

Nov. 30, 1965

S. YANDO

3,220,881

METHOD OF MAKING A NON-LINEAR RESISTOR

Filed Nov. 30, 1960

2 Sheets-Sheet 1

Fig. 1

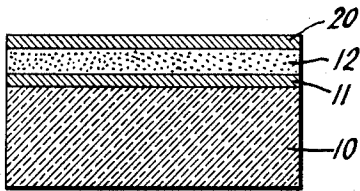


Fig. 2

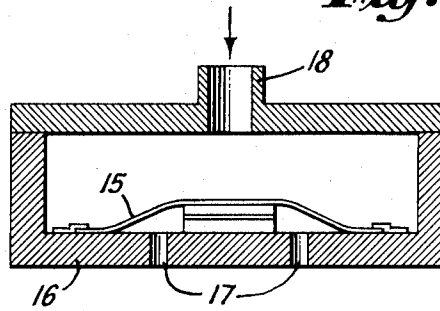
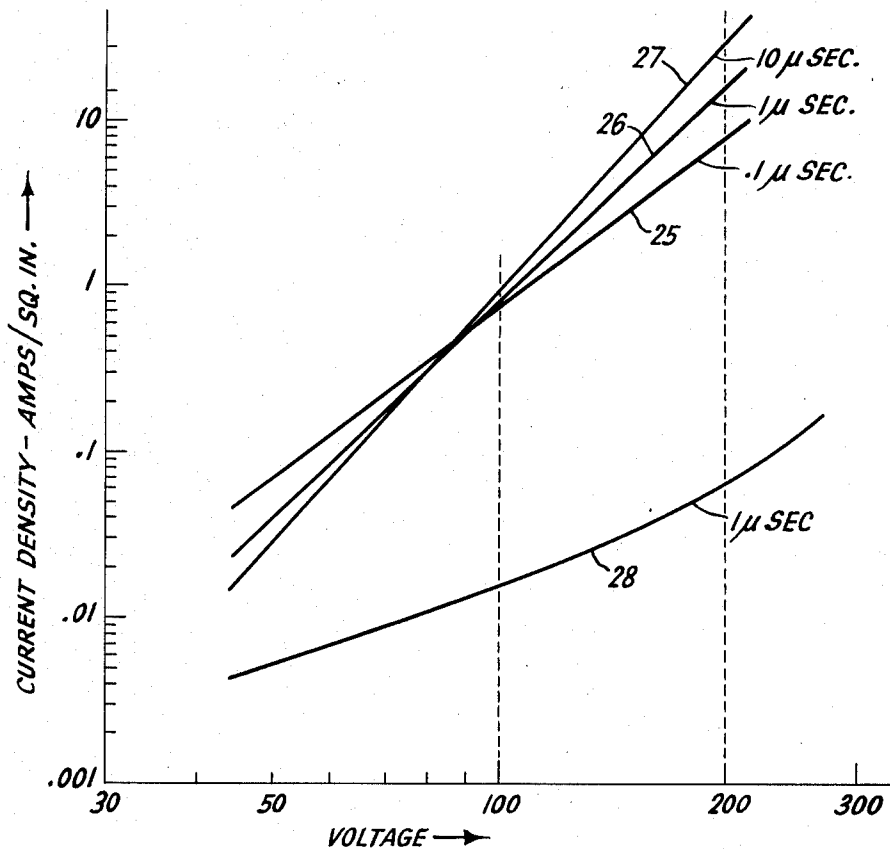


