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ELECTRICAL-RESISTANCE ALLOYS OF COPPER, MANGANESE, AND ALUMINUM

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ABSTRACT

An investigation has been made of the electrical properties of alloys containing from 4 to 15 percent of manganese and from 0 to 10 percent of aluminum, the remainder being copper. An alloy containing 85 percent of copper, 9.5 percent of manganese, and 5.5 percent of aluminum has properties very similar to those of manganin. Its thermoelectric power against copper is much smaller than that of manganin and this thermoelectric power may be brought to zero by the addition of a very small amount of iron. Resistance coils constructed from these alloys, with or without added iron, have been very stable in resistance. By properly baking, their temperature coefficients of resistance at 25° C may be made as nearly zero as is desired, and this coefficient changes less with temperature than does that of manganin.

CONTENTS

I. INTRODUCTION

The electrical properties of an alloy of copper, manganese, and aluminum have been under observation at the National Bureau of Standards since about 1910. At that time William B. Driver gave to this Bureau some samples of such an alloy, which he had developed as an electrical-resistance material. This material, which is of the type later called Therlo, had almost the same electrical properties as manganin, with the exception of its smaller thermoelectric power against copper. Chemical analyses of two samples of this alloy gave the following results: *sheet material*—copper, 84.35 percent; manganese 11.48 percent; aluminum, 4.2 percent; iron and nickel, traces; *wire*—copper, 84.05 percent; manganese, 11.54 percent; aluminum, 4.2 percent; and nickel, 0.12 percent.

Of the resistance standards constructed of these materials, two 10-ohm standards and a 0.01-ohm standard were kept under observation by Dr. Frank Wenner of this Bureau and in regular use for more than 20 years. During that time the two 10-ohm standards increased in resistance, respectively, by 100 and 30 parts in a million, while the 0.01-ohm standard increased by 220 parts in a million. Judging by the appearance of the sheet material, Dr. Wenner concluded that the original ingot was probably not free from blow holes, and that an appreciable amount of the aluminum had been oxidized and therefore was not in solution. However, on the basis of the results obtained with these samples, he advocated a thorough investigation of copper-manganese-aluminum alloys in the hope of developing a more suitable material for use in the construction of resistance standards and coils than any of the materials then available.

With the expectation that modern methods of producing alloys containing aluminum would yield better results, experiments were begun recently upon the production of alloys of copper, manganese, and aluminum. After a considerable amount of experimentation a technique for the production of satisfactory alloys of this type was developed; and alloys containing from 0 to 10 percent of aluminum and from 4 to 15 percent of manganese, the remainder being copper, have been investigated. For use in the construction of coils for electrical-resistance standards and measuring apparatus, the best composition was found to be approximately 85 percent of copper, 9.5 percent of manganese, and 5.5 percent of aluminum. This alloy has nearly the same resistivity as manganin, its temperature coefficient of resistance at 25° C can be brought to zero by a suitable heat treatment, and the change of the temperature coefficient with temperature is about half that of manganin. Its thermoelectric power against copper at 25° C is only about 10 percent of that of manganin, and this thermoelectric power may be further reduced by the addition of a very small percentage of iron without materially affecting the other properties of the alloy. The stability of the electrical resistance of these alloys, with or without added iron, is apparently as good as that of manganin.

II. PREPARATION OF ALLOYS

The copper and aluminum used in preparing these alloys were of high quality, the total impurities not exceeding 0.03 percent in either material. Unfortunately, the manganese available was not of a comparable purity. It was Standard Sample 67 of this Bureau, containing 97.25 percent of manganese, by analysis. The principal impurities were iron, 1.5 percent; silicon, 0.4 percent; and phosphorus, 0.2 percent. In weighing out the ingredients for these alloys, no allowance was made for the impurities. Hence, in what follows, unless otherwise stated, the percentage of any ingredient includes that of its impurities.

The alloys were prepared in Acheson graphite crucibles which were heated by means of an induction furnace. The copper was first melted in the crucibles under a heavy coating of cryolite (Na_3AlF_6 or $3NaF \cdot AlF_3$), a flux in which aluminum oxide is soluble. The manganese, in granular form, was then added, and finally the aluminum. The addition of the aluminum resulted in a considerable rise in temperature, so the induction furnace was then cut off and the charges were thoroughly stirred with graphite rods, and poured into graphite molds.

