Nov. 19, 1968 H. F. PUPPOLO ETAL 3,412,220

VOLTAGE SENSITIVE SWITCH AND METHOD OF MAKING

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Fig. 1.

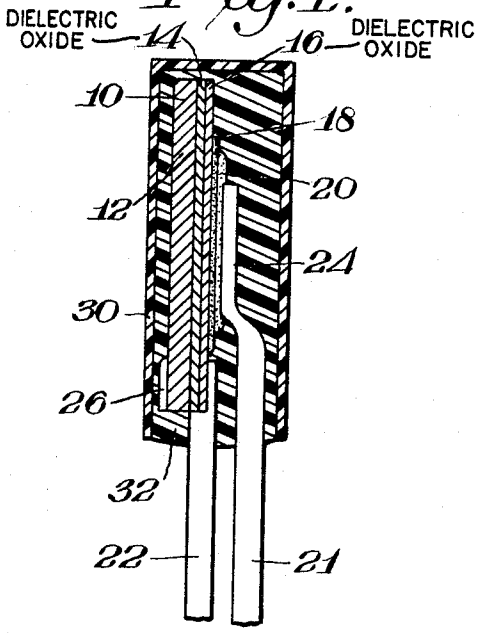


Fig. 2.

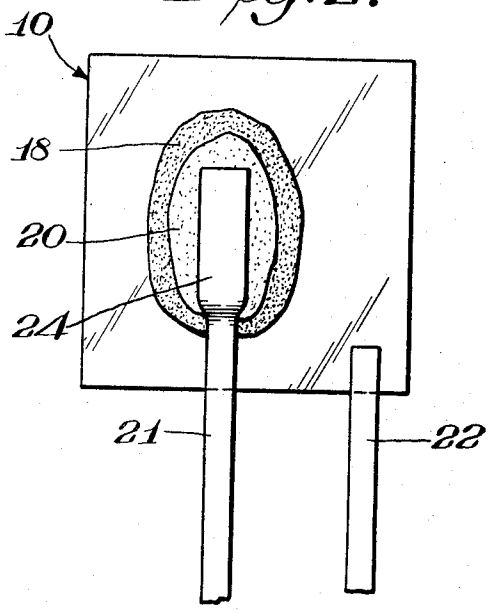
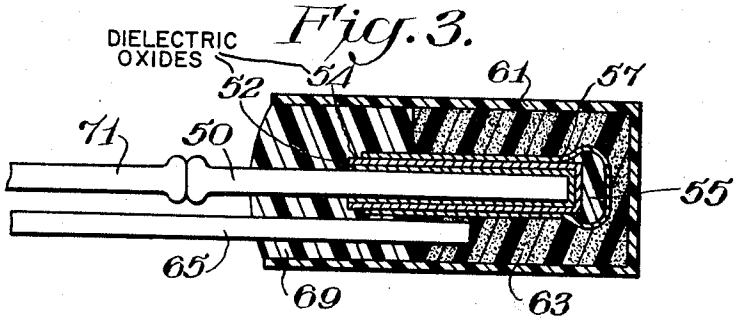


Fig. 3.



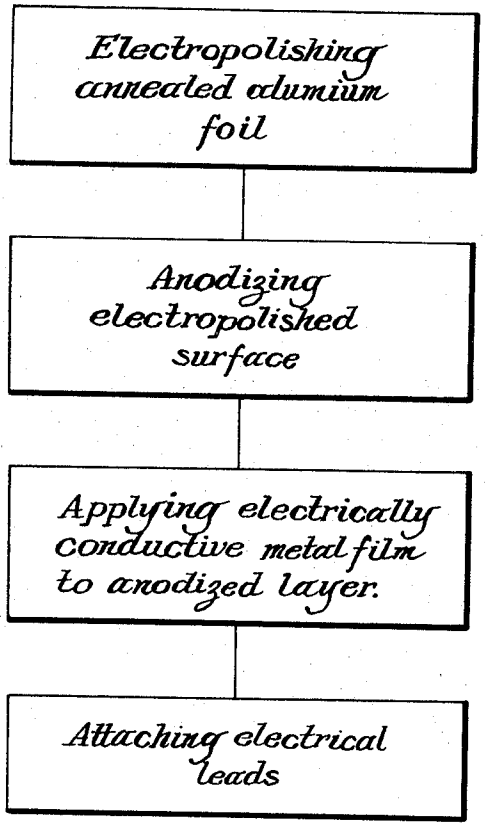
INVENTORS
HENRY F. PUPPOLO
ALBERT E. SCHERR, III
BY Connolly and Hutz
ATTORNEYS

