April 27, 1965 R. A. QUINN 3,180,807

METHOD FOR MAKING FILM RESISTORS

Filed Oct. 23, 1961

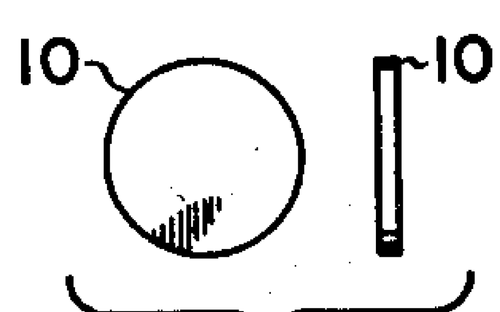

Fig. 1

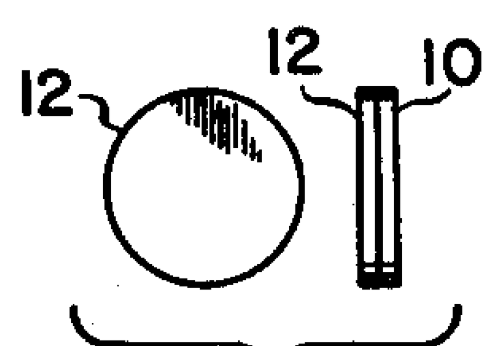

Fig. 2

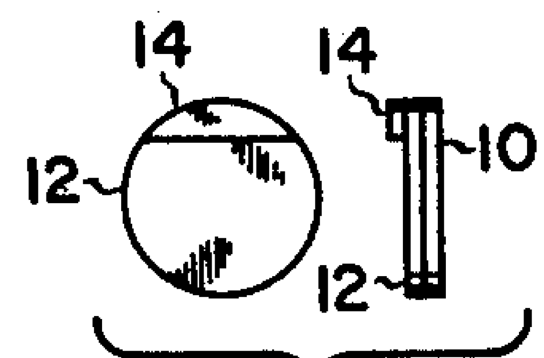

Fig. 3

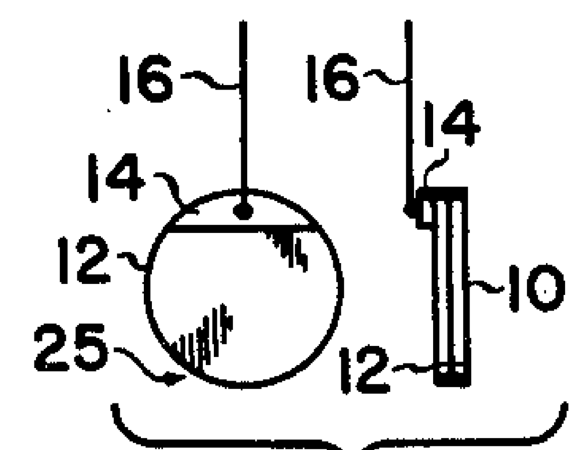

Fig. 4

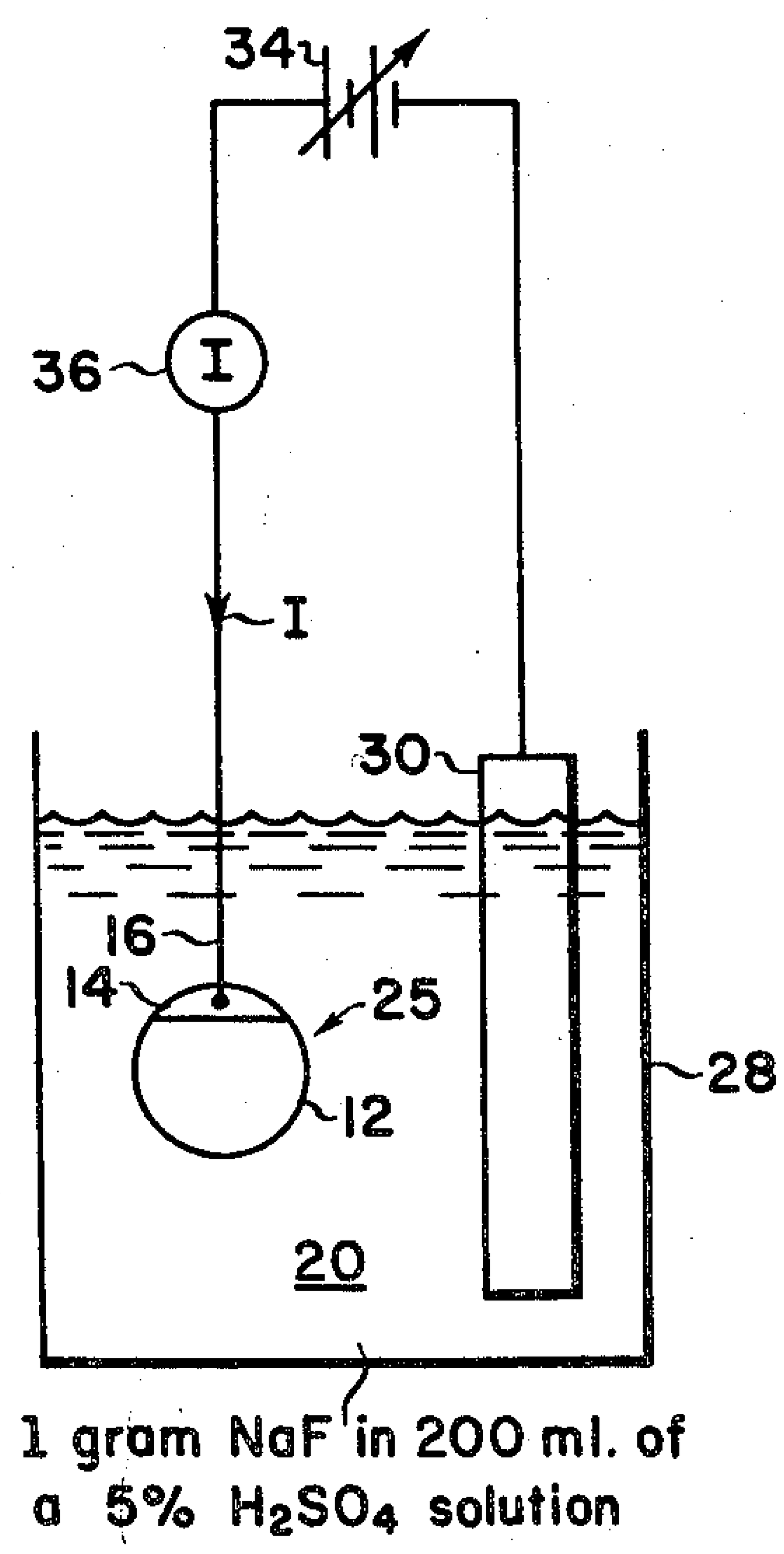

Fig. 5

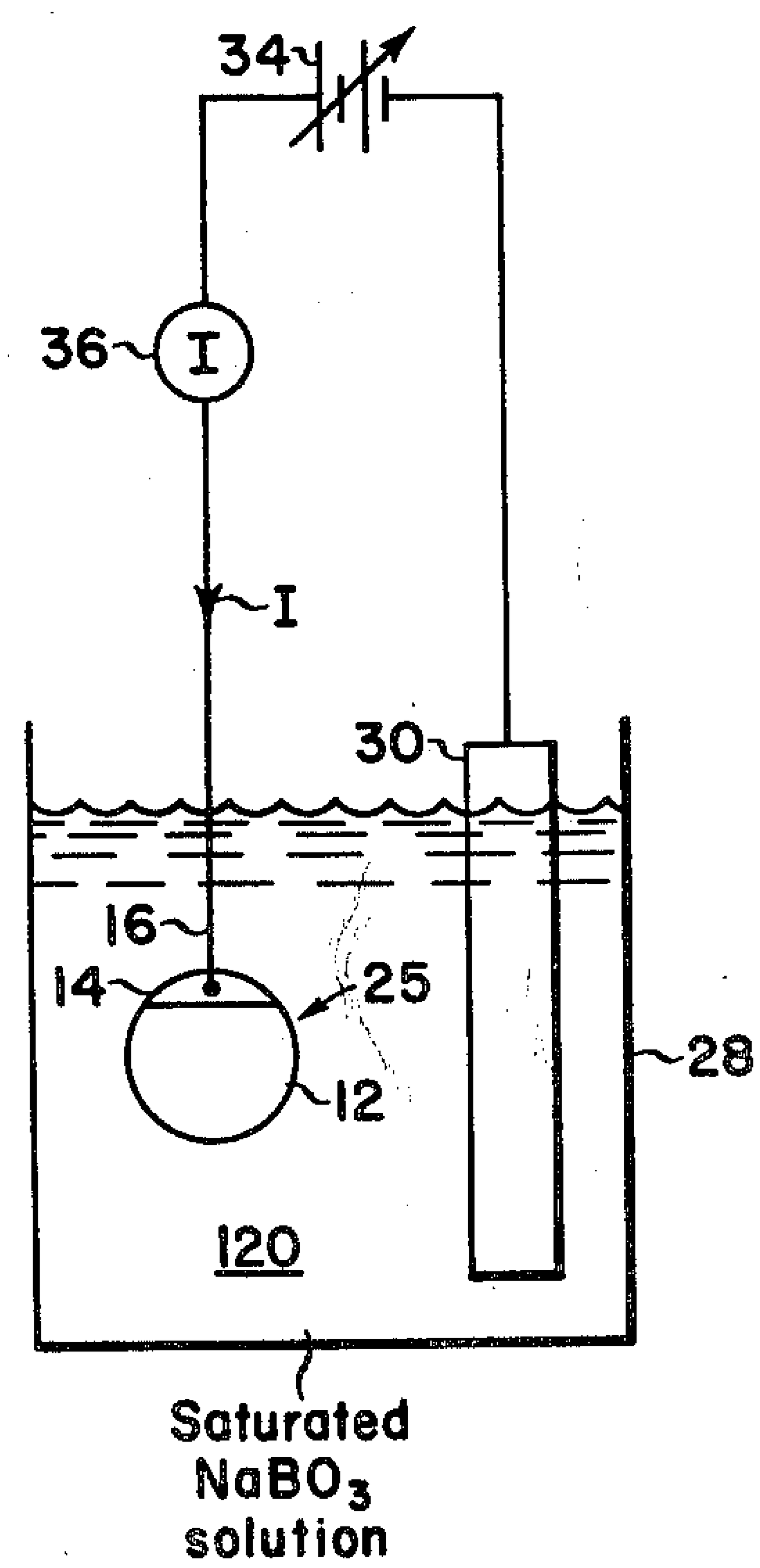

Fig. 6

INVENTOR.
ROSS A. QUINN

BY George C. Sullivan
Agent

United States Patent Office

3,180,807

Patented Apr. 27, 1965

3,180,807
METHOD FOR MAKING FILM RESISTORS

Ross A. Quinn, Palo Alto, Calif., assignor to Lockheed Aircraft Corporation, Burbank, Calif.

Filed Oct. 23, 1961, Ser. No. 147,711
4 Claims. (Cl. 204—38)

This application is a continuation-in-part of application Serial No. 8,480, filed February 11, 1960, now abandoned.

This invention relates generally to methods for making electrical resistor components, and more particularly to an improved method for making film resistors.