To obtain some idea of the losses during the melting and working into wire, a chemical analysis of one sample was made. The alloy selected for this analysis had been worked into wire 0.53 mm in diameter, and the composition, as calculated from the chemical analyses of the ingredients, was: copper, 84.92 percent; manganese, 9.24 percent; aluminum, 5.50 percent; iron, 0.22 percent; and impurities, 0.12 percent. The chemical analysis of the finished wire showed: copper, 85.2 percent; manganese, 9.2 percent; aluminum, 5.2 percent; iron, 0.20 percent; remainder, 0.2 percent. The difference between the chemical analysis and the calculated composition could be almost entirely explained by the assumption of a loss in aluminum amounting to 0.3 percent of the weight of the alloy. Such a loss of aluminum is entirely possible, as aluminum would probably reduce any oxide present as well as remove any oxygen dissolved in the molten alloy.

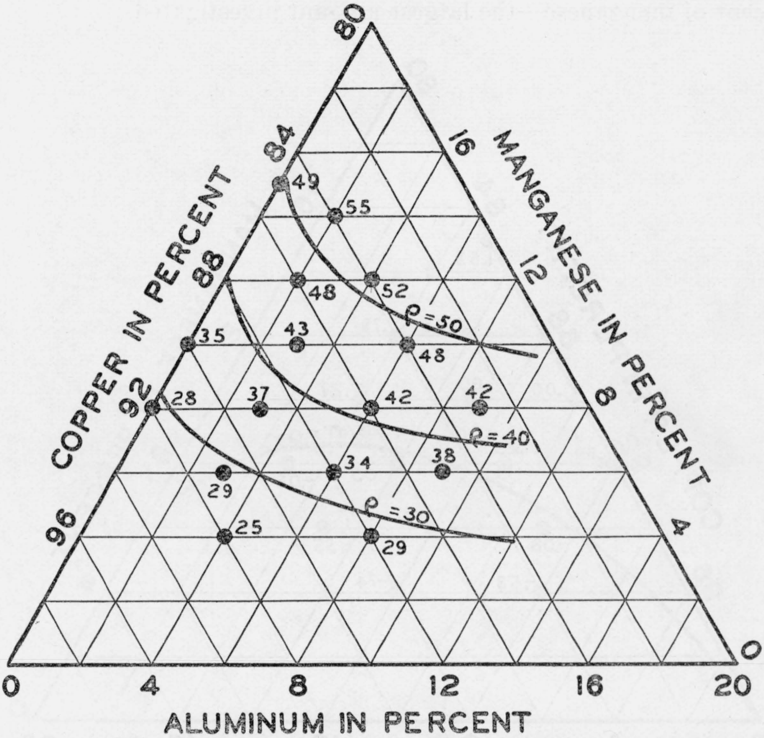

FIGURE 1.—*Resistivities of copper-manganese-aluminum alloys.*

The resistivities are for hard-drawn wires at 25° C and are expressed in microhm-centimeters. The compositions shown were calculated from the weights of the impure ingredients.

The ingots were heated in air and hot-forged into the form of rods 5 or 6 mm square. They were then cold-rolled and swaged into wire about 1 mm in diameter, after which they were drawn through steel dies to a diameter of about 0.5 mm. The material was annealed several times during the rolling and swaging, but the wire was not annealed during the drawing. In annealing, the material was heated only to a dull red, as higher temperatures would sometimes produce a hardening. The wire was not pickled to remove the oxide from the surface, but at the beginning of the drawing its surface was carefully cleaned with sandpaper.

The difficulty of working the alloys into wire was found to increase with the percentage of aluminum. No alloy containing more than 9 percent of aluminum was worked into wire, although an ingot containing 10 percent of aluminum and 10 percent of manganese was worked down sufficiently to get an estimate of its resistivity. No difficulty was encountered in handling ingots containing up to 15 percent of manganese—the largest amount investigated.

