

April 13, 1937.

J. E. LILIENFELD

2,076,904

FILMING METAL COATINGS AND METHOD OF FORMING THE SAME

Filed Aug. 29, 1931

Fig. 1.

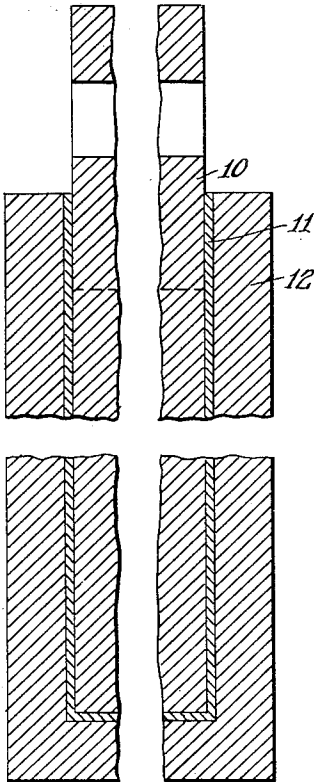


Fig. 2.

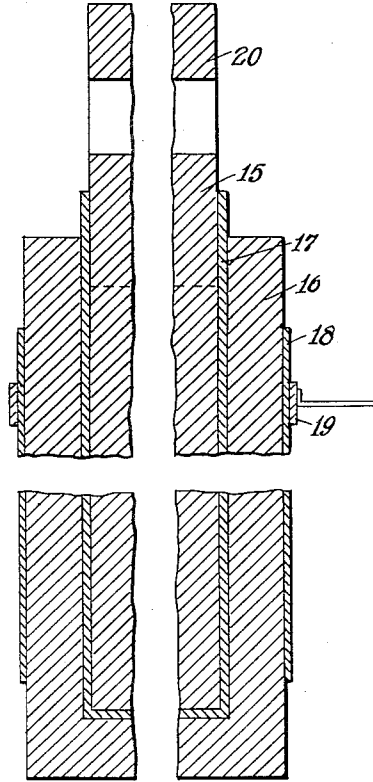
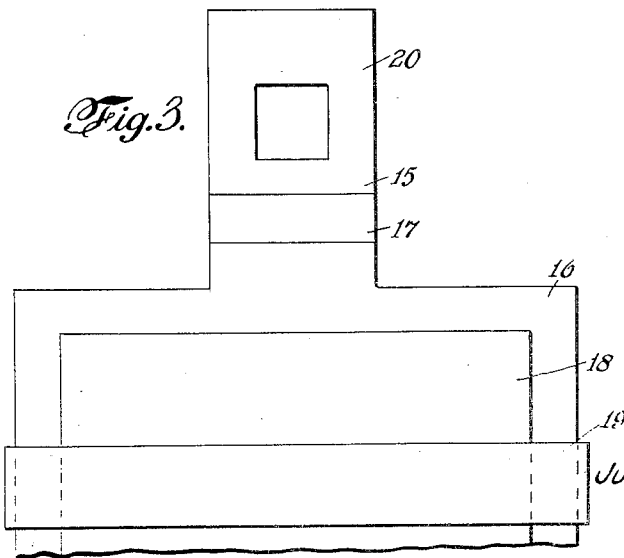


Fig. 3.



INVENTOR
JULIUS EDGAR LILIENFELD
BY *Ben N. Lehotsky*
ATTORNEY

UNITED STATES PATENT OFFICE

2,076,904

FILMING METAL COATINGS AND METHOD
OF FORMING THE SAME

Julius Edgar Lilienfeld, Winchester, Mass., assignor, by mesne assignments, to The Magnavox Company, Fort Wayne, Ind., a corporation of Arizona

Application August 29, 1931, Serial No. 560,141

42 Claims. (Cl. 175—315)

The invention relates to integral coatings or films produced on filming metals such as aluminum, tantalum, etc., and comprising compounds of such metals which are molecularly associated therewith. This application is in part a continuation of my copending application Ser. No. 462,251, filed June 19, 1930.

Coatings of this nature have been variously formed, as by electrolytic action or oxidation, and there are, generally speaking, two classes of these layers or films—one which is very thin (of immeasurable thickness—approximately 10^{-4} to 10^{-5} mm.) and which apparently does not build up beyond this limit irrespective of the duration of the formation. The film provides an insulating coating on the anode if the metal is positive even in the presence of water or water vapor, and is hereinafter designated as the "active" layer or film.

