Sept. 20, 1960 B. F. TELLKAMP 2,953,484

COBALT-CHROMIUM ELECTRICAL RESISTANCE DEVICE

Filed July 22, 1957

Fig. 1.

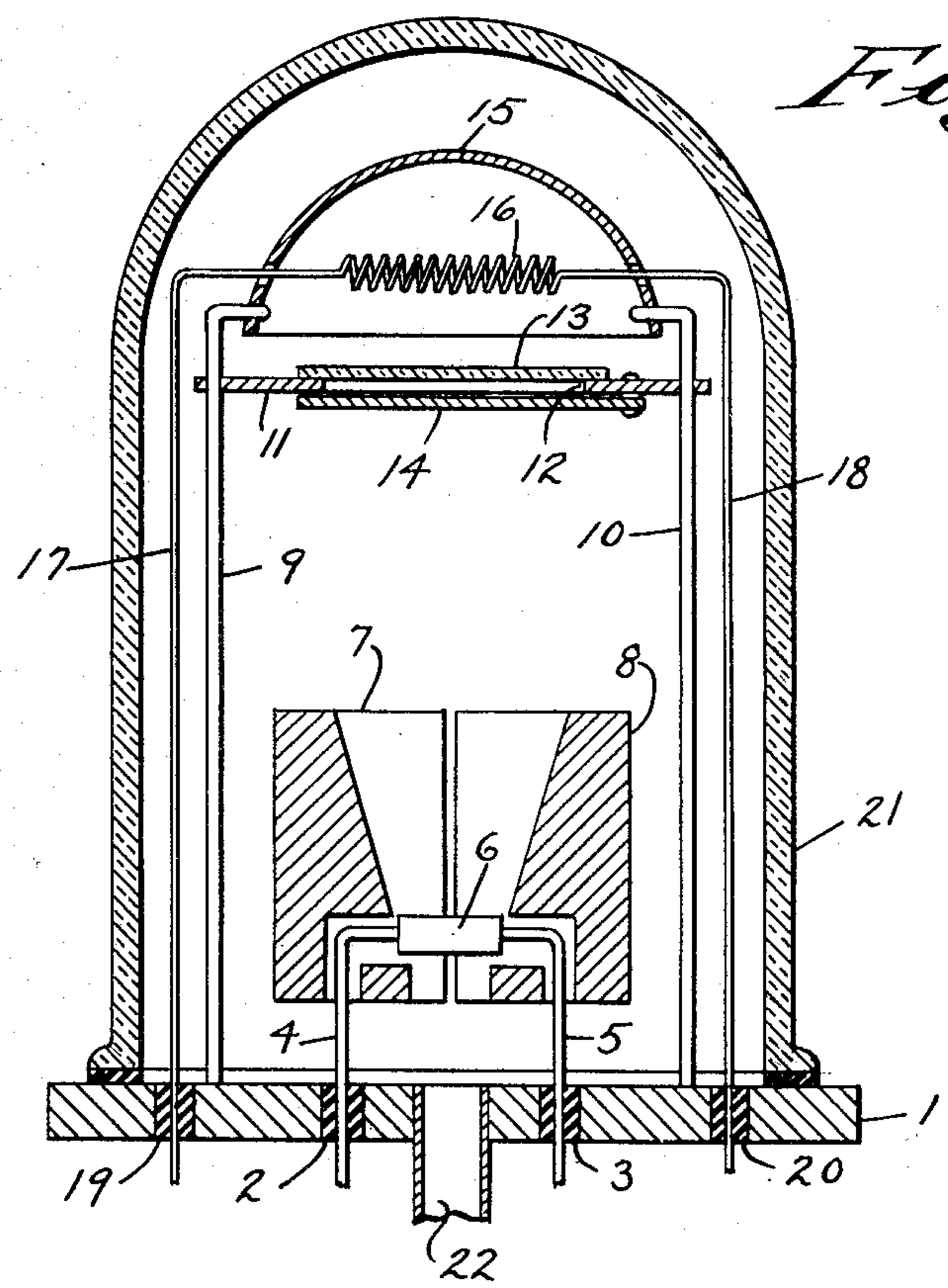
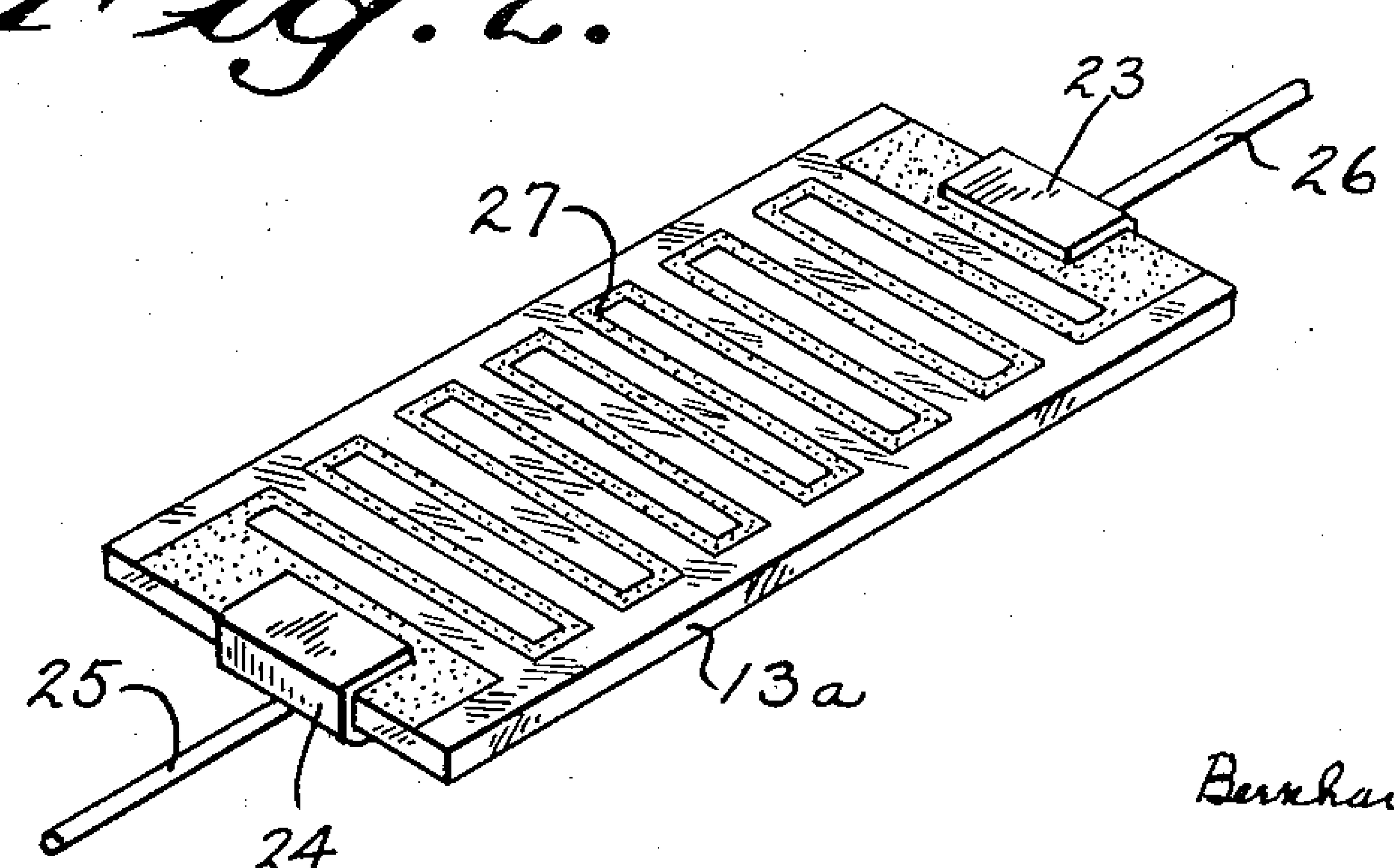


