

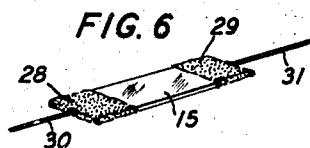
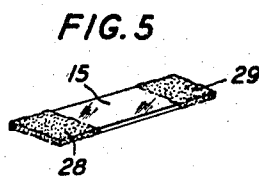
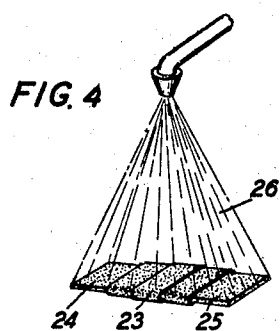
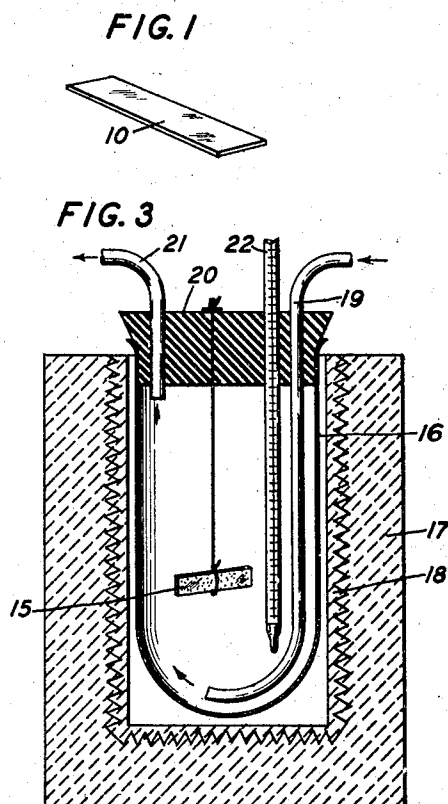
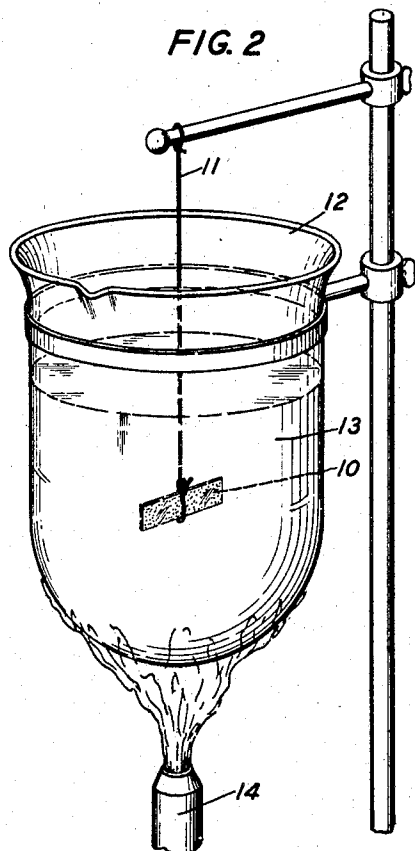
May 11, 1937.

R. O. GRIDALE

2,079,690

METHOD OF MAKING RESISTANCE DEVICES

Filed Jan. 2, 1936



INVENTOR
R. O. GRIDALE
BY *J. MacDonald*
ATTORNEY

UNITED STATES PATENT OFFICE

2,079,690

METHOD OF MAKING RESISTANCE DEVICES

Richard O. Grisdale, New York, N. Y., assignor to
Bell Telephone Laboratories, Incorporated, New
York, N. Y., a corporation of New York

Application January 2, 1936, Serial No. 57,180

6 Claims. (Cl. 91-70)

This invention relates to the preparation of electrical resistances from silver sulphide and more particularly to electrical resistances formed by the deposition of silver sulphide on supporting base members.

An object of the invention is to produce an electrical resistance unit which has a large negative temperature coefficient and in particular one whose resistance decreases with increase of temperature from room temperatures to 200° C. A further object is to produce a resistance element whose resistance is reproducible and reversible. That is, one whose resistance will have the same value at any given temperature regardless of the direction from which this temperature is approached.