The other class comprises layers or films which apparently continue to grow in thickness indefinitely with prolonged formation and attain under proper conditions mechanically measurable thicknesses. These layers in the presence of water or water vapor are not active as a dielectric, being conductive above a certain voltage, and are also unsuited as rectifiers. Such layers or films are hereinafter designated as "inactive" layers or films.

In making this distinction between the active layer being insulating and the inactive layer conducting, the following is to be noted:

The distinction holds true only in the presence of a liquid electrolyte or aqueous vapor. In perfectly dry condition both kinds of layers are insulating. In the presence of water vapor—provided the water pressure be increased sufficiently closely to saturation—some inactive layers will conduct very well, e. g. those produced by etching the filming metal in hydrochloric acid and subsequently boiling the same, those which are formed in carbonates, as well as those formed in sulphuric acid.

Other inactive layers, of which the layer formed in phosphoric acid is an example, will not increase their conductivity to an appreciable extent unless a partial pressure of an alkaline component such as ammonia be present.

Furthermore, the active layer does not allow an increase of voltage beyond a certain limit without breaking down—sparking or, in other words, a disruptive and destructive discharge taking place, and it will not grow indefinitely. An inactive layer will upon increase in voltage transmit a large current and continue to grow, eating up

the base metal. However, it is true that with a sufficiently low voltage even an inactive layer will present a relatively high resistance to the current. This voltage level varies in different cases, with the layers formed with sulphuric acid the voltage being only a few volts, with carbonates the voltage is below 120 volts, and when formed with phosphoric acid the voltage is below 150 volts.

The foregoing discussion of the resistance of different layers is concerned with current passing from the positive metal across the layers to an electrolyte or to a spattered coating; it is also limited to the case of simple layers, and does not include bilaminate coatings comprising both types of layers as hereinafter set forth. With respect to such coatings the statements necessarily remain true for the active layer even if it is underimposed beneath the inactive layer. The inactive layer, on the other hand, when superimposed over the active one presents in an electrolyte, in some instances also in an aqueous vapor, a negligible resistance to current even at low voltages which manifests itself in the fact that at frequencies of the order of 1000 cycles the power loss of the bilaminate condenser may be a small fraction of one percent if the resistance of the electrolyte is chosen sufficient low.

The capacity due to the presence of the active layer is changed by its underimposition under the inactive one—such as formed in phosphoric, sulphuric acid and carbonates—comparatively little and the change amounts to a relatively small decrease by 25% or less of the capacity. Other superimposed layers than the ones indicated provide for even lesser losses, for example, those produced by etching in hydrochloric acid with subsequent boiling. The reduction of the capacity is due probably to the fact that a very thin active stratum is produced in some cases at the border between an underimposed active and an inactive layer superimposed thereover.

The present invention has for an object the provision of a novel coating embodying both of the aforesaid layers. Further objects of the invention reside in novel devices embodying this filming metal coating.

I have discovered in relation to these two types of layers that while it is possible to first form the inactive layer and then to underimpose beneath the same the active layer, this process is irreversible, it being impossible to reverse this sequence of operation. That is to say, the active layer may not first be formed on the anode metal and an inactive layer built thereon.

I have further found that the extremely thin

active layer is particularly vulnerable and is readily scratched or mechanically injured, while the heavy inactive layers are comparatively hard to break and remove mechanically, thus affording protection for an underlying layer when required.

For example, in electrolytic condenser work, the anodes have first to be formed and then to undergo mechanical assembly operations, and protection against mechanical injuries of the active layer is, therefore, especially desirable. In some cases it is highly desirable to space the cathodes as closely as possible to an anode, and then the use of the bilaminate coating is helpful to prevent injury to the layer. Higher breakdown voltages of the active layer are also attainable by the use of the bilaminate coating.

In the provision of a filming metal with a coating formed with an active layer underimposed beneath the inactive layer, a very useful and important element is obtained which is adaptable to many further applications and a number of which are set forth herein. Other adaptations will form the subject matter of additional patent applications, the present application being drawn broadly to the novel filming metal coating, the method of providing the same and novel condenser structures embodying the coating applied to the anode thereof.

The nature of the invention, however, will best be understood when described in connection with the accompanying drawing, in which:

Fig. 1 is a transverse section, on a greatly exaggerated scale, through an anodic electrode for a condenser and provided with the novel coating, said anode being suitable for use in an electrolyte of a viscosity which may vary from a low degree such as pure aqueous solutions to a degree of viscosity sufficiently high to afford a plastic mass.