Fig. 2.



INVENTOR
Bernhard F. Tellkamp

BY Quarles, Fox, Seidel,
Bateman & Hoar

ATTORNEYS

United States Patent Office

2,953,484

Patented Sept. 20, 1960

2,953,484

COBALT-CHROMIUM ELECTRICAL RESISTANCE DEVICE

Bernhard F. Tellkamp, Muskego, Wis., assignor to Allen-Bradley Co., Milwaukee, Wis., a corporation of Wisconsin

Filed July 22, 1957, Ser. No. 673,290

12 Claims. (Cl. 117—212)

This invention relates to electrical resistance elements and more particularly to elements which are suitable for use as standards in electrical measuring apparatus and in other circuits where it is important to minimize change in resistance value with change in temperature and other ambient conditions, such elements being at times referred to as precision resistors, and the invention resides more particularly in an article wherein the electrically conductive element is composed of a metallic film supported on a solid dielectric base, the metallic film comprising co-deposited cobalt and chromium.

In attempting to meet the requirements of electrical instrument makers and others, who require resistors of or approaching instrument grade, wire wound devices have been commonly resorted to. Wire wound resistors are open to several serious objections, among them, chiefly in the higher resistance values, expense, inductive properties, bulk, capacitor properties, moisture susceptibility and limited load carrying capacity. Although wire wound resistors have the disadvantages noted, their properties have been found superior to other constructions including carbon composition resistors, non-metallic deposited film resistors, and metallic deposited film resistors, as heretofore formed.

Among the deficiencies of deposited metallic film resistors, as heretofore produced, has been their fragility and the undesirably high temperature co-efficient of resistance which has usually been equal to or in excess of that of the wire wound resistors. Such shortcomings are overcome in the practice of the present invention. In a preferred practice of the invention resistance films are formed by evaporation deposition in high vacuum, employing for the purpose a hermetically closed receiver containing means for bringing a metallic mass of cobalt and chromium to a temperature at which vapor is evolved. Within the receiver, provision is made for exposing to the heated metallic mass insulating bodies upon which the evaporated metal may be deposited in a thin conductive film of substantial electrical resistance. The deposition surface, which receives the deposited film is preferably the surface of a body of high chemical and electrical stability, and in most cases a high quality glass carefully cleaned to accept and tightly hold the deposited film is chosen as the base for the film.

The receiver, in which deposition takes place, is evacuated to a pressure at which the mean, free path of the evaporated metallic vapor particles is increased to a distance exceeding the spacing between the heated metal source and the deposition surface. For practical purposes, a pressure below 10^{-4} mm. of mercury will be found necessary and pressures as low as 10^{-6} mm. of mercury or lower may, at times, be employed to advantage.

The deposition surface of the glass plate or other body is advantageously maintained at a temperature receptive of the coating to be deposited and this temperature may be held for most practical purposes between 150° C.

and 500° C. For certain purposes a glass of low ionic mobility is selected, to form a more stable resistance unit in which initial resistance value will be maintained for greater time. So-called alkali lead silicate glass is an example, and has been satisfactorily employed for a resistor of high resistance value produced by forming a film in grid configuration with small dimensions.

The metal mass from which evaporation occurs may be a mixture or an alloy melt of cobalt and chromium with substantial proportions of each by weight. This melt is held at a temperature of about 2500° C. to 3000° C. within a receiver with the surface of the melt in a position directly facing the surfaces upon which deposition is to take place. The metals, cobalt and chromium, may be heated as separated evaporative sources if desired where such sources are spaced closely and are positioned to deposit simultaneously upon the deposition surface. Deposition may also be accomplished by the sputtering method.

Where a figurate film is required the glass, or other deposition surface, may be masked with a suitable substance such as a photosensitive resist, or other masking substance which can be easily removed, along with parts of the deposited film. Removal of the film with metal deposited thereon produces the desired figuration.

The deposition process, when carried on under the conditions above described, produces a deposited film containing substantial proportions by weight of each the cobalt and the chromium, and the proportions may vary within ranges discussed herein. To achieve the desired proportions in the film, the proportions of the metallic mass from which evaporation occurs is altered accordingly.

An object of this invention is to provide a deposited metallic film resistor wherein the temperature coefficient of resistance over a wide temperature range will be dependably low in terms of instrument makers' requirements.

Another object of this invention is to provide a deposited metal film resistor having chromium and cobalt as principal constitutents of the film.

Another object of this invention is to provide a deposited metal film resistor in which the temperature coefficient of resistance remains substantially constant for a wide range of film thickness.

It is another object of this invention to provide a deposited film type resistor in which the resistance film and the insulating base have compatible temperature coefficients of expansion.

It is another object of this invention to provide a method of producing a deposited film type resistor by evaporation of two metals compatible in evaporation rate and structural form.