Fig. 3



INVENTOR
STEPHEN YANDO
BY
R. J. Frank
ATTORNEY

Nov. 30, 1965

S. YANDO

3,220,881

METHOD OF MAKING A NON-LINEAR RESISTOR

Filed Nov. 30, 1960

2 Sheets-Sheet 2

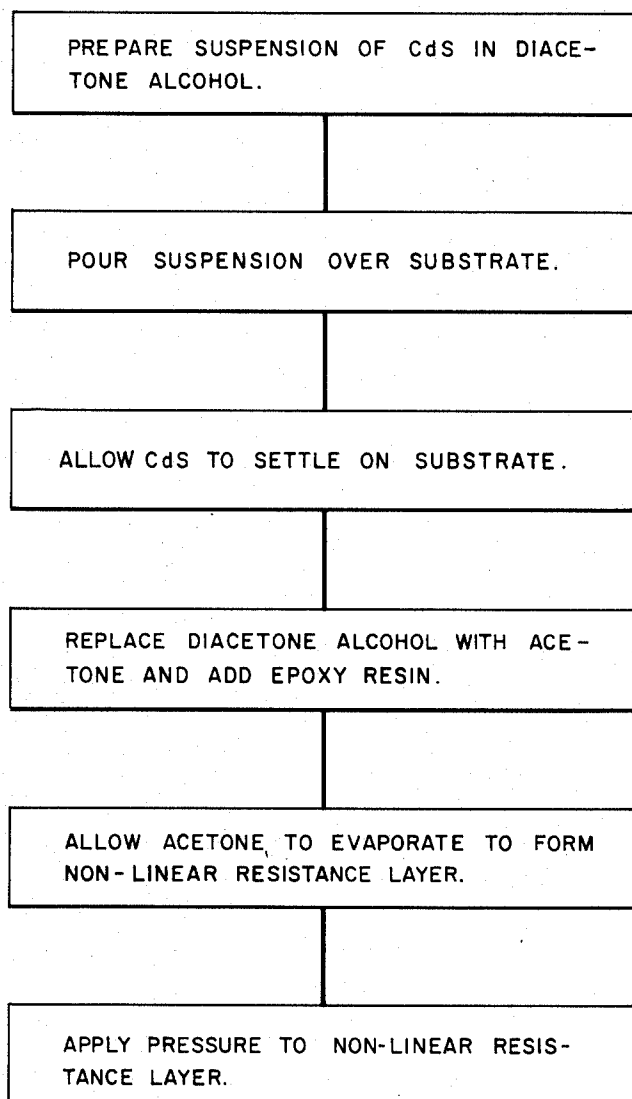


Fig. 4.

INVENTOR.

STEPHEN YANDO

BY

R. J. Frank
ATTORNEY

1

3,220,881

METHOD OF MAKING A NON-LINEAR RESISTOR
Stephen Yando, Cold Spring Hills, Huntington, N.Y.,
assignor to General Telephone and Electronics Laboratories, Inc., a corporation of Delaware
Filed Nov. 30, 1960, Ser. No. 72,789
4 Claims. (Cl. 117—217)

This invention relates to electrical resistors and, in particular, to a method of manufacturing resistors having non-linear voltage-current characteristics.

Non-linear resistors are manufactured in a variety of forms and are utilized in many types of electrical and electronic circuits. I have invented a new non-linear resistor which has characteristics making it especially suitable for excitation by voltage pulses. Further, I have invented a method of making a non-linear resistance layer for use in resistors having these desired characteristics.

A non-linear resistance layer suitable for pulse excitation should have a high resistance when no voltage is applied across it and should present a low resistance to the pulse voltage source immediately upon application of the pulse and also during the entire period that the pulse is applied. In addition, to assure a rapid response, the capacitance of the layer should be as low as possible. Further, the power handling capacities of the resistance layer should not be easily exceeded.

Accordingly it is an object of my invention to provide a non-linear resistor which is particularly well suited for pulse excitation.

Another object is to provide a non-linear resistance layer having a relatively low capacitance component.

Still another object is to provide a non-linear resistance layer which has a relatively high current conductivity.

A further object is to provide a non-linear resistance layer having a comparatively high power density rating.

Yet another object is to provide a non-linear resistor which is simple and inexpensive to manufacture.

In accordance with the principles of my invention, particles of a non-linear resistive material are settled uniformly on to a substrate and then bonded together by a small amount of resin in a manner assuring clean contact between the particles. Settling is the precipitation of insoluble materials held in suspension in a liquid and then gradually accumulated at the bottom of a vessel by gravitation while a non-linear resistive material may be defined as one forming a non-linear resistance layer when it is settled on to a substrate. After bonding, the substrate and layer are heat-treated under pressure to cure the resin. If desired, the substrate can be made conductive thereby forming one electrode of the device while a second electrode can be applied to the other side of the non-linear layer.