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Fig. 4.



INVENTORS
HENRY F. PUPPOLO
ALBERT E. SCHERR, III
BY Connolly and Hutz
ATTORNEYS

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3,412,220

VOLTAGE SENSITIVE SWITCH AND METHOD OF MAKING

Henry F. Puppolo, North Adams, and Albert E. Scherr III, Williamstown, Mass., assignors to Sprague Electric Company, North Adams, Mass., a corporation of Massachusetts

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5 Claims. (Cl. 200—2)

ABSTRACT OF THE DISCLOSURE

An electrode overlies porous and dense oxides formed on the surface of an aluminum foil. Contact is made to the electrode by an electrically conducting resin. A second lead is welded to the aluminum foil. The assembly is potted in a non-conducting quantity of the same resin.

The present invention relates to electrical switches connected by leads to close a circuit between those leads when the voltage at the leads reaches or exceeds a predetermined value, but holding the circuit open so long as the voltage is lower. Switches of this type are described in U.S. Patents 2,909,122 granted Oct. 20, 1959, and 2,986,660 granted May 30, 1961, as well as in a paper by Otley et al. in the Proceedings of the IRE, vol. 46, pages 1723–30 (1958).

Among the objects of the present invention is the provision of novel switches of the above type which are simple to manufacture in large quantities and show a high degree of uniformity when so manufactured.

Additional objects of the present invention include the provision of novel methods for making the above switches.

The foregoing as well as additional objects of the present invention will be more fully appreciated from the following description of several of its exemplifications, reference being made to the accompanying drawings wherein:

FIG. 1 is a sectional view of a complete switch assembly representative of the present invention;

FIG. 2 is a plan view of the interior of the assembly of FIG. 1 showing its principal components;

FIG. 3 is a sectional view similar to FIG. 1 of a modified form of switch assembly in accordance with the present invention; and

FIGURE 4 is a flow chart illustrating a method of producing the switch assembly of the present invention.

As described in the above cited prior art, switches of the type here involved are generally of the one-shot type. That is, they will close the circuit once by a heavy flow of current through an aluminum oxide layer, and this flow will generally render the layer permanently conductive so that opening the circuit calls for disconnecting the switch. The aluminum oxide layer is originally non-conductive and will remain so as long as the voltage across it is below that at which the heavy electrical flow is initiated. The electrical breakdown resulting from the flow then reduces the resistance across the aluminum oxide layer to a very low value.

The construction of FIG. 1 has a piece of aluminum foil **10** which can be relatively small in size, having about 99.99% purity and fully annealed. One surface **12** of the foil is electropolished so that it is extremely bright and smooth. On this surface a combination of anodized layers **14**, **16** is formed. Anodized layer **14** is a relatively porous aluminum oxide while anodized layer **16** is a relatively dense aluminum oxide. Over a minor portion of the anodized layers is then applied a conductive film **18** of finely divided metal particles bonded to the anodized surface. An electrical lead **21** is electrically connected and

anchored to the film **18** by means of a body of epoxy resin **20** containing a sufficient concentration of finely divided metal to provide the desired electrical conductivity. A second electrical lead **22** is welded directly to the foil **10** at a location spaced from film **18** to complete the principal components of the switch.

In order to protect the switch from ambient influences such as handling, moisture and the like, it can be potted in resin **32** with or without a container **30** as shown in FIG. 1. A suitable container for this purpose is made of plastic so that it needs no further insulation. The space within container **30** can then be filled with a potting compound, one suitable type of which is an epoxy resin as described for example in U.S. Patent 2,553,718, although many other resins can be used.