Another object of this invention is to provide a deposited metallic film for a resistor which is strong mechanically so that it may be handled by ordinary means following deposition and until encased without danger of substantial alteration of electrical properties.

Another object of this invention is to provide a deposited metallic resistance film which may be encased by protective substances without alteration of electrical properties due to stress imposed by the encasing medium.

The foregoing and other objects and advantages of this invention will appear from the description to follow. In the description reference is made to the accompanying drawing, which forms a part hereof and in which there is shown by way of illustration and not of limitation specific means of practicing the invention.

In the drawing:

Fig. 1 shows in cross-section and in elevation an evacuated receiver in which the process of this invention may be conducted, and

Fig. 2 is a perspective view of an electrical resistance element formed in accordance with this invention.

In Fig. 1, there is shown an evacuated receiver having a metallic bed plate **1** through which insulated terminal bushings **2** and **3** enter the space to be evacuated. The bushings **2**, **3** surround and carry conductor support members **4** and **5**. Bridging the support members **4** and **5** is an electrothermal boat **6** intended to receive and heat the cobalt-chromium melt which is brought, thereby, to a vaporizing temperature. Surrounding the boat **6** are shield members **7** and **8** that confine the heat evolved and act, to some extent, as a path limiting guide for evaporated metal leaving the boat **6**.

A pair of support columns **9** and **10**, secured to the bed **1**, carry a horizontal platform **11** above the boat **6** which has an open center **12** over which is placed a sheet of ceramic, glass or other non-conductive supporting base material **13**. The base **13** is directly above and faces the cobalt-chromium melt to receive the film to be deposited. Interrupting the path between the boat **6** and the base **13** is a shutter **14**, pivoted to the platform **11**, that is employed to open and close the center **12**.

The upper ends of the support columns **9**, **10** turn inwardly to mount a reflector **15** having a resistance heating element **16** for maintaining the base **13** at a desired temperature. Conductors **17**, **18** are connected to the heater **16** and lead from the apparatus through insulating bushings **19**, **20** in the bed plate **1**.

The assembly described is surrounded by a receiver shell **21** joined hermetically at its lower margin to the bed plate **1**. An entrance opening **22** through the bed plate **1** is connected to pump means, not shown, for exhausting the interior of the apparatus.

The base **13**, upon which the film is to be deposited, may present a clear surface, or it may be masked by a substance responsive to solvent attack in a pattern which will produce a plurality of resistance elements each in grid configuration. It has been found that a convenient masking material is a photoengraver's resist, wherein albumin photosensitively insolublized by a substance such as an alkali dichromate is a major constituent. A figurate mask is easily formed photographically from such material and that which is not set by the photographic step is washed away to expose a portion of the underlying base **13**, having a configuration of the contemplated finished resistor units.

With the base **13** in place, the receiver shell **21** seated upon the bed plate **1**, and the shutter **14** closed, the interior of the apparatus is first exhausted and then the cobalt-chromium mixture in the boat **6** is brought to vaporizing temperature. The heater **16** raises the temperature of the base **13**, for enhancing the receptiveness to the metal to be deposited. The shutter **14** is opened, and the metallic vapors, which depart from the melt at a high energy level travel directly upward toward the base **13**. By reason of the pronounced directional effect of vapor deposition in a high vacuum the platform **11** will accumulate little deposit and the vaporized metal will strike the base **13** to form a uniform evenly distributed cobalt-chromium film.

After deposition of the metallic film has reached the desired thickness, the process may be terminated by closing the shutter **14**, and after cooling and reestablishing atmospheric pressure in the shell **21**, the base **13** is removed. If masked, the several individual resistance elements delineated on the base **13** may be cut apart from one another either before or after subjecting the same to solvent attack for removal of the masking material. An alkali solution that is a solvent for the photo resist forming the mask may be used to attack the mask at its margins to dissolve it from under the co-deposited cobalt-chromium film. The mask is thereby removed, together with the portion of the film deposited thereon, and although this attack proceeds over the space of a few hours the co-deposited cobalt-chromium film on the base **13** is, apparently, inert and suffers no perceptible attack by the solvent.

A resistor formed in this fashion may appear as illustrated in Fig. 2, where **13***a* represents a portion cut from the base **13**, upon which the co-deposited film of evaporated cobalt-chromium is arranged in grid configuration as indicated at **27**. Terminals **23** and **24** with leads **25** and **26** may be attached, as shown, and if desired the entire resistor may be encased in a protective insulated jacket, not shown.