As a result of recent developments in printed circuitry and the need for microminiaturization in present-day electronics, the demand for film resistors of high stability has increased enormously. However, the provision of such film resistors, particularly where high stability in the presence of high temperatures is required, has been a considerable problem, requiring expensive and complicated methods and apparatus, which as far as is known are still not entirely satisfactory for producing high resistivity film resistors of high stability.

It is the broad object of the present invention, therefore, to provide an improved method for making high resistivity film resistors of high stability and reproducibility.

A more specific object of this invention is to provide an improved method for making film resistors of high stability and uniformity in which a low resistivity titanium film is converted into a film of high resistivity.

Another object is to provide an improved method for making very thin films of metal and metal oxide.

An additional object is to provide methods in accordance with any or all of the above mentioned objects which are simple and relatively inexpensive.

The above objects are accomplished in accordance with the present invention by a method in which a low resistivity film of convenient and non-critical thickness such as titanium, is converted into a highly stable film of high resistivity by means of a specially chosen simultaneous anodizing and etching treatment to which the low resistivity film is subjected.

The specific nature of the invention as well as other objects, uses and advantages thereof, will clearly appear from the following description, and from the accompanying drawing in which:

FIGURES 1–4 are each front and edge views of a ceramic or glass disc illustrating the preparation of a low resistivity titanium film on the ceramic disc with a suitable lead attached thereto.