Fig. 2 is a transverse section, on a greatly exaggerated scale, of a semi-dry condenser for operation in a moist atmosphere.

Fig. 3 is a plan thereof.

Referring to the drawing, more particularly to Fig. 1, 10 designates an anode of filming metal, such as aluminum, tantalum, etc., adapted to be provided over a surface with the novel bilaminate integral coating which is to be molecularly associated therewith. The proximate layer 11 constitutes the usual dielectric or active film which may be formed by any of the well-known electrolytic processes, in the case of aluminum providing a thin film of oxide of aluminum whose thickness is immeasurable and of the order of magnitude of approximately 10^{-4} to 10^{-5} mm.

The outer layer 12 is in the nature of an inactive layer as hereinbefore referred to and affords a protective coating to an underimposed active layer. This layer is conductive in the presence of water or water vapor above a certain voltage, and is similarly a compound of the anodic metal, for example, a phosphate. This latter layer, however, may be formed of measurable thickness, say 1/1000 of an inch, the thickness being dependent upon the duration of treatment.

The following explanation is offered with respect to the difference in properties, as hereinbefore referred to, of these two layers in the presence of water or water vapor.

A compound of a filming metal (aluminum) may or may not be permeable to the OH ion. Different compounds of the filming metal may react differently in this respect, and even the same compound, speaking in terms of an ele-

mental analysis, may be in a molecular condition in which it is or is not permeable to OH ions. An example of the latter is aluminum oxide of which an active or inactive layer can be formed according to the molecular structure of this compound, inasmuch if the molecules form an organized pattern the layer is active, otherwise it is inactive.

The permeability again is explained by the fact that the molecules of aluminum compounds according to their condition of organization or polymerization may or may not be hydratable or capable of attaching OH ions to the molecule. A hydratable layer is then a conductive layer in the presence of a medium containing OH ions, and a non-hydratable layer is an insulating layer in the presence of such medium. In other words, the active layer may be said to be but slightly if at all hydratable while the inactive layer is highly hydratable, and the hydratability of such inactive layers may be varied by different treatments in production. The hydratability of the inactive layers may be enhanced in certain instances by persistent boiling in water after formation or by the addition of ammonia. Boiling serves also to increase somewhat the hydratability of the active layer but to a much lesser extent than that of the inactive layers.

As hereinbefore noted, the provision of these films or layers must be in a particular sequence, that is to say, the inactive layer 12 must first be formed on the anodic metal and the active layer 11 then underimposed thereunder.

In applying the respective layers, an anode may be formed to provide an inactive layer in various electrolytes, for example, in $\frac{1}{2}$ normal phosphoric acid at a temperature of 30°-35° C. and at a current density of 5 m. a. per sq. cm., or may be variously oxidized or etched. Before underimposing the active layer beneath this inactive layer, the formed anode is thoroughly washed for 5 to 10 minutes in boiling distilled water, whereupon formation is effected, for example, in an electrolyte consisting of boric acid with or without the addition of a small amount of sodium borate.

Other reagents may be utilized in the formation of the inactive layers, for example, sulphuric acid, carbonates, etc., or the layer may be attained by etching the aluminum in hydrochloric acid and subsequently boiling the etched material (see my copending application Ser. No. 8,925, filed March 1, 1935, as a continuation in part hereof). The active layer is best prepared by electrolysis of the filming metal, after formation of the inactive layer, as in boric acid or boric acid with a small amount of sodium borate.

The value of the protecting inactive layer is particularly evident in condensers in which the electrodes are closely spaced to prevent mechanical injury of the active film or layer, especially when the anodic and cathodic electrodes are separated merely by a highly viscous electrolyte comprising a condensation product of an alcohol and an acid with admixture of a suitable filler, all of which is more particularly set forth in my copending applications: Ser. No. 560,140 (since issued as Patent No. 2,013,564, dated September 3, 1935) and Ser. No. 560,142 (since issued as Patent No. 1,989,622, dated January 29, 1935), both filed of even date herewith; Ser. No. 670,084 (since issued as Patent No. 2,021,455, dated November 19, 1935); and Ser. No. 711,286, (since issued as Patent No. 1,986,779, dated January 1, 1935).

More particularly in connection with the ad-

mixture of a dust filler to a viscous electrolyte, which serves to hold the electrolyte in place between electrodes, such admixture, when the filler is of a conducting nature, will tend to reduce the

5 sparking or breakdown voltage to a considerable degree in the absence of a protective layer, such as the inactive layer hereinbefore referred to. However, when a bilaminate integral coating is applied to the anode metal as hereinbefore described, no appreciable change in the breakdown voltage is observed whether a conducting filler be employed or not in connection with the electrolyte.