When a voltage step or pulse is applied to the two electrodes, a high initial current flows through the layer. This current remains relatively constant or increases during the interval that the pulse is applied. When the magnitude of the voltage pulse is increased, the current magnitude increases in a non-linear manner. In particular, a small increase in voltage results in a relatively large increase in current and consequently a sharp decrease in resistance. Stated another way, the current through the layer equals KV^n where V is the applied voltage, n is a number greater than 1, and K is a constant of proportionality.

In one method of carrying out my invention, cadmium sulphide powder is suspended in a first fluid having a relatively high viscosity. The fluid is poured over a substrate and the cadmium sulphide particles allowed to settle slowly and uniformly over the substrate. The first

2

fluid is then replaced by a second fluid having a lower viscosity and a much higher evaporation rate than the first fluid. A small amount of an epoxy resin containing a curing agent is dissolved in the second fluid and the second fluid allowed to evaporate at room temperature. The substrate and settled layer are then subjected to pressure to increase the conductivity of the layer.

The above objects of and the brief introduction to the present invention will be more fully understood and further objects and advantages will become apparent from a study of the following description in connection with the drawings, wherein:

FIG. 1 is a cross-sectional view of a non-linear resistor made in accordance with my invention;

FIG. 2 is a cross-sectional view of the curing fixture used in preparing the non-linear resistor;

FIG. 3 is a graph illustrating the relationship between current density and voltage at various time intervals after the application of a voltage step across the resistor;

FIG. 4 is a flow sheet illustrating the steps of the process.

In carrying out my method, a measured amount of cadmium sulphide powder is first suspended in 50 milliliters of diacetone alcohol. A substrate consisting of a glass blank 10 having a gold electrode 11 affixed to its top surface is next placed in the bottom of a 150 milliliter settling beaker. The agitated suspension is then poured over the substrate and the cadmium sulphide powder allowed to uniformly settle over the substrate for about one-half hour.

The amount of cadmium sulphide powder suspended in the diacetone alcohol is dependent upon the desired thickness of the layer. Using a 150 milliliter settling beaker having a bottom area of about 3 square inches, 1.25 gram of cadmium sulphide powder suspended in 50 milliliters of diacetone alcohol produces a settled layer approximately 10 mils thick. Settled cadmium sulphide layers between 5 and 35 mils thick have also been used successfully. The cadmium sulphide powder may be produced by the process set forth in the copending application of G. Morrison et al., Serial No. 792,977 filed February 13, 1959, and now abandoned except that better results appear to be obtained when a copper concentration of about .01% by weight is used instead of the .02-1% disclosed in the application. Diacetone alcohol is used as the settling vehicle because it has a relatively high viscosity of approximately 3.2 centipoise at 20° C. and therefore allows the cadmium sulphide powder to settle slowly and uniformly over the substrate. Further, diacetone alcohol is a good solvent for the epoxy resin which is used, as will be explained hereinafter, to bond the powder.

The next step involves bonding the cadmium sulphide layer by an epoxy resin and requires that the diacetone alcohol, having a low vapor pressure, be replaced by a quickly evaporable solvent for the resin constituents. To prevent turbulence and surface tension from disturbing the cadmium sulphide layer, the diacetone alcohol is replaced by acetone in such a way that the liquid level never goes below the settled layer. This is accomplished by gently removing diacetone alcohol from the bottom of the 150 milliliter beaker with a pipette while slowly adding acetone to the top according to the following schedule: (1) remove 30 ml. of diacetone alcohol from the bottom of the beaker and add 20 ml. of acetone to the top, (2) remove 20 ml. of the mixture from the bottom and add 20 ml. of acetone to the top, (3) remove 20 ml. of the mixture from the bottom and add 20 ml. of acetone to the top, (4) finally remove 20 ml. of the mixture from the bottom and add 20 ml. of acetone

3

with .05 gram of an epoxy resin and .0065 gram of a catalyst dissolved therein to the top of the beaker.