FIGURES 5 and 6 are diagrammatic views illustrating the two-bath treatment to which the ceramic disc of FIGURE 4 is subjected to convert the low resistivity titanium film into a highly stable film of high resistivity, in accordance with the invention.

In order to permit the present invention to be better understood, the following background information is now provided.

A method which is presently used with some success for providing film resistors involves the vacuum deposition of metals and alloys on a suitable substrate. This method has yielded films with resistivities of good stability up to only about 500 ohms per square. Also, this method is relatively inconvenient for mass production and can be quite expensive.

In the search for cheaper and more adaptable methods and apparatus for making film resistors, a variety of more direct approaches have been employed, but for the most part these have been unsuccessful or impractical. One such method involves forming a low resistivity metal layer on a suitable substrate, and then etching away the

layer in an etching bath so as to reduce its effective resistance. However, it has been found that the etching process will not produce stable films with thicknesses small enough to provide a useable value of resistivity. The main reason appears to be the lack of uniformity in the etching process which causes some parts of the metal film to be etched at a faster rate than other parts.

Another method which has been employed for making film resistors involved the use of an anodizing process. As is well known, anodizing is an electrolytic process for converting the surface of a suitable metal into a metal oxide. Because this metal oxide is of a high resistance, attempts have been made to use this anodizing process for making film resistors by anodizing the surface of the metal film. This anodizing process, however, has not proved successful because the oxide layer only penetrates a short distance beyond the surface of the film, the layers below the surface (which are effectively in parallel with the high resistance surface layer) remaining essentially at their low resistance value. The resultant resistivity of the film, therefore, is raised only slightly. Attempts to increase the depth of penetration of the oxide layer produced by anodizing have been unsuccessful because arcing usually occurs which destroys the film. To achieve any success in making film resistors by anodizing, therefore, it is necessary to have a very thin film to begin with so that the depth of penetration of the oxide layer is significant when compared to the total thickness of the film. As indicated previously, the provision of such thin film is quite a problem in itself.

I have discovered that, by combining the above two heretofore unsuccessful approaches of anodizing and etching in a predetermined manner, it is possible to produce high resistivity films of remarkably high stability, including the high resistivity values previously unobtainable. And, because of the relative convenience of anodizing and etching techniques as compared to vacuum deposition techniques, the method of the present invention is inherently cheaper and more readily adaptable to production techniques.

In accordance with the present invention film resistivities of high stability are obtained by converting a low resistivity metal film of convenient and non-critical thickness into a highly stable film of high resistivity by means of a specially chosen simultaneous anodizing and etching treatment to which this low resistivity metal film is subjected. I have found that titanium is a particularly desirable low resistivity metal film from which highly stable film resistors of high resistivity can be produced, and for this reason titanium will be used for illustrative purposes in the description of the invention to follow. It is to be understood, however, that other suitable low resistivity films could be converted into stable high resistivity films by means of the present invention, and the invention is not to be considered as limited to titanium, although at present titanium appears preferable. The invention will now be described in detail, using titanium as the low resistivity film.

FIGURES 1–4 illustrate the steps that might be followed in providing one side of a disc **10** or a suitable substrate with a low resistivity titanium film of convenient and non-critical thickness, which will be subjected to the simultaneous anodizing and etching treatment in accordance with the invention. For purposes of illustration, the thicknesses of the various layers shown are exaggerated. In FIGURE 1, a ceramic disc **10**, such as alumina, is suitably plated with a film **12** of titanium of convenient and non-critical thickness, as shown in FIGURE 2. This may be accomplished by a method such as is disclosed in U.S. Patent No. 2,746,888. A suitable lead tab **14**, which may be of copper, is then plated onto one edge of the titanium film **12** as shown in FIGURE 3 and a lead wire 16 soldered thereto as shown in FIGURE 4 to form the resultant disc 25. The titanium film 12 on the disc 25 may conveniently have a resistance of the order of 0.2 to 15 ohms per square. Although a round disc is shown in FIGURES 1–4, it is obvious that any desired shape or size may be used, such as might be required for printed circuitry.