Films deposited, as above directed, exhibit extremely small temperature coefficients of resistance and this is true of extremely thin films as well as films of substantial thickness. The formation of continuous films having a resistance per square area of from below 20 ohms to above 2000 ohms can be formed wherein the temperature coefficient of resistance is as low as plus or minus 30 parts per million per degree centigrade over the temperature range of minus 60° C. to plus 200° C. The formation of resistors of a wide range of resistance values without resort to figuration is thus possible. The arrangement of the film in a grid configuration may, of course, be resorted to where higher resistances are desired.

The co-deposited cobalt and chromium metal films of this invention also exhibit excellent stability of resistance over long periods of time both at room temperature and at operating temperatures well above room temperature. Excellent stability is also exhibited over a wide range of operating voltages. To enhance such stability, heat treatment after deposition may be availed of. The films also produce resistors which contribute negligible electrical noise even in the highest resistance values. The hardness and durability of the film is such that it will withstand considerable mechanical abrasion by all but the very hard materials. This latter property is of importance where it is not feasible to encase the film. For example, films thin enough to permit light transmission may be provided to permit electrical heating of a transparent element for fog and frost dispelling purposes.

For obtaining a high degree of stability over an extended life the selection of the material for the base **13** should be such as not to detract from the several advantages of the cobalt-chromium co-deposited film. If the material selected has appreciable conductive properties at elevated temperatures, or has a coefficient of expansion differing materially from that of the film the beneficial properties of the resistance film may be adversely masked. A satisfactory base material, with a low ionic conductivity, is a sodium and potassium content lead glass known as lead alkali silicate electrical glass. Other preferable glasses, as deduced from tests, are non-alkali barium, aluminum, boro-silicate glass; alumino-silicate glass; borosilicate electrical glass; and lead alkali silicate high lead content glass.

Films of excellent properties, both from the standpoint of continuity and mechanical excellence and from the standpoint of electrical properties, are obtainable through a range of proportions for the cobalt and chromium. For attaining a temperature coefficient of resistance within the vicinity of, or less than, plus or minus 50 parts per million per degree centigrade the proportion of chromium may vary from approximately 80 percent to 40 percent by weight with the balance being substantially cobalt. Such low temperature coefficients of resistance are held through a substantial range of film thickness, which makes possible the provision of a wide range of resistance values, for any given resistance grid configuration, through variation of film thickness. For purposes of controlled production in which the temperature coefficient of resistance is to be confined within narrow limits it is preferable that the amount of chromium be within 60 percent to 70 percent by weight, and substantially the entire balance be cobalt. This preference has been substantiated by extensive test runs. In one group of 120 depositions, made from metallic masses of between 60 percent to 70 percent chromium, greater than 95 percent of the depositions had a temperature coefficient of less than 40 parts per million per degree centigrade, and there were substantial numbers of both positive and negative coefficients. As the chromium content is increased beyond this rang the coefficients become markedly negative and increase in value. A decrease in chromium from the range causes a shift to the positive and likewise an increase in value.

For precision resistors film thickness should be sufficient to overcome surface conditions that render resistance values unpredictable, if they are permitted to be dominant. Oxidation at the surface, for example, and electron flow at the boundary may interfere with controlled production, if films are extremely thin. The exact nature of thin metallic films, as herein described, is not fully known, and the phenomena giving rise to the low temperature coefficient of resistance, for the co-deposited cobalt-chromium films of this invention, is likewise not certain. Some similarities in the characteristics of cobalt and chromium are of apparent aid to the manufacture of the co-deposited films of this invention. As a melt the vaporization temperatures of the metals are not widely divergent, and the rates of vaporization are sufficiently alike that excessive fractionation does not occur.