The acetone is then allowed to evaporate at room temperature. After all of the acetone is evaporated, the epoxy which remains bonds the particles of cadmium sulphide together forming non-linear resistance layer 12. An epoxy resin which has been found highly satisfactory for this purpose is known by the tradename Epon 828 and is sold by the Shell Chemical Co., New York, N.Y. The catalyst used with this resin is a polyamine known as Epon Curing Agent D.

After all of the acetone has evaporated, the substrate with the resistance layer 12 is placed in a curing fixture as shown in FIG. 2. A sheet 15 composed of a plastic material, such as Teflon, is placed over the substrate and fastened securely (around its periphery) to the housing 16 of the fixture. The space enclosed by sheet 15 is vented to the atmosphere by openings 17 in the bottom of housing 16. Air pressure at about 8.5 p.s.i. is admitted to the fixture through intake 18 for approximately one hour during which time the temperature of the substrate is maintained at about 100° C. The substrate is then taken from the curing fixture and a gold electrode 20 evaporated or painted on to the cadmium sulphide-epoxy layer. These steps are illustrated graphically in the flow sheet of FIG. 4.

FIG. 3 shows the response of a resistor having a 10 mil. cadmium sulphide-epoxy settled resistance layer to the application of a step voltage, i.e. to the sudden application of a D.-C. voltage of predetermined magnitude across electrodes 11 and 20. For example, curve 25 shows that 0.1 microsecond after the application of a 100 volt step to the resistor, a current density of 0.7 ampere per square inch is obtained while 0.1 microsecond after a 200 volt step is applied the current density is about 7.5 amperes per square inch. Similarly, curve 26 indicates that the current density 1.0 microsecond after the application of a 100 volt step is about 0.8 ampere per square inch while the current density 1.0 microsecond after application of a 200 volt pulse is about 15 amperes per square inch. Ten microseconds after a voltage step is applied, the current density is still higher. Thus, as shown by curve 27, the current density is about 0.9 ampere per square inch, 10 microseconds after a 100 volt step is impressed across the resistor and 28 amperes per square inch 10 microseconds after application of a 200 volt step. The degree of non-linearity, as measured by the value of the exponent 17 in the relationship $I=KV^n$, is about 3.4, 4.2 and 5.0 for curves 25, 26 and 27 respectively. Furthermore, measurements indicate that the capacitance of a typical layer is 500 micromicrofarads per square inch for a 10 mil thick layer while initial power densities as high as 25 watts per square inch have been applied to the resistor without changing its characteristics.

Curve 28 shows by way of comparison, the current-voltage characteristics of a cadmium sulphide non-linear resistor manufactured by conventional methods rather than by the settling technique described herein. Comparison of curves 26 and 28 indicates that one microsecond after application of a 100 volt step to the two resistors the conductivity of the settled cadmium sulphide layer is about 50 times as great and that one microsecond after application of a 200 volt step to the two layers, this ratio increases to about 250. Thus, the high initial conductivity, low capacitance, and high power handling ability make the non-linear resistor of this invention especially useful for applications involving excitation by voltage pulses of relatively short duration. In addition to its good response to voltage pulses, the resistor also exhibits high conductivity and maintains its non-linearity when subjected to steady state A.-C. and D.-C. voltages.

While FIG. 1 shows a non-linear resistor having first and second electrodes 11 and 20 and a glass base 10, these are not essential to my invention. As disclosed in

4

my copending application Serial No. 72,788 filed November 30, 1960, and now Patent No. 3,072,821 the non-linear layer may be settled upon a piezoelectric sheet or on any other suitable base and may be used without metallic electrodes. Also, a non-linear resistor may be made in the form of a gap cell by settling the cadmium sulphide layer between two spaced electrodes having coplanar surfaces.