This is of particular importance since heretofore the only way known in which to secure a high voltage breakdown limit of electrolytic condensers was to increase the resistance of the electrolyte. This, however, increased the power loss in the operation of the condenser. The present invention offers a means of reducing the total resistance, and therefore the power loss, of a condenser while preserving the protective feature of a high resistance electrolyte. This is obtained by the admixture of a conducting filler, such as lamp black, etc. to the electrolyte which will reduce very considerably the total resistance of the mixture when utilized with the active layer underimposed beneath the inactive layer. The following may be added in order to provide for a better understanding:—The bodily presence of the dust or filler particles upon an active layer will disturb the field of and also exert a mechanical influence upon such active layer. In the present instance with an active layer underimposed, such filler being relatively coarse, will not enter into the superimposed inactive layer and will not, therefore, affect the breakdown characteristics of the active layer underimposed beneath said inactive layer.

40 The permeability of the aforesaid inactive layer to OH ions in conjunction with an underimposed active layer is of value, also, in the construction of a condenser of a different type and which I shall term the "semi-dry" type. Such condenser is shown in Figs. 2 and 3, the filming metal 15, such as aluminum, being provided with the inactive layer 16 and under which is provided the active layer 17.

A contact layer 18 is provided over the inactive layer, this being effected in any well-known or special manner, as by cathodically spattering gold or copper thereon and as is more fully set forth in my copending applications, Serial Nos. 265,372 and 265,373 both filed March 28, 1928, and since issued, respectively as Patents Nos. 1,900,018 (March 7, 1933) and 1,906,691 (May 2, 1933). A terminal band or foil 19 may overlie the said contact layer for convenient connection to one element, the other connection then being had to the filming metal lug 20.

In a dry condition, the specific capacity of this condenser is low because of the presence of the heavy inactive layer which in the dry condition is insulating. However, when the condenser is then exposed to an aqueous vapor or to an atmosphere containing aqueous vapor, for example, hydrous ammonia, carbonic acid, etc. the inactive layer becomes conductive—on account of the phenomenon of hydration, as hereinbefore set forth—and the specific capacity increases to a value substantially corresponding to that of the underimposed active layer.

I claim:

75 1. A filming metal with bilaminate integral

coating molecularly associated therewith, the proximate layer being an active and relatively non-conductive compound thereof and the other a compound thereof which is inactive and conductive in the presence of water or an aqueous vapor.

2. A filming metal with bilaminate integral coating molecularly associated therewith, the proximate layer being an active and substantially non-hydratable compound thereof and the other a compound thereof which is inactive and highly hydratable.

3. An anodic electrode of a filming metal, comprising two non-metallic strata molecularly associated therewith, the proximate stratum being a dielectric and a compound of said metal, and the other stratum a compound of the metal and permeable to OH ions.

4. An anodic electrode of a filming metal, comprising two non-metallic strata molecularly associated therewith, both being compounds of the filming metal and only the proximate layer possessing dielectric breakdown properties in the presence of water or an aqueous vapor.

5. The combination with an electrolyte, of a filming metal electrode having a bilaminate integral coating molecularly associated therewith, the proximate layer being a compound of the filming metal, of a thickness of the order of magnitude of 10^{-4} to 10^{-5} mm. and affording a high specific capacity between the metal electrode and electrolyte, and the other being a compound of the filming metal of a thickness greater than the proximate layer and conductive in the electrolyte.

6. The combination with an electrolyte, of a filming metal electrode having a bilaminate integral coating molecularly associated therewith, the proximate layer being a compound thereof, of a thickness of the order of magnitude of 10^{-4} to 10^{-5} mm. and having a high specific capacity with respect to the electrolyte, and the other being a compound of the filming metal, of a thickness greater than the proximate layer and conductive in the electrolyte, and a more conductive layer overlying the layer of mechanically measurable thickness.

7. A filming metal electrode with bilaminate integral coating molecularly associated therewith, both layers consisting of a compound of said metal and the outer being of greater hydratability and conductivity than the proximate layer.

8. A filming metal electrode with bilaminate integral coating molecularly associated therewith, both layers consisting of a compound of said metal and the proximate layer being an oxide thereof and a dielectric, and the other a compound of the filming metal which is conductive in the presence of water or an aqueous vapor.