The resistance between the copper tab 14 and a point diametrically opposite thereto on the disc 25 may be expressed by the well-known relationship

$$R=\frac{\rho L}{A}$$

in which R is the total resistance, ρ is the specific resistivity of titanium film 12, L is the length of the resistance path, that is, the distance from the tab 14 to the point opposite the tab 14 and A is the area of the resistance path which is proportional to the thickness of titanium layer 12. As the thickness of titanium layer 12 is reduced in accordance with the invention, the area A in the above equation is reduced, thereby causing the resistance R to increase. The thickness of the titanium layer 12 is reduced by converting its surface to titanium dioxide which has a very high specific resistivity and has a negligible shunting effect on the titanium layer 12.

As shown in FIGURE 5, the disc 25 is now immersed into a specially chosen bath 20 which contains an anodizing electrolyte and suitable additional material for etching purposes, the choice of which will be considered in detail a little later. The bath 20 is contained in a suitable container 28 into which is also immersed a suitable cathode 30, such as graphite. Obviously, the container 28 should not deleteriously react with the bath. In the anodizing process the graphite 30 serves as the cathode while the disc 25 serves as the anode. A variable D.-C. power source 34 has its negative side connected to the graphite 30 and its positive side connected to the lead 16 of the disc 25 through a current measuring device 36. During anodizing, an anodizing current I flows from the power source 34 as shown in FIGURES 5 and 6.

The choice of the bath 20 will now be considered in detail since it is important in providing the proper type of simultaneously anodizing and etching treatment necessary to produce highly stable films of high resistivity in accordance with the invention. First, etching material is provided in the bath 20 of a type which will etch the metal oxide layer formed by anodizing. For etching the oxides of titanium, fluoride ions are quite suitable.

The concentration of etching material in the bath 20 is then chosen in conjunction with the particular anodizing system so that the metal film is anodized at a rate which is at least sufficiently faster than the rate of etching to cause only the metal oxide layer to be etched, the bare titanium being converted into oxide by the anodizing process before it is attacked to any significant extent by the etching material. Essentially, therefore, the thickness of the original titanium film 12 is reduced as a result of the etching of the metal oxide surface layer produced by anodization, and not by the etching of the titanium itself.

I have discovered that this simultaneous anodizing and etching treatment as just described achieves an amazingly uniform and more controlled reduction in the thickness of the original metal film than could be obtained by any known etching process, thereby making it possible to obtain very thin films of high resistivity and stability. An additional advantage which is also derived is that the resistivity of the film increases not only because of the reduction in its thickness due to etching, but also, because when the film becomes very thin the very high resistance oxide layer produced by anodizing will have penetrated by an amount which produces a very significant increase in the resistivity of the film. And, both these effects are obtained in a single treatment.

It will now be understood that the concentration of etching material provided for a given bath 20 and a given anodizing system must be less than some predetermined concentration so that the surface of the titanium film is anodized to an oxide before it is attacked to any significant extent by etching. The smaller the concentration of etching material provided below this predetermined concentration, the slower the rate at which the thickness of the film will be reduced. This is because in a given anodization process, penetration is only possible for a predetermined short distance beyond the surface of the film. Thus, if etching is relatively slow, once this penetration is made, anodization can only proceed as fast as the anodized oxide surface is etched. Consequently, while any concentration of etching material below this predetermined concentration may be used, the actual concentration used in a given bath and a given anodizing system is usually dictated by the film thickness and treatment time desired.

Using the above described simultaneous anodizing and etching treatment, the titanium film 12 on the ceramic disc 25 can be converted into a highly stable film of high resistivity in a single bath by means of an arrangement such as shown in FIGURE 5. However, in order to provide greater control and more accuracy in the final value of resistivity obtained, I find it more advantageous to use a two-bath treatment in which the first bath converts the titanium film 12 into a very thin film of relatively high resistivity by means of the above described simultaneous anodizing and etching operation, and then obtain the final value of resistivity in a true anodizing bath without any etching material. FIGURE 6 diagrammatically illustrates the second bath set-up which is essentially the same as that of FIGURE 5 except for the use of a different bath 120.

