group consisting of the alkali and alkali earth metals which are electropositive with regard to the aluminum and of the easily reducible salts of these metals.

6. In the manufacture of electrolytic condensers, the process of providing a fine crystalline structure for the aluminum which comprises the treatment of molten aluminum with .1% to .2% sodium.

7. In the manufacture of electrolytic condensers, the process which comprises the steps, forming an aluminum electrode having closely adjacent protruding portions, in an electrolyte having as major constituent a weak acid which is soluble in water and comprising an agent which forms a protective layer for the film during its formation in said electrolyte.

8. In the process of providing film-forming electrodes for electrolytic condensers and the like, the steps of combining with a film-forming metal such as pure aluminum, a relatively smaller but appreciable quantity of another metal not normally associated with said film-forming metal as an impurity, thereafter exposing said metal composition to the action of a chemical agent adapted to etch out said added metal without readily affecting said film-forming metal.

9. In the process of treating film forming electrodes for electrolytic condensers and the like, the step of exposing an electrode composed substantially of pure aluminum but containing an appreciable though smaller quantity of at least one other element intentionally added to the aluminum, said added element being normally not present as an impurity in aluminum to the action of a solution adapted to readily etch out said added element without substantially etching out the aluminum, whereby the effective film forming surface of said electrode is materially increased.

10. In the process of providing film forming electrodes for electrolytic condensers and the like, the steps of combining with a pure film forming metal such as aluminum, a relatively smaller but appreciable quantity of another metal not normally associated with said film forming metal as an impurity, thereafter exposing said metal composition to the action of an etching solution to remove said added metal from the surface of said composition.

11. In the process of providing film forming electrodes for electrolytic condensers and the like, the steps of combining with aluminum of a purity of at least 99.2% a relatively smaller but appreciable quantity of another metal not normally associated with aluminum as an impurity, thereafter exposing said metal composition to the action of a solution adapted to etch out said added metal from the surface of said metal composition.

PRESTON ROBINSON.