A particularly practical technique for making the switch is set forth in the following example:

Example

A length of 0.003 inch thick aluminum foil of 99.99% purity and fully annealed is electropolished in a solution made by mixing 138 cc. of 60% perchloric acid (in water) with 483 cc. of acetic anhydride. The foil is placed in the solution with one face of the foil opposite a stainless steel cathode electrode also immersed in the solution. An anodic current density of 0.12 ampere per square inch of said foil surface is passed through the combination for 2½ minutes, the electrolyte being kept at 25° C. and actively agitated. The foil is now much brighter in appearance and after rinsing is then subjected to a sequence of two anodizing steps. In the first the electrolyte is a 6% aqueous solution of chromic acid, the anodic current density 0.013 amperes per square inch and the anodizing time 10½ minutes. A porous aluminum oxide is formed. After rinsing and drying the anodized foil is again anodized, this time in a 1% aqueous solution of ammonium dihydrogen phosphate. Here the voltage is kept at 7.2 and the anodizing carried on for four minutes with the electrolyte heated to 86° C. A dense aluminum oxide is formed. The resulting anodized foil is again rinsed and dried and a conductive film applied from an electrically conductive silver paint such as that described in the Bureau of Standards Circular 468, pp. 5 through 7. The conductive film is of relatively small area, preferably no more than 3 millimeters wide by 3 millimeters long, or 5 to 20 square millimeters in area, and located so that it occupies only a minor portion of the foil **10** and leaves plenty of room for attaching electrical lead **22** well spaced from the film.

An electrical lead **21** is then bonded and electrically connected to film **18** by means of the epoxy cement described above. One such cement is a mixture of Bisphenol-A with epichlorhydrin in a ratio of approximately 2 mols of epichlorohydrin for each mol of Bisphenol-A, about 80 to 85% weight percent finely divided gold being added, based on the weight of the metal-free mixture, and triethylene tetraamine added as a curing catalyst in the proportion of one part by weight for every 25 parts by weight of the gold-filled mixture. A quantity of the above cement is placed over a portion of film **18**, preferably so that it does not extend beyond the film. Lead **21**, which can have an offset flattened tip **24**, is then placed over the cement so that the tip rests on it and the offset keeps the remainder of the lead spaced from the surrounding portions of the anodized foil. The parts are kept in this relationship and the epoxy cement then cured. There is no need to press the tip against the foil; the weight of the tip itself will be sufficient.

Lead **22** is then spot-welded in place against the anodized surface of the foil, preferably using a grooved electrode against the lower surface of the foil and pressing down with another electrode on the tip of lead **22** so that

the foil is pushed into the groove of the lower electrode and takes its shape as indicated at **26**.

The resulting product will show a resistance between leads **21**, **22** of more than 1000 megohms at DC voltages (either polarity) up to about 5. With the lead **21** connected to the positive terminal of a DC supply and lead **22** connected to the negative terminal, increasing the voltage to 10 reduces the resistance somewhat, but further increase in voltage causes the switch to break down at 13.5 plus or minus 1 volt. It will then show a resistance of approximately 1 ohm between its two leads. It will also carry a current as high as 10 amperes.

The switch is no sturdier mechanically then the thin foil from which it is made, and is accordingly preferred to be protected as by potting. The potting case **30** shown in FIG. 1 can be made of pre-molded diallyl phthalate resin, and the potting compound **32** can be the same epoxy resin used for the body of cementing resin **20**, but without the gold filler. Other fillers can be used in the potting resin, as for example to color it and thereby code the switches.

Other metal particles can be used in place of the gold in the bonding resin **20**, but the gold gives best results, particularly if the units are to have the greatest current-carrying ability (after breakdown) and the maximum life. Other metals can also be used in place of the silver in the film **18**, and gold, bronze, platinum, palladium or the like provide good results there.

