July 11, 1939. J. L. THOMAS 2,165,316

ELECTRICAL RESISTANCE ELEMENT, ALLOY, AND PRODUCTION THEREOF

Filed June 25, 1937

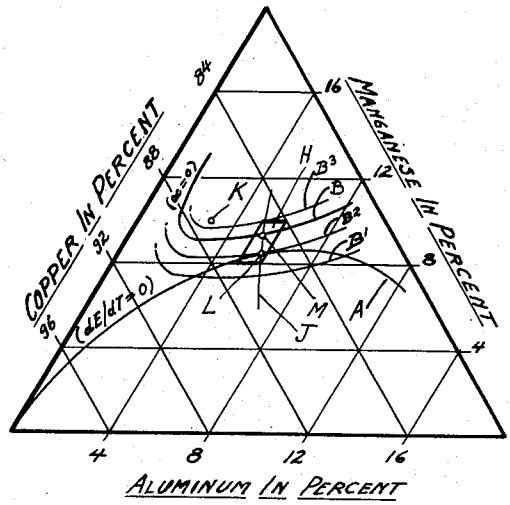


Fig. 1.

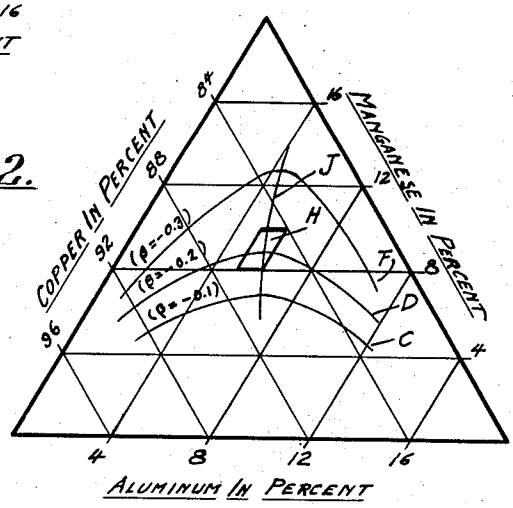
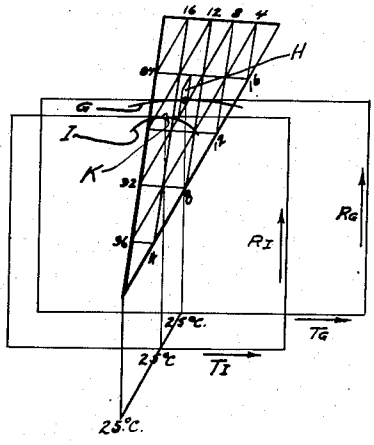


Fig. 2.

Fig. 3.



JAMES L. THOMAS,

INVENTOR

BY J. Motherhead

ATTORNEY

Patented July 11, 1939

2,165,316

UNITED STATES PATENT OFFICE

2,165,316

ELECTRICAL RESISTANCE ELEMENT, ALLOY, AND PRODUCTION THEREOF

James L. Thomas, Garrett Park, Md., assignor to the Government of the United States of America, represented by the Secretary of Commerce

Application June 25, 1937, Serial No. 150,334

12 Claims. (Cl. 201—76)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

The invention herein described may be manufactured and used by or for the Government of the United States for governmental purposes, without the payment to me of any royalty thereon.

This invention relates to electrical resistance elements and alloys and the production thereof, and aims generally to provide improved elements and alloys of this character, together with an improved method of producing the same.

Generally in electrical measuring apparatus and electrical resistance standards, coils of wire are utilized and difficulty has always been encountered in obtaining a wire whose electrical resistance remains stable or substantially constant. It is known that the resistance of coils of wire changes with age and also with ordinary changes in room temperature. The change which takes place with age may be due to chemical action of the air upon the surface of the wire, or to changes in the crystal arrangement therein.

Further, besides stability, resistance alloys should have low temperature coefficients of resistance and low thermoelectric powers against copper at ordinary room temperatures in order that they may be readily measured to a high precision.