While avoidance of extraneous material in the deposited film is desirable, it is an advantage of this invention that substantial quantities of impurities may be present without materially impairing the properties of the film. For example, up to five percent of the metallic impurities aluminum, beryllium, iron, manganese, molybdenum, silicon, tantalum and titanium have been present in the melt without increasing the temperature coefficient of resistance to more than plus or minus 100 parts per million per degree centigrade over an ordinary range of operating temperature. Such limits for a temperature coefficient are low and well within the requirements for most precision applications. Substances such as carbon, tungsten and others, present in trace tmounts, are equally harmless. Impurities up to the concentrations indicated may be tolerated, and where it is herein stated that substantially the entire balance of the composition consists of cobalt, such statement is intended to mean that said balance may be cobalt and impurities in amounts not exceeding values that mask the advantages of the invention. It is a further discovery that nickel may be introduced in substantial amounts in place of an entire balance of cobalt. Where the chromium is at least 40 percent of the composition, the nickel content may run as high as 50 percent of that which is otherwise a balance of cobalt. The introduction of nickel in such amount does not materially increase the temperature coefficient of resistance over limits applicable for precision resistor application.

I claim:

1. An electrical resistance device comprising a non-conductive solid base having a film supporting surface and an electrically resistive adherent metallic film upon said surface consisting of a mixture that is substantially, entirely of the metals cobalt and chromium in proportions of 40 to 80 percent by weight of chromium and substantially the entire balance cobalt.

2. An electrical resistance device in accordance with claim 1 in which said base is a glass substance.

3. An electrical resistance device in accordance with claim 1 in which said base is a glass selected from the group of lead alkali silicate electrical glass; nonalkali barium, aluminum, boro-silicate glass; aluminosilicate glass; borosilicate electrical glass; and lead alkali silicate high lead content glass.

4. An electrical resistance device comprising a non-conductive solid base having a film supporting surface and an electrically resistive metallic film adhering to said surface consisting substantially, entirely of the metals cobalt and chromium in proportions of 40 to 80 percent by weight of chromium and substantially the entire balance cobalt co-deposited from mixed vapors of the said metals by simultaneous condensation thereof on the supporting surface.

5. An electrical resistance device in accordance with claim 4, wherein the non-conductive solid base is a glass substance.

6. An electrical resistance device comprising a non-conductive base and an electrically conductive thin metallic film deposited upon said base comprised of co-deposited chromium and cobalt with the amount of chromium being 60 to 70 percent by weight and substantially the entire balance being cobalt.

7. An electrical resistance device comprising a non-conductive base and an electrically conductive thin metallic film deposited upon said base comprised of a mixture of chromium, cobalt and nickel of which 40 to 80 percent by weight is chromium substantially the entire balance is cobalt and nickel with the nickel being no greater than 50 percent of the balance.

8. An electrical resistance device comprising a non-conductive base and an electrically conductive metallic film deposited upon said base, which film is deposited upon said base by heating a mixture of from 40 to 80 percent by weight of chromium with substantially the entire balance being cobalt to temperatures that vaporize the metallic mixture, and exposing the base to metallic vapors emitted from the mixture.

9. The method of forming an electrical resistance film which consists in heating a mixture of from 40 to 80 percent by weight of metallic chromium and the balance substantially, entirely metallic cobalt in a vessel in an evacuated enclosure wherein the pressure is less than 1×10^{-4} mm. of mercury, to a temperature sufficient to melt and vaporize said metals simultaneously at similar rates of vaporization, while exposing a cooler non-conductive body within said receiver to the vaporizing mass, at a distance not exceeding approximately the mean free paths of the vaporized metals at the pressure prevailing.

10. The method of forming an electrical resistance film in accordance with claim 9, wherein the metal mixture subjected to heating contains approximately 60 to 70 percent by weight of chromium and substantially the entire balance cobalt.

11. The method of forming an electrical resistance film in accordance with claim 9, wherein the deposit receiving surface of the non-conductive body bears a removable figurate mask and the method includes the step of removing said mask to provide a figurate resistance film.

12. An electrical resistance device comprising a non-conductive base selected from the group of lead alkali silicate electrical glass; non-alkali barium, aluminum, boro-silicate glass; aluminosilicate glass; borosilicate electrical glass; and lead alkali silicate high lead content glass; an electrically resistive metallic film upon said base consisting of a mixture that is substantially entirely of the metals cobalt and chromium with the chromium being within 40 to 80 percent by weight of the mixture; and lead wires attached to opposite ends of the film.

References Cited in the file of this patent

UNITED STATES PATENTS

2,586,752	Weber et al.	Feb. 19, 1952
2,798,140	Kohring	July 2, 1957
2,803,729	Kohring	Aug. 20, 1957
2,809,139	Bloom et al.	Oct. 8, 1957