Welding of lead **22** to the anodized surface of the foil does not provide a connection that is mechanically very strong, although electrically it is perfectly sound. The use of a grooved spot-welding electrode, as described above, increases the mechanical strength of the welded joint without detracting from the electrical characteristics of the switch as a whole. The welding of electrical lead **22** can also be carried out against the opposite face of the foil **10**, particularly where that face has not been anodized, and it will then give a still stronger joint, but it is difficult to carry out the welding on that face without causing the welding equipment to engage and damage the adhesion of film **18**.

The electropolishing of the foil can be carried out with other electropolishing techniques, as described for example in The Electrolytic and Chemical Polishing of Metals by W. J. McG. Tegart, published 1959 by Pergamon Press, but with results that are not quite as good. With other electropolishing techniques the switches are not as uniform in their electrical characteristics. Whichever technique is used, the polishing is carried out just long enough to cause a noticeable brightening, and need not remove rolling marks or the like.

The chromic acid anodization can be carried out with different concentrations of chromic acid in the anodizing bath, and the chromic acid can be replaced by other electrolytes known to produce porous oxide films similar to that produced with chromic acid. Oxalic acid and sulfuric acid are instances of such other electrolytes. The ammonium dihydrogen phosphate in the second anodization can be replaced by other electrolytes known to produce dense oxide films, such as diammonium hydrogen phosphate, disodium hydrogen phosphate, orthophosphoric acid, without much change in characteristics. The combination of any of these phosphate anodizing treatments with the prior chromic acid anodizing makes a particularly effective and highly desirable switch.

The switch can be made to break down at voltages other than indicated above by varying the anodizing times or voltages, or by using different concentrations of solute in the anodizing baths. Shortening the times or voltages, or making the baths more dilute will provide switches that break down at as little as ten volts. On the other hand, lengthening the times or increasing anodizing voltages will give switches that break down at voltages anywhere up to 100 volts or even higher. In general it is preferred to have the chromic acid anodizing take about one to five times as long as the phosphate anodizing, as in the current practice used for manufacturing anodized aluminum for electrolytic capacitors. Varying the thickness of the aluminum foil from 0.002 inch to 0.020 inch does not affect its electrical characteristics appreciably.

While the foils from which the switches of the present invention are made can be longer and/or wider than indicated in the above example, the increased size does not contribute much. It is preferred to make the foils small, as in the example, and to cut them from larger foils after films **18** are applied. Thus a large foil can be electropolished, anodized and then coated with a multiplicity of rows and columns of suitably spaced films **18**, each a relatively small dot. The large foil can then be cut into individual foils 5 millimeters by 5 millimeters in size, or into strips containing one or two rows of dots each, for further processing.

In the interest of simplicity the electropolishing and anodizing can be confined to one face of the foil, but either or both of these treatments can also be spread to both faces if desired, without detracting from the effectiveness of the switch. Both treatments show considerable throwing power and will make themselves felt to some degree on the back face of a foil whose front face is juxtaposed close to and parallel with whatever is used as the surface of the cathode in these treatments.

Copper leads with electrolytic platings of pure tin, or lead, or coated with alloys of tin and lead weld very readily to the anodized or unanodized aluminum. For welding to the anodized surface a spot-welding current supply of 740 volts is very effective when used with a force of 14 pounds between a cylindrical 22 AWG lead and the foil. Lower voltages are useful when welding to essentially unanodized foils.

As pointed out in the above cited prior art, the breakdown voltage of switches such as those produced by the example, will be different if the polarity of the leads is reversed and if the voltage is applied in extremely short pulses. On the other hand, the switches of the present invention, although made for breakdown at a specific voltage, can be operated by lower voltages when the lower voltages are provided by alternating currents. Thus the alternating currents can be passed through a series-resonant LC circuit having an inductance and capacitance tuned to the frequency of the alternating current. The switch of the present invention can then be connected across the capacitor of the series-resonant circuit or the switch itself can be the capacitor of such circuit so that with a high Q inductor the voltage across the capacitor can be made several times that of the AC supply voltage. A switch that normally breaks down at 10 DC volts can then be made to break down with an AC voltage as low as 3 R.M.S. volts or less and with AC frequencies of from 25 cycles to 1 megacycle per second. When the same AC voltages are applied to the switch from circuits not using the foregoing resonance feature, the switch breaks down at an R.M.S. voltage about 40% higher than the DC voltage.