In addition, such elements should have tolerance as large as possible for changes from the standard temperature at which they are intended to be used.

To the best of my knowledge, no alloy has heretofore been developed which possesses these qualities to the desired degree. While special alloys have been developed for which the changes in resistance with temperature and time are comparatively small, these alloys do not sufficiently attain other desirable properties. "Manganin", an alloy of copper, manganese, and nickel, is the resistance alloy now most generally used, but this alloy does not possess the desired qualities to a sufficiently high degree.

In accordance with the present invention an alloy element may be obtained having not only adequate stability of characteristics, but also exceedingly constant characteristics of temperature coefficient of resistance and thermoelectric power against copper, and a minimum change of resistance with variation from the standard temperature at which the element is intended to be used, represented hereinafter by the usual figure 25° C.

In addition, this invention provides a method and alloy in which the proportions of constituents are so related to their properties that the constituents requiring closest percentage control are those most easily controlled.

In developing this invention, experiments were conducted with alloys of copper, manganese, and aluminum, with and without the addition of small percentages of iron, for the purpose of obtaining an alloy resistance element of not only great stability but also having both a substantially zero thermoelectric power against copper, and a substantially zero temperature coefficient of resistance at standard temperature, as 25° C.

Specifically, the research and tests included a number of different alloys composed of copper with the addition of approximately from 4 to 15 percent of manganese by weight, together with from 0 to 10 percent of aluminum by weight, and from 0 to 0.5 percent of iron by weight. As the results of the research, it was discovered that the most desirable alloy comprises approximately 85 percent of copper, 9.5 percent of manganese, 5.3 percent of aluminum, and 0.2 percent of iron, all percentages by weight. Moreover, the discoveries in this research show that all copper-manganese-aluminum alloys containing by weight from 8 to 10 percent of manganese, together with over 5, and not more than about 6, percent of aluminum and 0 to 0.5 percent of iron, possess the desired electrical qualities to a higher degree than has heretofore been obtained.

The first difficulty encountered in the experiments was to find a method by which the ingredients could be properly alloyed. The best method, it was discovered, is to melt the copper in graphite crucibles under a heavy coating of cryolite, the coating of cryolite being for the purpose of excluding air and thus preventing oxidation of the alloys, and to dissolve any aluminum oxide which might be present in the aluminum subsequently added. Preferably after the copper has melted, the manganese is added and then the aluminum and iron. After being well stirred by means of a graphite rod, the alloys are preferably heated to about 1100° C. and poured into graphite molds, the graphite crucibles and molds being preferred because graphite absorbs oxygen and will assist in the prevention of oxidation. While other methods of preparation would serve the purpose, such as alloying in a vacuum or in an atmosphere of dry hydrogen, the method just described is preferred because of its simplicity and the good results obtained by it in practice. The use of a vacuum or dry hydrogen atmosphere requires a complicated and expensive apparatus and does not render any better, if as good, results.

After being molded, the ingots may be hot-forged into the form of rods 5 or 6 mm. square. They are then preferably cold rolled and swaged to a diameter of 2 mm., after which they may be annealed as by being heated to a red-heat in air or in a vacuum, and subsequently swaged and drawn down to the desired size through appropriate dies, such as sapphire or steel dies.

After the wire has been formed into a coil it is put through a baking process which has the effect of ageing it artificially—that is to say, after the coils are baked from 1 to 5 days in air at 100 to 300° C., their change in resistance, with time, is much slower than for the unbaked coils. This baking has another effect besides that of artificially ageing the resistance of the coils. When the coils are baked at a temperature of 100 to 300° C., the temperature coefficients of resistance are increased. The amount of this increase in the temperature coefficients was found to depend upon both the baking temperature and upon the length of time the coils were baked. By properly choosing the temperature and length of time of baking, it is possible to adjust the temperature coefficient to zero for coils having a negative temperature coefficient before baking. For example, an unbaked coil of the alloy containing, by weight, copper 85%, manganese 9.5%, aluminum 5.5%, and iron 0%, had a negative temperature coefficient of about 40 parts per million per degree centigrade at 25° C. After being baked at 140° C. for one day, the temperature coefficient was approximately zero at 25° C. The following table is illustrative of the temperature-resistance changes of a 100-ohm coil of the composition and after the baking just described:

Temperature, ° C.	Resistance
20	99.9996
22.5	99.9999
25	100.0000
27.5	99.9998
30	99.9994

For the best quality of manganin the changes in resistance with temperature are approximately twice as large as those shown above for this embodiment of the new alloy.

