May 12, 1942. S. RUBEN 2,282,344

RESISTANCE DEVICE

Filed Dec. 15, 1939

Fig. 1

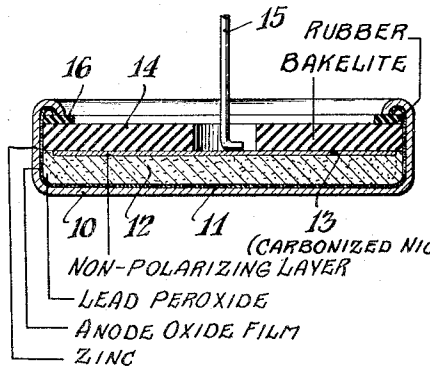


Fig. 2

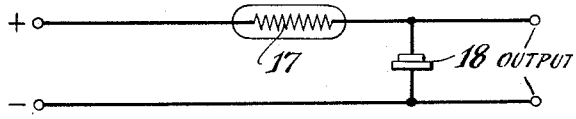


Fig. 3

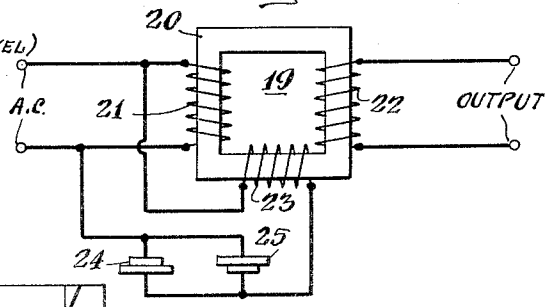


Fig. 6

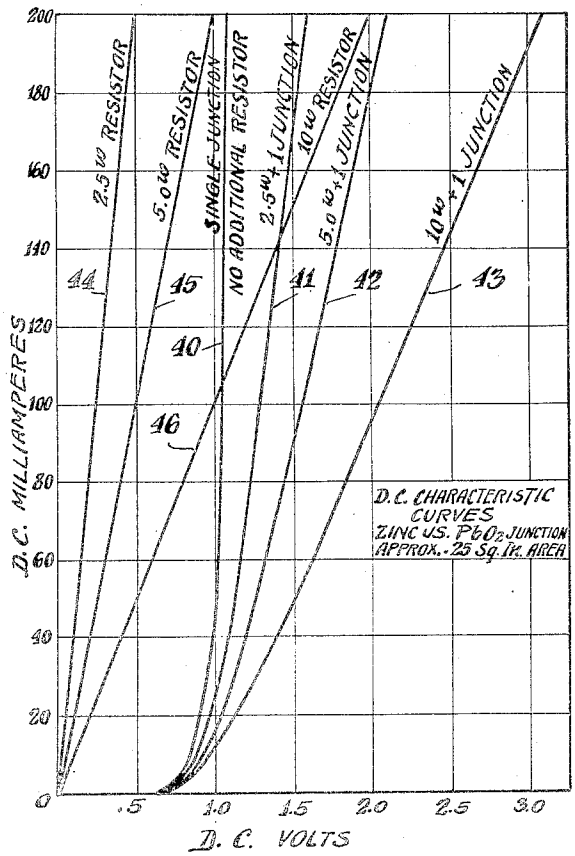


Fig. 4

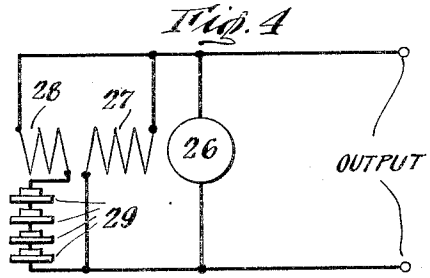
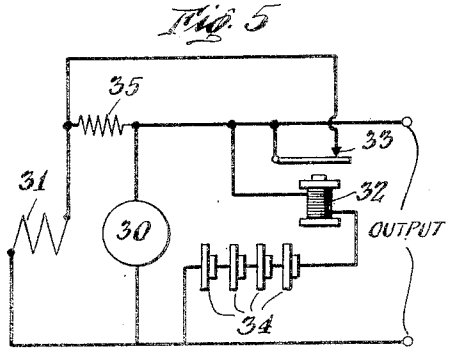


Fig. 5



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RESISTANCE DEVICE

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8 Claims. (Cl. 201—63)

This invention relates to an electric device whose resistance decreases rapidly with increasing applied voltage above a predetermined threshold voltage.