Another object of the invention is to produce an electrical resistance unit having a large negative temperature coefficient of resistance whose resistance is independent of frequency or time and of voltage except insofar as an increase of voltage resulting in an increased power dissipation may cause a consequent decrease in resistance.

A still further object of the invention is to provide methods of making electrical resistances possessing the characteristics set forth above.

Many materials are known to have negative temperature coefficients of electrical resistance; and, in fact, this property is possessed to some degree by most non-metallic conductors and in particular by the so-called semi-conductors. Most of these materials, however, are not satisfactory for use in electrical apparatus either because their temperature coefficients of resistance are not great enough, or because their specific electrical resistances are not of the correct magnitude, or because they are not stable or reversible, or because of their chemical natures, they are not readily fabricated into suitable forms.

Silver sulphide possesses a combination of properties which make it uniquely suitable for use in electrical devices as a means of compensating for resistance changes in metallic conductors which possess positive temperature coefficients of resistance or as a control or compensatory device to operate when the change in temperature attains some predetermined value.

I have determined that by the following procedures resistance units which are suitable for use in electrical devices of the above-mentioned varieties can be prepared.

In my method, which will hereinafter be de-

scribed in detail, silver sulphide resistance units are formed by depositing silver sulphide on base members. These base members may be rods or plates of glass, ceramic, or other insulating materials or they may be of metals or alloys. The base members coated with silver sulphide may then be heat treated in an atmosphere of dry nitrogen to remove volatile impurities from the silver sulphide.

According to my method, silver sulphide film can be deposited directly on glass, ceramic, or metal supports by the chemical decomposition of solutions of complex sulphur bearing silver salts. For example, when a small quantity of a dilute solution of sodium hydroxide is added to solution of silver nitrate or acetate in combination with thiourea, at 30° C., silver sulphide is deposited on clean surfaces which have been immersed in the solution just after the addition of the sodium hydroxide. The deposit of silver sulphide may then be heat treated in an atmosphere of dry nitrogen to drive off impurities such as excess sulphur and to set the deposited material so that the resistance characteristic will not change with age or normal use.

In Fig. 1 a support or base member 10 is shown. This support may be of glass, ceramic, or other insulating material or of a metal or an alloy. The surfaces of the support 10 should preferably be free from dirt or grease, such materials being removed by mechanical action or by suitable chemical agents such as the mineral acids, ether, benzene, alcohol, or other organic solvents.

In Fig. 2 the support 10 is suspended by a string 11, or other supporting device in a vessel 12, containing a solution of a complex sulphur bearing silversalt 13 to which has been added a small quantity of sodium hydroxide solution, the support 10 being completely immersed in the solution 13. The vessel 12 and the solution 13 are preferably maintained at a temperature of 30° C. by a source of heat 14. The object or support 10 which is to be coated is preferably immersed in the solution 13 immediately after the small quantity of alkali hydroxide has been added to this solution. The alkali hydroxide is added in order to catalyze the chemical reaction which results in the deposition of the silver sulphide. This reaction is completed in a relatively short time, an immersion of eight minutes being sufficient to produce a satisfactory coating. If desired, successive deposits of silver sulphide may be produced on the same base member by repeating the above procedure.

After the support 10 has been subjected to

immersing in the solution 13 it becomes the silver sulphide coated unit 15 shown in Fig. 3.

An alternative method of producing silver sulphide film on supporting base members is the following. I have found that such film can be produced by immersing the object to be coated in a solution of silver nitrate or acetate in combination with sodium thiosulphate or sodium thiocyanate. When such a solution is employed it is preferable that it be heated to a temperature between 80° C. and 120° C. In order that the silver sulphide obtained by this method will adhere well to the base member, it is preferable that it be thoroughly cleaned and then washed in a fresh dilute solution of stannous chloride. The time required to produce a satisfactory film by this method will depend upon the temperature of the solution and may vary from a few minutes to an hour or longer.