Besides serving to bring the temperature coefficient of resistance of this alloyed element to zero, the baking is an essential step in its artificial ageing, and has the advantage of doing away with, or at least substantially reducing, the ageing that would ordinarily take place as the element ages with time. The stability of these elements after ageing is as great, if not greater, than for similar manganin elements.

Besides being as stable in resistance as manganin and having a smaller change in resistance with temperature at laboratory temperatures, the new alloys are far superior to manganin in that they have much smaller thermoelectric powers against copper than does manganin. Without the addition of iron, these copper alloys containing from 8 to 10 percent of manganese and between 5 and 6 percent of aluminum, both by weight, all have thermoelectric powers against copper which are only about one-tenth as large as for manganin against copper. By adding the proper percentage of iron, not exceeding 0.5 percent, the thermoelectric powers of these alloys against copper may be made to be zero at any chosen room temperature. This is a great advantage over manganin or any other alloy now known, as it facilitates precise measurements of the resistance elements. Moreover, resistance measuring apparatus containing elements of these new alloys may be used to a higher precision, as the stray thermoelectromotive forces in them will be substantially zero. These and other advantages residing in the range of alloys of my discovery will be more apparent by considering the diagrammatic figures of the accompanying drawing, in which:

Fig. 1 is a three phase diagram showing the preferred range of copper-manganese-aluminum alloy dealt with in this invention, together with curves of zero thermoelectric power against copper, zero temperature coefficients of resistance, and optimum tolerance for departure from standard temperature.

Fig. 2 is a three phase diagram showing the rate of change in such alloys of the temperature coefficient of resistance on departure from the standard temperature at which the element is intended to be used, showing derivation of the curve of optimum tolerance for departure from standard temperatures, and

Fig. 3 is an exaggerated phantom perspective presentation of the diagram of Fig. 1 showing normal to its plane, the relatively great tolerance of alloys of the preferred range as compared with alloys removed therefrom.

Referring to the drawing indicative of the results of the research in the ranges of alloys described above, curve A (Fig. 1) indicates the copper-manganese-aluminum compositions of elements prepared as above for which thermoelectric power against copper (dE/dT) is zero for a temperature of 100° C. at the hot junction and 0° C. at the cold junction, and thus zero at room temperature, say 25° C., the elements falling below and above curve A having negative and positive coefficients, respectively.

Again referring to Fig. 1, curve B indicates the compositions for which, after preparation and artificial ageing as herein set forth, the temperature coefficient of resistance (α); that is, the slope of the resistance-temperature curve, is zero at 25° C., such coefficients being positive for compositions outside and negative for those inside the curve B.

In Fig. 2, the curves C, D and F indicate the contours for compositions of elements prepared as above and artificially aged as herein described, which have, respectively decreasing tolerances for departure from the temperature at which the elements are intended to be used. Thus these contours show decreasing rates of change (β) indicated in parts per million per ° C. per ° C. for temperatures at or near 25° C., of the temperature coefficient of resistance on departure upwardly or downwardly from 25° C.

In Fig. 1, any alloy lying on curve A has a thermoelectric power against copper of zero; and any alloy lying on curve B, after artificial ageing as set forth, has a temperature coefficient of resistance (alpha) of zero. Curves B^1, B^2, B^3, show, respectively, what alloys will have alpha=0 for different degrees of heat treatment. The curves C, D and F on Fig. 2, represent the constancy of the temperature coefficients of the alloys lying thereon, as explained above, interpolation applying between these lines.