An object of the invention is to produce an improved device of negative voltage resistance characteristic such as it suitable for use in current control systems of various types.

Other objects of the invention will be apparent from the following description and accompanying drawing taken in connection with the appended claims.

The invention comprises the features of construction, combination of elements, arrangement of parts, and methods of manufacture and operation referred to above or which will be brought out and exemplified in the disclosure hereinafter set forth, including the illustrations in the drawing.

In the drawing:

Figure 1 is a sectional view of a device according to the present invention;

Figure 2 shows one form of regulating circuit in which my device may be used to advantage;

Figure 3 shows a transformer regulating circuit using my device;

Figures 4 and 5 show generator voltage regulating systems using my device; and

Figure 6 is a graph illustrating the electrical characteristics of the device.

In many electrical systems such as those shown in the drawing of the present application, for example, it is desirable to have a unit which can control the current flowing in parts of such systems as a function of the applied voltage. Some devices of this type have been used heretofore such as various combinations of junctions having a negative coefficient of resistance versus applied voltage, for example, copper-cuprous oxide junctions, nickel iron alloy-selenium junctions and magnesium-cupric sulfide junctions. Such junctions have been used for such purposes as improving the positive action of a relay by connecting the junction in series therewith, and as means of obtaining a greater than proportional current rise through a coil with increasing voltage. These junctions have also been applied to various forms of voltage regulating systems.

The copper-cuprous oxide junctions and the nickel-iron-selenium junctions possess the disadvantage of having large variation in resistance with temperature and hence the resistance voltage characteristics are not constant but vary markedly with the temperature at which the device is operated. Such devices have also been subject to considerable instability in that they have failed to consistently maintain the original resistance values for given applied voltages when any appreciable amount of current has been carried by the junction. These prior art junctions have also been limited to circuit applications where a very low threshold value of conduction was applied to each junction. Hence with normal applications a large number of junctions were required in series in order to produce a device which would operate in the range of voltages used.

The magnesium-cupric sulfide junctions have also been subject to considerable variation due to mechanical and atmospheric conditions and variations in the processing of these elements have rendered them difficult to use where reproduceable characteristics are required within close limits.

I have now discovered that a junction produced by a contact combination of lead peroxide with metallic zinc, the surface of which has been electrolytically oxidized, produces a resistance which is much superior in operating characteristics to the devices heretofore used and which has a much higher threshold value of conductivity. I have found that with a junction formed of an anodized zinc element against a lead peroxide element, when connected in a circuit in which the zinc comprises the negatively charged electrode (cathode) practically no current will flow until an applied voltage of 0.7 volt is reached and that only a very small amount of current will flow until the voltage drop across the junction reaches about 0.85 volt. As the voltages rises above 0.85 volt, there is a rapid rise of current with increasing voltage, indicating a rapid drop in the resistance of the junction above this voltage value. Again as the voltage applied to the junction is decreased the current falls rapidly to a very small value as the same threshold voltage is passed. The function of the junction appears to be reproduceable for an indefinite period without any noticeable change in characteristics or deterioration of the junction.

The operation of the junction is dependent upon voltage effects and the critical voltage values will decrease somewhat with temperature.

The oxide coating produced on the zinc by the anodizing process prior to assembly of the device is a low resistance material and hence the function of the junction differs materially from junctions using oxidized aluminum or magnesium as one electrode. The oxides of aluminum and of magnesium are insulating and in order

for such junctions to function the oxide layer must be broken down or punctured by a current surge. Hence aluminum and magnesium have heretofore found application as electrodes in lightning arresters where a rapid breakdown takes place when a high voltage is applied. With the anodized zinc electrode no puncturing or breaking down of the oxide layer takes place and the increase and decrease in conductivity with applied voltage is a continuous curve rather than a discontinuous one. Hence the device of the present invention differs materially in mode of operation from the "breakdown" devices of the prior art.

While a preferred embodiment of the invention is described herein, it is contemplated that considerable variation may be made in the method of procedure and the construction of parts without departing from the spirit of the invention. In the following description and in the claims, parts will be identified by specific names for convenience, but they are intended to be as generic in their application to similar parts as the art will permit.