To drive off excess sulphur and impurities the unit 15 may be heat treated in an atmosphere of pure dry nitrogen. This may be done by suspending the unit 15 as shown in Fig. 3 in the vessel 16 supported in the heating chamber 17 heated by the heating coil 18. Pure dry nitrogen is supplied to the vessel 16 through an inlet pipe 19 and is fed into the lower portion of the vessel 16. A plug 20 is provided in the top of the vessel 16. The plug 20 is apertured to accommodate the inlet pipe 19 and to support an outlet pipe 21 the outlet 21 serving as an outlet for the nitrogen and gases developed in the vessel 16. The temperature of the interior of the vessel 16 is indicated by the thermometer 22. I have found that if a temperature of about 200° C. is maintained in the vessel 16 and the unit 15 is allowed to remain in the vessel 16 for about one hour in the atmosphere of nitrogen, that the excess sulphur is removed from the silver sulphide coated unit 15 and the unit 15 will possess the required resistance characteristic and be stable in service.

After the unit 15 is removed from the vessel 16 it is ready to have the terminals or lead-in wires secured thereto.

Due to the character of the resistance unit 15 the well-known method of mounting or securing connections to resistances or the like cannot be used. It is therefore necessary to provide a different method of making connections to this resistance unit.

As shown in Fig. 4 the central portion of the resistance is masked by means of tape or some other similar material 23. The exposed portions 24 and 25 on the ends of the resistance are then sprayed with a conducting metal 26 by means of the gun 27 preferably in the manner of the well-known Schoop process. A coating of conducting metal is therefore formed at 28 and 29 on the ends of the resistance 15 as shown in Fig. 5. Lead-in wires 30 and 31 are then secured to the respective ends 28 and 29 of the resistance 15. It will be understood that I do not limit my-

self to the precise apparatus herein disclosed as the same is only used in an illustrative sense and that the invention is only limited to the scope of the appended claims.

What is claimed is:

1. A method of producing resistor units having a large negative temperature coefficient of resistance for use in electrical circuits which comprises the deposition on a supporting member by chemical reaction of solutions of silver nitrate in combination with thiourea and sodium hydroxide, and heat treating the coated supporting member in an atmosphere of pure dry nitrogen.

2. A method of producing resistor units having a large negative temperature coefficient of resistance for use in electrical circuits which comprises the deposition on a supporting member by chemical reaction of solutions of silver nitrate in combination with thiourea and sodium hydroxide, and subjecting the coated supporting member to a temperature of about 200° C. in an atmosphere of pure dry nitrogen.

3. A method of producing resistor units having a large negative temperature coefficient of resistance for use in electrical circuits which comprises subjecting a support to a bath of a solution of complex sulphur bearing silver salts in combination with alkali hydroxide, and heat treating the coated support in an atmosphere of pure dry nitrogen.

4. A method of producing resistor units having a large negative temperature coefficient of resistance for use in electrical circuits which comprises subjecting a support to a bath of a solution of complex sulphur bearing silver salts to obtain a coating of silver sulphide on the support, and then subjecting the coated support to a temperature of about 200° C. for about one hour in an atmosphere of pure dry nitrogen.

5. A method of producing resistor units for use in electrical circuits which comprises adding a small quantity of a dilute solution of sodium hydroxide to a solution of silver nitrate in combination with thiourea maintained at a temperature of about 30° C., immersing a base member in the solution of silver nitrate immediately after adding the dilute solution of sodium hydroxide, removing the base member from the solution after a sufficient coating of the silver solution has been obtained on the base member and subjecting the coated base member to a temperature of about 200° C. in an atmosphere of dry nitrogen.

6. A method of producing resistor units for use in electrical circuits which comprises immersing a clean support in a solution of silver acetate in combination with sodium thiocyanate maintained at a temperature between 80° C. and 120° C., removing the support from the solution when a required coating is obtained on the support and subjecting the coated support to a temperature of about 200° C. in an atmosphere of dry nitrogen.

RICHARD O. GRISDALE.