Figs. 1 and 2 are drawn in the plane T=25° C.; and to represent the changes corresponding to curves C, D, and F, on departure from 25° C., a third dimension, at right angles to the planes of Figs. 1 and 2 is necessary.

Accordingly in Fig. 3, the diagram of Figs. 1 and 2 is viewed in perspective with the curves of

resistance change on departure from 25° C. shown normal to the plane of the 3-phase diagram. The transparent planes T_I—R_I and T_G—R_G are the planes in which the curves I and G lie, and T and R in each case are the temperature vs. resistance ordinates and abscissas of curves I and G, respectively.

The curves A and B of Fig. 1 are not reproduced on Fig. 3, it being deemed preferable for clarity to merely indicate the area H of Fig. 1 thereon. The curve G (Fig. 3) represents the desirable flattened curve of decrease in absolute resistance from the peak resistance at 25° C., of an element within the preferred range H in close proximity to curve D (Fig. 2). The curve I (Fig. 3) represents the less desirable sharper and greater curve of decrease in absolute resistance from a peak resistance at 25° of an element outside the preferred range, and thus removed toward the curve F in Fig. 2.

In accordance with these diagrams illustrative of my discoveries, it will be perceived that the curves A and B approach one another most closely between the 4% aluminum and 7% aluminum lines. It will also be perceived that the curves in one region near the center of these limits nearly parallel one another and most nearly parallel the aluminum axis.

Further referring to Figs. 1 and 2 there is shown thereon by line J the locus of peaks of the curves C, D and F. This locus J coincides with the highest incidence on the diagram of zones of best tolerance, for departures from the standard temperature of use, 25° C. From the diagram it is seen that this locus J for the alloys here concerned traverses the range of compositions at which the curves A and B (Fig. 1) most closely approach one another; this traverse occurring about on the line aluminum 6-manganese 8 to aluminum 5.2-manganese 10%.

In connection with these factors, this invention contemplates that as aluminum is the most easily oxidized metal of the three primary constituents of my alloy, it will effect reduction of any oxides of manganese or copper developed during the process of preparing the elements of my invention. Referring to Fig. 1 it will be seen that at the portion of the zone of closest relative approach of the curves A and B lying between aluminum 5% and aluminum 6% the slope of the curves with reference to the aluminum axis is small so that variations in proportions of this element in the alloy will, within this range, not produce appreciable change in the characteristics of the alloy. This range, then, is a particularly advantageous one inasmuch as the aluminum content is the one constituent difficult to control exactly because of losses due to oxidation.

In view of this last mentioned factor and the position of the curve J discovered as indicated in Figs. 1 and 2, in accordance with this invention, the range of copper-manganese-aluminum alloy base within which the best alloys are attained is limited to an area in close proximity to the point of juxtaposition of the curves A (Fig. 1) and J (Figs. 1 and 2).

To better illustrate this, consider an alloy base K (Fig. 1) rather widely removed from the contemplated range and lying in the neighborhood, say, of 87% copper, 10% manganese and 3% aluminum. In this case, firstly, as the slope of the curve A is much steeper at the point where it crosses the 3% aluminum line than it is within the range H, the effect of variations of aluminum content on the characteristics of the alloy would be much more marked. Thus, much more accurate determination of the amount of excess aluminum to be added during melting to compensate for loss of aluminum by oxidation would be required than in the range of my discovery. Secondly, if such base K were used, it would lie so far to the left of the curve J (Fig. 2) that it would lie closely adjacent to the curve F (Fig. 2) rather than the curve D thereon. Accordingly, the curve of tolerance for temperature variation from standard (curve I with abscissas T_I and ordinates R_I Fig. 3), for the composition K would be more sharply peaked, and the tolerance be much poorer, than that indicated by the curve G with abscissas T_G and ordinates R_G (Fig. 3) for the range particularly characterizing my invention.

As above mentioned, the heat treatment of alloys in accordance with this invention effects artificial ageing, increases the temperature coefficients of resistance, and produces a decrease in absolute resistance.