Referring to the drawing Figure 1 shows a preferred form of construction for my device. The zinc electrode **10** is in the form of a zinc cup having the anodized coating **11** on the inside thereof. The cup is filled with lead peroxide **12** and a non-polarizing electrode disc of carbonized nickel **13** is pressed on top of the lead peroxide and spaced from the side walls of the cup. A Bakelite pressure disc **14** is placed over the carbonized nickel disc **13** and a soft rubber sealing ring **16** on the Bakelite disc and the top edge of the zinc cup **10** is then spun over the rubber ring to seal the unit and press the carbonized nickel disc firmly against the lead peroxide composition within the cup. A terminal wire **15** is welded to the middle of nickel disc **13** to afford a suitable connecting terminal. The other terminal of the device is the zinc cup **10** itself. However, if desired a wire conductor may also be welded to the zinc cup.

The anodizing of the zinc is accomplished by immersing it in a weak alkaline solution and applying a positive potential to it. The voltage applied and the time will depend upon the alkaline concentration. With a 5% solution of sodium hydroxide, for example, a potential of 4 volts for 30 seconds is satisfactory. The preferred alkaline anodizing electrolyte is a saturated solution of calcium hydroxide (0.18 gram calcium hydroxide per 100 cc. of water). With this electrolyte a voltage of 8 volts applied for one minute at a temperature of 25 degrees C. is most suitable. An excessively thick film should be avoided since in such cases a practically non-conductive condition is had resulting in punctures taking place when the couple is assembled with consequent overloading effects at the punctured points resulting in decomposition of the lead peroxide. The anodizing can be controlled so as to give a cell of minimum internal resistance and a steep characteristic curve. The current at the low voltage values is dependent upon the thickness of the oxide film and the preferred condition is that giving a minimum resistance drop at the higher voltages. No forming or aging is required after assembly.

The lead peroxide is preferably pressed into the zinc cup under relatively high pressure such as 2000 pounds per square inch. However, it can also be applied as a spray onto the anodized zinc surface. The spray material may be formed by grinding the lead peroxide in a 3% solution of copolymer of vinyl chloride and vinyl acetate in a solvent of 50% acetone and 50% carbon dichloride. After spraying the coating is baked at 120 degrees C.

The anodized zinc element should be thoroughly washed after forming to eliminate any alkaline or water soluble salts. The anodized zinc cup and the lead peroxide should both be dried thoroughly prior to assembly to avoid any electrolytic effects.

Under normal operating conditions the junction appears to undergo no electrolytic changes or reduction, such as has been observed with aluminum-lead peroxide junctions, during operation. None of the lead peroxide appears to be changed to the non-conductive lead oxide during operation of the device. The junction shows unilateral conductivity and hence when used in alternating current circuits a pair of junctions should be used in inverse parallel relation to avoid any rectifying effect. There is less temperature effect with the anodized zinc-lead peroxide junction than with a cuprous oxide or selenium junction.

Any number of junctions can be connected in series to enable operation in higher voltage circuits. Also they may be used in series with fixed resistors.

When the zinc is made the anode or positively charged electrode in the circuit very little current will flow and therefore for use as a regulator in direct current circuits the zinc should be made the cathode.

Figure 6 is a graph containing a family of curves showing the non-linear voltage-current characteristics of a single junction with various series resistances. These are compared with the straight line curves representing the voltage-current characteristics of ordinary resistances.

Curve **40** is the characteristic curve for a single junction having no resistance in series therewith. It will be noted that very little current flows until about 0.85 volt is applied, after which the current increases rapidly. The steepness of the curve depends in part upon the area of the junction and the thickness of the anodized film. The single junction giving the curve illustrated in Figure 6 had a junction area of .25 square inch and the anodized film was formed by one minute formation in a saturated calcium hydroxide solution at 8 volts. The lead peroxide was compressed at 2000 p. s. i. to a thickness of .02". Curve **41** is a similar curve for a single junction connected in series with a 2.5 ohm resistor. Curve **42** shows the characteristics of a single junction connected in series with a 5 ohm resistor. Curve **43** is for single junction connected in series with a 10 ohm resistor. Curves **44**, **45** and **46** show the corresponding straight line characteristics of ordinary resistors of 2.5, 5 and 10 ohms respectively.

From these curves the most suitable combination for any one of a variety of operating conditions may readily be determined.

Figure 2 shows a direct current power supply circuit using a junction of the type described for voltage regulating purposes. An iron wire ballast resistor **17** is connected in series with the power supply leads and junction **18** is connected across the output terminals. If the output voltage rises above the practical critical value of about 0.85 volt per junction the large increase in current flow through the junction **18** will heat up the ballast resistor **17** thereby increas-

ing its resistance and hence increasing the voltage drop in the ballast resistor. It will be seen that by properly adjusting the system so as to operate the iron-wire ballast resistor at its most sensitive point a very sensitive and close control of the output voltage is possible.