The advantage of a two-bath treatment can be seen by realizing that the simultaneous anodizing and etching treatment provided by the first bath is basically controlled by the etching operation which reduces the film by a given thickness in a given time. Thus, as the film gets very thin, its resistivity changes much more rapidly with time, and hence is more difficult to control. By removing the disc 25 from the first bath when the film has a desired thickness and an intermediate value of resistivity, and then obtaining the final high resistivity by means of an anodizing operation in a second bath containing no etching material, the final value of resistivity can be controlled to a high degree without further thinning of the film. The second bath is chosen so that the anodizing process penetrates to a greater depth than did the anodizing process of the first bath, thereby permitting a greater portion of the thin film to be converted to oxide to increase the film resistivity. This increased penetration of the oxides by anodization is now able to exert a significant effect on the film resistivity because the first bath has greatly reduced the thickness of the original film. Also, this second bath is advantageous in that it permits a higher resistivity to be obtained for a greater thickness, since it converts more of the film to the higher resistance oxides.

The following specific example will now clearly illustrate the present invention. First, a disc 25 is provided as shown in FIGURE 4 having a titanium film 12 of convenient thickness with a resistivity of the order of 0.2 to 15 ohms per square.

The disc 25 is then immersed in the first bath 20 shown in FIGURE 5 consisting of 1 gram of sodium fluoride NaF in 200 milliliters of a 5% sulfuric acid H_2SO_4 solution for a time of approximately ten minutes with an anodizing current flow starting at 40 milliamperes per square centimeter and then decreasing, and a voltage source 34 adjustable up to 100 volts. Otherwise stated, the bath 20 consists essentially of 0.12 N (normal) sodium fluoride in 5% aqueous solution of sulfuric acid.

When the resistivity of the film reaches the order of

80 to 200 ohms per square, the disc **25** is removed from the first bath **20** as shown in FIGURE 5 and immersed in the second bath **120** as shown in FIGURE 6, which is a saturated sodium perborate $NaBO_3$ solution. The anodizing current flow starts at 8 milliamperes per square centimeter and the voltage source **34** is adjustable up to 250 volts. The disc **25** is held in the second bath **120** until the resistivity of the film **12** increases to the desired value. This may be determined by removing the disc **25** from the bath **120** and measuring its resistance in a conventional manner.

In the first bath **20** of FIGURE 5 consisting of 1 gram NaF in 200 milliliters of a 5% solution of H_2SO_4, the 5% H_2SO_4 solution serves as the anodizing electrolyte, while the fluoride ions produced when the NaF is dissolved in the 5% H_2SO_4 solution are able to etch the oxides of titanium produced by anodization. The fluoride ions can be obtained from any alkaline metal fluoride, from hydrofluoric acid or from any other metallic fluoride sufficiently soluble to provide the necessary fluoride concentration. The second bath **120** which is a saturated sodium perborate solution is provided only for anodizing and contains no etching material. Bath **120** may consist essentially of any conventional anodizing solution, such as boric acid, oxalic acid, sulfuric acid, sodium perborate, sodium borate, or ethyl acid phosphate. This anodizing bath **120** in conjunction with the higher voltage available from the source **34** in FIGURE 6, is able to provide a greater depth of penetration of the oxide layer than was possible with the anodizing set-up of FIGURE 5. The final high resistivity of the film may thus be produced by means of the set-up of FIGURE 6 by increasing the depth of penetration of the anodized oxide layer, which is able to cause significant increases in the resistivity of the film because the film is now very thin as a result of the first bath treatment.

Using the two-bath treatment of the above-described specific example, highly stable titanium films having resistivities as high as 5,000 ohms per square have been successfully produced.

Listed below are examples of other baths which I have found satisfactory in practicing this invention:

(1) With a titanium film having an initial resistance of 2.7 ohms per square, bath **20** consisted essentially of .06 N sodium fluoride in a 10% aqueous solution of sulfuric acid.

(2) With a titanium film having an initial resistance of 1.6 ohms per square, and a bath **20** consisting essentially of .12 N sodium fluoride and a 10% aqueous solution of sulfuric acid, a film resistance of 78 ohms per square was obtained after which anodization in bath **120**, which consisted essentially of saturated sodium borate, produced a resistor having a final value of 580 ohms per square.

(3) With a titanium film having an initial resistance of 1.5 ohms per square and a bath consisting essentially of .24 N sodium fluoride in a 2.5% aqueous solution of sulfuric acid. A film resistance of 92 ohms per square was obtained which was then anodized in bath **120** consisting essentially of a saturated sodium perborate solution to produce a final value of 492 ohms per square.