9. A filming metal with bilaminate integral coating molecularly associated therewith, the proximate layer being a dielectric oxide thereof and the outer layer a phosphate thereof.

10. A filming metal electrode with bilaminate integral coating molecularly associated therewith, both layers consisting of compounds of said metal, and the outer layer being relatively hydratable and conductive and the proximate layer highly insulating.

11. An electrical device embodying three molecularly associated layers, the two outer layers being conductive and one of said layers relatively hydratable, and the intermediate layer of a thickness of the order of magnitude of 1/1000 of an inch and a dielectric, the hydratable layer and the

intermediate layer being compounds of the said other conducting layer.

12. An electrical element comprising a filming metal, an active film of a thickness of the order of magnitude of 10^{-4} to 10^{-5} mm., and an overlying film of a thickness greater than the active film, both layers comprising compounds of the filming metal, the compounds being different and the layers molecularly associated with the filming metal and the overlying layer conductive in the presence of water or aqueous vapor.

13. An electrical device comprising a filming metal having a dielectric layer thereover comprising an oxide thereof and the said layer protected with a further overlying and relatively hydratable layer comprising a compound of the filming metal different from said oxide.

14. An electrical device comprising a filming metal having a dielectric layer thereover comprising an oxide thereof and the said layer protected with a further overlying and relatively hydratable layer comprising a phosphate of the filming metal.

15. An electrical device comprising aluminum provided with a layer of aluminum oxide protected with an overlying layer of aluminum compound molecularly associated therewith and of greater hydratability and conductivity than the underlying layer.

16. A filming metal with bilaminate formed layers embodying compounds of the metal, the proximate layer being formable only after the outer layer has been applied.

17. The method of providing an electrical element of a filming metal, which comprises first providing a relatively hydratable and conducting film thereover, the same being a compound of said metal and of a thickness of the order of magnitude of $1/1000$ of an inch, and then electrolyzing the metal to provide an underlying dielectric film of a compound of said metal and of a thickness of the order of magnitude of 10^{-4} to 10^{-5} mm.

18. The method of providing an electrical element of a filming metal, which comprises first forming the metal in an electrolyte to provide a relatively hydratable and conductive film thereover of a compound of said metal and of a thickness of the order of magnitude of $1/1000$ of an inch, and then electrolyzing the formed metal in a different electrolyte to provide an underlying dielectric film of a compound of said metal and of a thickness of the order of magnitude of 10^{-4} to 10^{-5} mm.

19. The method of providing an electrical condenser element, which comprises first forming a filming metal in an acid electrolyte to provide thereon an inactive highly hydratable layer, washing the formed element, and again electrolyzing the same in a different electrolyte to provide an underlying active dielectric layer of a compound of said metal and of a thickness of the order of magnitude of 10^{-4} to 10^{-5} mm.

20. The method of providing an electrical condenser element, which comprises first forming a filming metal in phosphoric acid, washing the formed element, and again electrolyzing the same in boric acid.

21. The method of providing an electrical element of a filming metal, which comprises first forming the metal in an electrolyte to provide a relatively hydratable film thereover of a compound of said metal and of a thickness of the order of magnitude of $1/1000$ of an inch, and then electrolyzing the formed metal in a different electro-

lyte to provide an underlying film of a compound of said metal and of a thickness of the order of the magnitude of 10^{-4} to 10^{-5} mm., and depositing a metal coating over the outer film and in molecular contact therewith.

22. In an electrical condenser: an anode of a filming metal with bilaminate integral coating molecularly associated therewith, the proximate layer being an active and relatively non-conductive compound thereof, and the other a compound thereof which is inactive and conductive in the presence of water or an aqueous vapor.

23. An anode for electrolytic condensers, comprising aluminum having an active proximate layer which is a compound of the aluminum and an outer layer which is a different compound of the aluminum and active and highly hydratable, both layers being molecularly associated with the underlying aluminum and the outer serving as a protective layer for the proximate one, and preventing lowering of the sparking voltage, which may be applied across said outer layer and the said underlying aluminum, when said outer layer is brought into contact with conducting filler material of the condenser electrolyte in which the anode is immersed.

24. An anode for electrolytic condensers, comprising aluminum having an active proximate layer which is an oxide of the aluminum and an outer layer which is a phosphate of the aluminum, both layers being molecularly associated with the underlying aluminum and the outer serving as a protective layer for the proximate one.