A similar result is obtained by connecting the switch across the inductor of such circuit rather than across the capacitor. Inasmuch as the switch will generally have a capacitance of about 0.002 microfarad, it will shunt some of the alternating current around the inductor and accordingly lower the effectiveness of such circuit somewhat.

It is not necessary to cement lead **21** to film **18** in the manner shown in FIG. 1. Instead, the lead can merely be embedded in a body of adherent electrically conductive resin in contact with the film. The electrically conductive resin can alternatively be used without the film **18**, but with results that are not as desirable.

FIG. 3 shows a voltage-sensitive switch built around a wire of aluminum rather than a foil. The aluminum wire is shown at **50** with one end anodized to form two layers **52**, **54** as in the construction of FIG. 1. A drop

55 of non-conductive resin such as the above-described epoxy resin, is adhered to the very tip of the anodized end to insulate the anodized layer at that tip. The anodizing does not give good results on sharp edges such as are present at the tip and it is important to keep such inferior oxide portions from lowering the quality of the switch as a whole.

The entire oxided end can then be coated with a film 57 of electrically conductive adherent material in the same manner as described above for film 18 in FIG. 1, except that in the construction of FIG. 3 such a film is readily applied by a dipping operation. The resulting multi-coated wire tip is then potted in a tubular container 61 with a body of electrically conductive plastic 63 in which is separately embedded a lead 65. The embedded end of lead 65 need not be in direct contact with film 57. On the other hand, the lead 65 should be well spaced from wire 50. The electrically conductive resin 63 is used in an amount small enough to keep from extending beyond the limits of the anodized layers 52, 54. A second body of resin 69 which can be the same resin used for potting except without electrically conductive fillers, can then be added over the electrically conductive body 63 to fill up the container 61 if desired.

Where it is not desired to use an aluminum lead for connection in the final circuit, a lead extension 71 can be secured to the wire 50. FIG. 3 shows such a lead extension made of tinned copper butt-welded to the aluminum in a manner similar to the lap-welding of the construction of FIG. 1.

The opposing lead 22 or 65 can be omitted by using an electrically conductive container in place of the non-conductive container 30 or 61. An electrically conductive potting compound will keep the container in electrical contact with the film 18 or 57 and if desired a lead can be soldered or welded to the container. Alternatively the container can be manufactured with an integral tail extending out and suitable for use as a connecting lead.

It is also practicable to have a lead of copper or other acceptable metal connected to the aluminum end of the anodized layers without welding as well as without soldering. In such modification the active portion of the aluminum is provided as a coating on a copper wire, for example. An aluminum coating of the desired high purity can be applied by a dip operation or by condensation from aluminum vapors, by cathode sputtering, or by spraying of the molten metal as in the Schoop process. The switch can then be formed on an aluminum surface so provided and the copper on which the surface is provided can then be used as a lead. The lead portion of the copper can be left uncoated as by masking it off, or the coating can be mechanically or chemically removed from the portion of the lead that is to be used for connection to a circuit.

Tantalum can be used in place of aluminum in either the foil or wire type switch assemblies, but again is not as desirable. With tantalum it is also important to polish its surface. Polishing techniques for tantalum are described on page 183 in "Anodic Oxide Films" by Lawrence Young, published by Academic Press, New York (1961). A chemical polishing procedure for tantalum is described in U.S. 2,808,542. Anodization techniques for tantalum are described on page 46 of the Young treatise and in U.S. 2,739,110. Non-electrolytic polishing also suitable for preparing tantalum for the purpose of the present invention includes polishing by a dip in an acid bath, as described in Transactions of the Faraday Society, vol. 53, page 841. A bath of 5 parts 96% aqueous H_2SO_4, 2 parts 70% aqueous HNO_3 and 2 parts 45% aqueous HF, all parts being by volume and used at 45° C., polishes tantalum very well in as little as 2 minutes.