The curve B (Fig. 1) is that for resistance elements baked for eighteen hours at 140° C., and having zero coefficient. As the baking has the effect of raising temperature coefficient of resistance, it thus has the effect of shrinking the curve B (Fig. 1) as indicated by curves B^1, B^2, B, B^3 representing, respectively, positions of $\alpha=0$ after increasing amounts of heat treatment.

From this factor it will be seen the heat treatment may, if desired, be made just sufficient to bring curve B into position B^2 in virtual tangency with curve A, which point of virtual tangency occurs in close proximity to the intersection of curves A and J. By this means an alloy element containing only copper, manganese and aluminum may be obtained having no appreciable thermoelectric power against copper and no appreciable temperature coefficient of resistance at 25° C. Under such conditions it is apparent that the most preferred embodiment containing only copper, manganese and aluminum also lies near the center of the range H of my discovery. Thus this most preferred embodiment, indicated by L (Fig. 1) comprises copper, 85.8%, manganese 8.5%, and aluminum 5.7%.

Another factor of my discovery mentioned above is that the addition of small amounts of iron will decrease the thermoelectric power against copper and increase the resistivity of the alloy with little effect on the temperature coefficient of resistance. Referring to Fig. 1, the effect of decreasing the thermoelectric power against copper by adding iron in amounts not more than one-half of 1 per cent, is to elevate the curve A slightly; that is, to reduce to zero what was theretofore a positive value of electromotive force against copper, without making any appreciable change in the curve B.

Thus if it is desired to obtain great stability by extended heat treatment, which would raise the temperature coefficient of resistance (having the effect of shrinking upwardly the curve B, Fig. 1) to a point as M (Fig. 1) at which the alloy having such zero coefficient of resistance would have a slightly positive thermoelectric power against copper, instead of the more desirable zero value, the alloy may be conditioned to have such virtually zero thermoelectric power against copper by the addition of a small amount of iron sufficient to effect a reduction to virtual zero of the thermoelectric power against copper after the heat treatment for ageing or stabilizing.

To summarize, my discovery shows that two

factors are available which may be balanced against one another.

Thus, if extensive heat treatment for maximum stability against ageing is not required, by applying my discoveries a copper-manganese-aluminum alloy containing virtually no iron may be made suitable; this being attained by proportioning the alloy in the range H in close proximity to the lines A and J (Fig. 1) and heat treating it only sufficiently to place the curve $\alpha=0$ at about the position B^2. The most preferred exemplification of this part of my invention is shown at L (Fig. 1) and comprises manganese 8.5%, aluminum 5.7% and copper 85.8%, moderately heat treated to bring its temperature coefficient of resistance to zero.

Again, where greater stability is required and a small positive thermoelectric power against copper is permissible, a similar copper-manganese-aluminum alloy with virtually no iron may be made suitable by my discoveries; this being attained by proportioning the alloy in the range H in close proximity to the lines B and J (Fig. 1) and heat treating it to an extended degree sufficient to place the curve $\alpha=0$ at about the position B. The most preferred exemplification of this part of my invention is shown at M (Fig. 1) and comprises manganese 9.5%, aluminum 5.5% and copper 85%, strongly heat treated to bring its temperature coefficient of resistance to zero.

Finally, if virtually zero electromotive force against copper is needed in a very stable alloy, then in accordance with my discoveries the alloy may have proportions of copper, manganese and aluminum similar to that shown at M (Fig. 1), which will reach zero temperature coefficient of resistance after extended heat treatment or ageing, and may contain such slight percentage of added iron as to in effect raise the curve A into virtual tangency with the curve B (Fig. 1) to obtain to the fullest all three desirable characteristics, stability, virtually zero temperature coefficient of resistance at standard temperature 25° C., and virtually zero thermoelectric power against copper. A preferred composition for such alloy may comprise manganese 9.5%, aluminum 5.3%, iron 0.2% and copper 85%, but slight variation of the percentages within range H and particularly variation of the iron in the range of less than one-half of 1 per cent, with or without similar variation in the non-critical aluminum content may be made while still obtaining the advantages of the invention.