25. A filming metal with bilaminate integral coating molecularly associated therewith, the proximate layer being a dielectric compound thereof and the outer layer substantially a phosphate thereof and inactive and conductive to OH ions.

26. The method of providing an anodic element of a filming metal, which comprises first electrolyzing a filming metal in phosphoric acid, and then in boric acid to form a further substantially non-hydratable film.

27. The process of treating anodes of condensers of the electrolytic type which comprises electrolyzing an anode in a bath of dilute sulfuric acid thereby forming a coating thereon and thereafter forming a further coating thereon beneath the first coating comprising a substantially non-hydratable oxide of the anode metal.

28. The process of treating anodes of condensers of the electrolytic type which comprises electrolyzing an anode in a bath of dilute sulfuric acid thereby forming a highly hydratable coating thereon, and thereafter forming a further substantially non-hydratable coating thereon beneath the first coating.

29. The process of treating anodes of condensers of the electrolytic type which comprises electrolyzing an anode in a bath of dilute sulfuric acid thereby forming a coating thereon, washing said coating to remove all sulfate ions therefrom, and thereafter forming a further relatively non-hydratable coating thereon.

30. The process of treating anodes of condensers of the electrolytic type which comprises electrolyzing an anode in a bath of dilute sulfuric acid thereby forming a film and thereafter forming a high-voltage film on said anode in an electrolyte of a different class.

31. The process of treating anodes of condensers of the electrolytic type comprising treating an anode to produce thereon an integral

coating of a compound of the anode characterized by being relatively conductive in the presence of moisture, and thereafter forming a high-voltage film on said anode in an electrolyte.

5 32. The method of producing an anodic element, comprising treating a filming-metal to produce thereon an integral coating of a compound of the anode characterized by being relatively conductive in the presence of moisture, and thereafter forming an underlying active dielectric film on said anode in an electrolyte.

10 33. The method of producing an anodic element, comprising treating a filming-metal to produce thereon an integral coating of a compound of the metal characterized by being highly hydratable, and thereafter electrolyzing the treated metal in boric acid to produce an active dielectric film.

20 34. In an electrical device, the combination of a filming-metal anode and an electrolyte containing a filler of solid particles, said anode having a proximate active dielectric film and an integral superposed substantially thicker protective layer conductive in the electrolyte and impermeable to said solid particles thereby protecting said dielectric film from contact with the solid particles in the electrolyte and preventing a reduction of sparking voltage.

25 35. The combination of a filming electrolyte containing conductive solid particles and a filming-metal electrode with bilaminate integral coating molecularly associated therewith, both layers consisting of compounds of said metal, the proximate layer being highly insulating and the outer layer being relatively conductive in the electrolyte and impermeable to said conductive solid particles, thereby preventing the latter from reducing the sparking voltage.

30 36. In combination, in an electrolytic condenser, a film-forming electrolyte containing a filler of lamp black and a filming-metal anode having a proximate active dielectric film and a superposed integral protective layer of a compound of the metal, said superposed layer being

relatively conductive in the electrolyte and affording mechanical protection to the active dielectric film.

37. An anode for electrolytic cells having a composite covering thereon, consisting of a porous coating presenting low dielectric properties and a film of high dielectric properties intimately associated with said coating.

38. An anode for electrolytic cells having a composite covering thereon, consisting of a porous coating presenting low dielectric properties and a film of high dielectric properties intimately associated with said coating, the coating being of a more highly adherent nature with respect to the anode than the dielectric film.

39. The process of treating anodes of condensers of the electrolytic type which comprises electrolyzing an anode in a bath of dilute sulfuric acid thereby forming a film, washing and heating the so-formed anode, and thereafter forming a high-voltage film in an electrolyte of a different class.

40. The process of treating anodes of condensers of the electrolytic type which comprises electrolyzing an anode in a bath of phosphoric acid thereby forming a coating thereon and thereafter forming a further coating thereon beneath the first coating comprising a substantially non-hydratable oxide of the anode metal.

41. The process of treating anodes of condensers of the electrolytic type which comprises electrolyzing an anode in a bath of phosphoric acid thereby forming a coating thereon, thoroughly washing said coating, and thereafter forming a high-voltage film on said anode in an electrolyte of a different class.

42. The process of treating anodes of condensers of the electrolytic type which comprises electrolyzing an anode in a bath of phosphoric acid thereby forming a film, washing and heating the so-formed anode, and thereafter forming a high-voltage film in an electrolyte of a different class.

JULIUS EDGAR LILIENFELD.