(4) With a titanium film having an initial resistance of 1 ohm per square and bath **20** consisting essentially of .12 N sodium fluoride in a 2.5% aqueous solution of sulfuric acid, anodization was continued until a film resistance of 68 ohms per square was attained and then treatment in bath **120**, a saturated sodium perborate solution, produced a resistor having a final value of 538 ohms per square.

(5) With a titanium film having an initial resistance of 3 ohms per square and a bath **20** consisting essentially of .12 N sodium fluoride in a 6% phosphoric acid solution, a film resistance of 75 ohms per square was obtained after which anodization in bath **120**, a 25 weight percent ethyl acid phosphate solution, increased the value to 1100 ohms per square.

The maximum useable concentration of fluoride ions occurs at about a .36 N solution above which the etching action proceeds at an uncontrollably rapid rate. Phosphoric acid was used in equivalent concentration for the sulfuric acid in the foregoing examples.

It is to be understood in connection with the present invention that the methods shown and described herein are only exemplary and that various modifications can be made in the construction, arrangement and steps thereof. The invention is to be considered as including all possible variations within the scope of the invention as defined in the appended claims.

I claim as my invention:

1. A process for making thin film resistors comprising the steps of plating an insulative substrate with titanium capable of being anodized, placing the plated substrate into an aqueous anodizing-etching bath in which anodizing and etching occurs simultaneously, said bath so constituted that the anodizing commences before the etching commences, applying an anodizing current between said titanium plating and said bath, and removing the plated surface from said bath when the titanium has reached the desired resistance, said bath consists essentially of an alkaline metal fluoride of .06 N to .36 N concentration in an aqueous solution of an acid from the group consisting of sulphuric acid and phosphoric acid in the range of about 2.5 weight percent to about 10 weight percent.

2. A process for making thin film resistors comprising the steps of plating an insulative substrate with titanium capable of being anodized, placing the plated substrate into an aqueous anodizing-etching bath of such chemical composition that the anodizing commences before the etching commences, applying an anodizing current between said titanium plating and said bath, removing the plated substrate from said anodizing-etching bath, placing the plated substrate in an anodizing bath different from said anodizing-etching bath, applying an anodization current between said titanium plating and last said bath, and removing the plated substrate from said bath when the titanium has reached a desired resistance; said anodizing-etching bath consists essentially of an alkaline metal fluoride of .06 N to .36 N concentration in an aqueous solution of an acid from the group consisting of sulphuric acid and phosphoric acid in the range of about 2.5 weight percent to about 10 weight percent.

3. A process for making film resistors comprising the steps of plating an insulative substrate with a relatively thin titanium coating whose entire thickness is capable of being anodized, placing the plated substrate into an aqueous anodizing-etching bath which is capable of substantially concurrently anodizing and etching said titanium coating, said bath being of such chemical composition that anodization of said coating commences before etching commences and said bath consists essentially of .12 N sodium fluoride in an aqueous solution of 5% sulphuric acid, applying an anodizing current between said titanium coating and said bath to anodize substantially the entire thickness of said coating, and removing the plated substrate from said bath when the anodized coating has reached a desired resistance.

4. A process for making thin film resistors comprising the steps of plating an insulative substrate with titanium capable of being anodized and placing the substrate into an aqueous bath where simultaneous anodizing and etching occurs, said bath having an anodizing acid constituent and an etching fluoride constituent for anodically treating said plated substrate which consists essentially of .06 N to .36 N of fluoride ions and a 2.5 w/o to 10 w/o aqueous solution of an acid selected from the group con-

sisting of sulphuric acid and phosphoric acid, to partially oxidize the titanium film and etch the resulting anodic oxide film.

References Cited by the Examiner

UNITED STATES PATENTS

1,985,118	12/34	Geel et al.	204—56
2,052,575	9/36	Lilienfeld	204—42
2,746,888	5/56	Ross	204—61
2,829,091	4/58	Missel	204—32
2,871,425	1/59	Burnham	204—56
2,874,102	2/59	Wainer	204—56
2,934,480	4/60	Slomin	204—37
3,025,225	3/62	Snyder et al.	204—145
3,030,286	4/62	Tao	204—141
3,148,129	9/64	Basseches et al.	204—38

OTHER REFERENCES

Colner et al.: Journal of the Electrochemical Society, November 1953, pages 485–489.

WINSTON A. DOUGLAS, *Primary Examiner.*

MURRAY TILLMAN, JOHN R. SPECK, *Examiners.*