Figure 3 shows a pair of the junctions applied to a transformer as a voltage regulator. The transformer 19 comprises an iron core 20 having a primary winding 21, a secondary winding 22 and a primary bucking winding 23 connected in shunt with the primary winding. A pair of junctions 24 and 25 are connected in inverse parallel relation with each other and in series with the bucking winding 23. As the applied A. C. voltage rises the junctions 24 and 25 pass an increasing amount of current resulting in a greater than proportional increase in current flow in the bucking winding 23. Since this winding has an opposite magnetizing effect on transformer core 20 than does primary winding 21 the resultant effect is a reduction of the magnetizing effect of the primary current on the core and hence the secondary output is maintained substantially constant.

Figures 4 and 5 show the junctions applied to voltage regulator systems for a D. C. generator.

In Figure 4 the generator 26 is provided with a shunt field winding 27 and a second shunt winding 28 connected in bucking relation thereto. A series of cells 29 of the type described herein are connected in series with the bucking winding 28. Should the generator output voltage exceed a predetermined value the current through the bucking winding will increase more than proportional resulting in a cutting down of the field strength of the generator and hence reducing the voltage. The system thereby acts as a regulator to maintain the generator voltage constant. A similar arrangement can be used with shunt wound motors for maintaining substantially constant speed with varying line voltages. In this case, however, the auxiliary field winding having couples in series with it is connected to aid the magnetizing effect of the main field winding.

Figure 5 shows another arrangement for maintaining the voltage constant wherein a generator 30 having a single field winding 31 has the winding 31 normally connected directly in shunt with the armature by contacts 33 of relay 32. Relay 32 is connected across the output of the generator and has cells 34 of the type described herein connected in series therewith. Should the voltage increase above the critical value the relay will receive a strong operating current and will pull up its armature opening contacts 33 which thereby introduce resistance 34 in series with the generator field winding 31 resulting in a decrease in current in the field winding and a reduction in the output of the generator. This system has an advantage over systems in use at present wherein a very sensitive relay is required and special contact materials are essential to prevent contact sticking due to the very weak pull of the relay in operating. The relay of Figure 5 will exert a strong and definite pull when the predetermined voltage is reached and hence affords a much more positive operation with a cheaper relay.

While the present invention, as to its objects and advantages, has been described herein as carried out in specific embodiments thereof, it is not desired to be limited thereby but it is intended to cover the invention broadly within the spirit and scope of the appended claims.

What is claimed is:

1. An electric device with negative resistance voltage characteristics comprising an electrode of lead peroxide, a non-polarizing contact engaging one surface thereof and a layer of zinc having an anodically formed oxide film thereon engaging the opposite surface thereof, said zinc and said non-polarizing contact forming the terminals of said device.

2. An electric device with negative resistance voltage characteristic comprising a layer of pressed lead peroxide powder, a non-polarizing contact element in contact with one side of said layer and an electrode of zinc having an anodically produced oxide film on its surface in contact with the other of said lead peroxide layer, said non-polarizing contact and said zinc forming the terminals of said device.

3. An electric device with negative resistance voltage characteristic comprising a zinc cup, an anodically formed oxide film on the inside of said cup and a layer of closely compacted peroxide of lead within said cup in intimate contact with said film, a non-polarizing contact disc engaging the exposed surface of said lead peroxide layer and pressure applying means pressing said disc against said lead peroxide layer and insulating said disc from said zinc cup, and a terminal conductor connected to said non-polarizing disc.

4. An electric device with negative resistance voltage characteristic resulting in a non-proportional increase in current flow with applied voltage above 0.7 volt, said device comprising an electrode of lead peroxide and a layer of zinc having an anodic oxide film thereon in contact with said lead peroxide, said film having a threshold value of conductivity in the order of 0.7 volt when said zinc is the negatively charged electrode.

5. An electric device comprising an electrode of zinc having an electrolytic anodic oxide film formed thereon and a cooperating layer of lead peroxide in contact therewith.

6. An electrical device comprising an electrode having a surface of an electrolytically formed compound comprising zinc oxide and a cooperating electrode of lead peroxide in contact therewith.

7. An electric junction device comprising zinc having an anodic oxide film on the surface thereof and a layer of lead peroxide in contact with said film.

8. An electric device comprising an electrode of zinc having an anodic oxide film thereon resulting from anodization in an alkaline electrolyte and a cooperating layer of lead peroxide in contact therewith.

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