From the foregoing it will be apparent that my invention is not limited to the particular embodiments set forth to illustrate the same.

I claim as my invention:

1. An electrical resistance element composed of a heat treated copper-manganese-aluminum alloy containing iron and comprising manganese 9.5%, aluminum 5.3%, and iron 0.2%, the remainder being virtually all copper; said element having substantially zero thermoelectric power against copper, great stability against change of resistance with ageing, and substantially zero temperature coefficient of resistance at about 25° C.

2. A copper-manganese-aluminum alloy containing iron and comprising manganese 9.5%, aluminum 5.3% and iron 0.2%, the remainder being virtually all copper, said alloy having substantially zero thermoelectric power against copper, and said alloy adapted to attain substantially zero temperature coefficient of resistance at about 25° C. after such extended heat treatment as will produce great stability against change of resistance with ageing.

3. An electrical resistance element composed of a heat treated copper-manganese-aluminum alloy comprising manganese 8.5% and aluminum 5.7%, the remainder being substantially all copper; said element having substantially zero thermoelectric power against copper, substantial stability against change of resistance with ageing, and substantially zero temperature coefficient of resistance at about 25° C.

4. A copper-manganese-aluminum alloy comprising manganese 8.5% and aluminum 5.7%, the remainder being substantially all copper; said alloy having substantially zero thermoelectric power against copper, and said alloy adapted to attain substantially zero temperature coefficient of resistance at about 25° C. after such heat treatment as will produce substantial stability against change of resistance with ageing.

5. An electrical resistance element composed of a heat treated copper-manganese-aluminum alloy comprising manganese 8 to 10 per cent, and aluminum 5.1 to 6.0 per cent, the remainder being substantially all copper; said element having substantially zero thermoelectric power against copper, stability against change of resistance with ageing, and substantially zero temperature coefficient of resistance at about 25° C.

6. An element according to claim 5, containing iron in an amount not exceeding 0.5%.

7. A copper-manganese-aluminum alloy comprising manganese 8 to 10 per cent and aluminum 5.1 to 6 per cent, the remainder being substantially all copper, said alloy having substantially zero thermoelectric power against copper, and said alloy adapted to attain substantially zero temperature coefficient of resistance at about 25° C. after such heat treatment as will produce stability against change of resistance with ageing.

8. An alloy according to claim 7, containing iron in an amount not exceeding 0.5%.

9. The method of making an electrical resistance element which comprises alloying copper with 8 to 10 per cent of manganese, and an amount of aluminum within the range 5 to 6% and preferably near the middle thereof, the copper constituting substantially all the balance of 100%, whereby there is obtained an alloy which will have a thermoelectric power against copper of substantially zero, a minimum rate of change of temperature coefficient of resistance on departure up or down from 25° C., and a zero temperature coefficient of resistance after such extended baking as will impart to the element stability against change of resistance with ageing, and in which extreme control of aluminum content is not essential beyond keeping it within the aforesaid range; forming the alloy into a resistance element, and baking the element for such extended period, ranging from a number of hours to several days, as to impart stability to it and at the same time adjust its temperature coefficient of resistance to substantially zero.

10. A method according to claim 9, further including the step of incorporating in the alloy iron in an amount not exceeding 0.5%.

11. The method of making an electrical resistance element which comprises alloying copper with an amount of aluminum within the range of 5 to 6 per cent and preferably near the middle thereof, and with an amount of manganese within the range 8 to 10 per cent and preferably near

the upper limit thereof; to enable the element to attain a temperature coefficient of resistance of substantially zero only after such extended baking as will produce substantial stability against change of resistance with ageing, and preferably only after such extended baking as will produce great stability thereagainst; forming the alloy into a resistance element, and baking the element for an extended period until its temperature coefficient of resistance becomes zero.

12. A method according to claim 11, further comprising the step of incorporating in the alloy iron in an amount not exceeding 0.5% to lower the thermoelectric power of the element against copper to substantially zero for the percentage of manganese included.

JAMES L. THOMAS.