Flexing of the foil or the wire during the making of the switch has a very deleterious effect on its characteristics and should be scrupulously avoided unless confined to areas that are not anodized.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed:

1. In a voltage sensitive switch, the combination of a fully annealed aluminum foil with at least one bright smooth electropolished surface, a first anodized layer on said surface anodically formed from a chromic acid electrolyte said first anodized layer being relatively porous, a second anodized layer on said surface superimposed over the first anodized layer and formed from a phosphate electrolyte, said second anodized layer being relatively dense as compared to said first layer a conductive film of finely divided metal particles on the superimposed anodized layers and bonded thereto, and an electrical lead connected to the film by a body of epoxy resin containing sufficient finely divided gold to be electrically conductive whereby the area between the conductive film and the aluminum foil overlain by the conductive film has a controlled uniform voltage for electrical breakdown initiation.

2. The combination of claim 1 in which a second electrical lead is welded to the foil and the combination is potted in a non-conducting epoxy resin.

3. In a voltage sensitive switch, the combination of a fully annealed aluminum foil having a purity of about 99.99% with at least one bright smooth electropolished surface, a first anodized layer on said surface anodically formed from a chromic acid electrolyte, said first anodized layer being relatively porous, a second anodized layer on said surface superimposed over the first anodized layer and formed from an ammonium dihydrogen phosphate electrolyte, said second anodized layer being relatively dense as compared with said first layer, a conductive film of finely divided silver particles about 5 to 20 square millimeters in area on the super-imposed anodized layers and bonded thereto, and an electrical lead connected to the film by a body of epoxy resin containing sufficient finely divided gold to be electrically conductive, the body of resin being out of direct contact with the anodized surface around the film, and a second electrical lead welded directly to the foil whereby the area between the conductive film and the portion of the aluminum foil overlain by the conductive film has a controlled uniform voltage for electrical breakdown initiation.

4. A method for making a voltage sensitive switch which method comprises electropolishing a surface of a fully annealed small sheet of aluminum foil, anodizing the electropolished surface first with a chromic acid electrolyte and then, second, in the same location with an aqueous electrolyte selected from the group consisting of ammonium dihydrogen phosphate, diammonium hydrogen phosphate, disodium hydrogen phosphate and orthophosphoric acid, applying a conductive film of finely divided metal particles to a minor portion of the resulting anodized layer, applying solely to the conductive film a soft layer of curable thermosetting resin cement containing an electrically conductive concentration of conductive particles, placing an electrical lead on said resin cement layer in the soft condition, then electrically bonding said electrical lead to the film by curing said cement layer, and welding a second electrical lead to the anodized surface of the foil alongside but out of contact with the metal film.

5. In a voltage sensitive switch having controlled and uniform breakdown properties, the combination of a fully annealed aluminum foil with at least one bright smooth electropolished surface, a first dielectric oxide anodically formed on said surface from a chromic acid electrolyte, said first formed dielectric oxide being relatively porous, a second dielectric oxide formed on said surface from a phosphate electrolyte, said second dielectric oxide being relatively dense so as to form with said first dielectric oxide a combination of dielectric oxides providing a uni-

form dielectric film substantially free of irregularities on the electropolished surface, a conductive film of finely divided metal particles overlying a portion of the uniform dielectric film and bonded thereto, a body of electrically conductive curable thermosetting resin containing an electrically conductive concentration of finely divided metal adhered to the conductive film out of direct contact with the dielectric film, an electrical lead electrically connected to the conductive film by the resin body, and a second electrical lead welded directly to the foil whereby the area between the conductive film and the portion of the aluminum foil overlain by the conductive film has a controlled uniform voltage for electrical breakdown initiation.

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LEWIS H. MYERS, *Primary Examiner.*

E. GOLDBERG, *Assistant Examiner.*