It shall be noted that, in the process disclosed, the particles are not wetted by a viscous resin and therefore clean particle to particle contact is achieved. This is accomplished by allowing settling to take place out of a resin solvent which is then displaced by a considerable less viscous acetone (having a viscosity at 20° C. of about 0.32 centipoise). Another important aspect is that only a very small amount of resin is employed (about 4% by weight) and, probably more significant is the fact that the resin is applied after the clean particle to particle contact of the cadmium sulphide powder has been established.

It has been found that pressures up to about 8.5 p.s.i. improve the conductivity of the layer but that pressures above this amount produced rapid degradation of the layer. While the reason for this is not completely understood, it is believed that excessive pressure causes displacement or fracture of the cadmium sulphide particles thereby allowing the resin to get between the particles. This tends to disrupt the clean particle to particle contact achieved by the settling process.

As many changes could be made in the above construction and many different embodiments could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The method of making a non-linear resistor comprising the steps of suspending cadmium sulphide powder in a first fluid having a relatively high viscosity, pouring said first fluid over a substrate and allowing said cadmium sulphide powder to settle in a uniform layer on the surface of said substrate, slowly replacing said first fluid with a second fluid having a relatively high evaporation rate, adding an epoxy resin to said second fluid, the quantity of epoxy resin being about 4% of the quantity of cadmium sulphide, allowing said second fluid to evaporate, and applying pressure to said layer, the resulting non-linear resistor having an extremely high conductivity.

2. The method of making a non-linear resistor comprising the steps of suspending cadmium sulphide powder in diacetone alcohol, said diacetone alcohol having a relatively high viscosity, pouring said diacetone alcohol over a substrate and allowing said cadmium sulphide powder to settle slowly in a uniform layer on the surface of said substrate, slowly replacing said diacetone alcohol with acetone having a relatively high evaporation rate, adding an epoxy resin to said acetone, the quantity of epoxy resin being about 4% of the quantity of said cadmium sulphide, allowing said acetone to evaporate, and applying pressure to said layer, the resulting non-linear resistor having an extremely high conductivity.

3. The method of making a non-linear resistor comprising the steps of suspending cadmium sulphide powder in diacetone alcohol having a relatively high viscosity, pouring said diacetone alcohol over a substrate and allowing said cadmium sulphide powder to settle in a uniform layer on the surface of said substrate, slowly replacing said diacetone alcohol with acetone having a relatively high evaporation rate, adding an epoxy resin to said acetone, the quantity of epoxy resin being about 4% of the quantity of cadmium sulphide, allowing said acetone to evaporate, heating said substrate and layer to about 100° C., and applying pressure to said substrate and layer for about one hour, said pressure not exceeding 8.5 pounds per square inch.

5

4. The method of making a non-linear resistor comprising the steps of suspending cadmium sulphide powder in diacetone alcohol, applying a first electrode to the surface of an insulating base, pouring said diacetone alcohol over said base and electrode, allowing said cadmium sulphide powder to settle in a uniform layer on the surfaces of said base and electrode, slowly replacing said diacetone alcohol with acetone, adding an epoxy resin and a polyamine catalyst to said acetone, the quantity of epoxy resin and catalyst being about 4% of the quantity of cadmium sulphide powder, allowing said acetone to evaporate, heating said substrate to about 100° C., applying pressure to said substrate and layer for about one hour, said pressure not exceeding 8.5 pounds per square inch, and applying a second electrode to the surface of said uniform layer.

6

References Cited by the Examiner

UNITED STATES PATENTS

2,792,447	5/1957	Kazan	252—501
2,860,219	11/1958	Taft et al.	338—15
2,866,878	12/1958	Briggs et al.	252—501
2,871,330	1/1959	Collins	338—15
2,937,353	5/1960	Wasserman	252—501
2,944,916	7/1960	Evans	117—33.5
2,997,408	8/1961	L'Heureaux	117—201
2,997,409	8/1961	McLean	117—201

FOREIGN PATENTS

564,981 10/1944 Great Britain.

15 RICHARD D. NEVIUS, *Primary Examiner*.
RAY K. WINDHAM, *Examiner*.