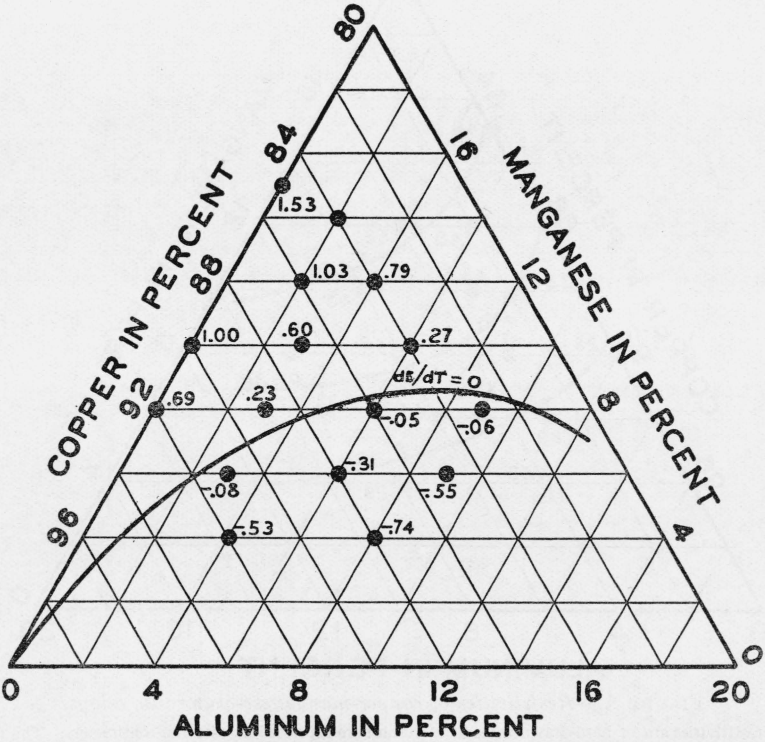

FIGURE 2.—*Thermoelectric power against copper of hard-drawn wire of copper-manganese-aluminum alloys.*

Average thermoelectric powers from 0 to 100° C, in microvolts per degree C.

III. ELECTRICAL PROPERTIES

1. RESISTIVITY

After the alloys had been worked into wire about 1 mm in diameter, their resistivities were measured. These were determined for the cold-worked wire, and the results are shown in figure 1. In this figure the resistivities in microhm-centimeters are marked at the points that represent the compositions on the three-phase diagram. Contour lines have been drawn connecting compositions having the same resistivities. These resistivities apply only to the cold-worked wire, as there was a considerable change when the wires were annealed, amounting in some cases to over 10 percent.

2. THERMOELECTRIC POWER

To measure their thermoelectric powers against copper, pieces of the wire were soldered to copper wires. One junction was kept at the temperature of ice and the other at steam, and the emf were measured with a low-resistance Diesselhorst potentiometer. For most of the alloys only this one temperature interval was used, so the values obtained were averages between 0 and 100° C. These thermoelectric powers, in microvolts per degree centigrade, are marked on figure 2 at points corresponding to the compositions. The curve shown in that figure is the contour line connecting compositions for which the average thermoelectric power against copper is zero. The data given are for the hard-drawn wire. For a few alloys, the temperature-emf curve was investigated in detail in the interval 0 to 100° C. The results are discussed in section V.

3. TEMPERATURE COEFFICIENTS OF RESISTANCE

For these copper-manganese-aluminum alloys the relation between resistance and temperature in the interval 20 to 30° C was found to be represented with sufficient accuracy by the equation:

$$R_t = R_{25}[1 + \alpha(t-25) + \beta(t-25)^2].$$

Here, R_t is the resistance at t° C and R_{25} is the resistance at 25° C. The constants α and β depend upon the composition and upon the mechanical and thermal history of the wires.

To measure their temperature coefficients of resistance, samples of the alloys were worked into wire 1 mm in diameter, annealed, and then hard-drawn to diameters that ranged from 0.43 to 0.55 mm. A coil of each was wound on a silk-insulated brass spool, the turns were

TABLE 1.—*Resistance coefficients*

Alloy	Mn	Al	Diameter of wire	Baking temperature	Baking time	$\alpha \cdot 10^6$	$\beta \cdot 10^6$
	%	%	mm	°C	hr		
A	4	4	0.43	140	18	124	0.00
B	4	8	.46	140	18	151	.00
C	6	3	.43	140	18	52	−.14
D	6	6	.43	140	18	57	−.08
E	6	9	.56	140	18	76	−.08
F	8	0	.48	140	18	45	−.46
G	8	3	.43	140	18	12	−.24
H	8	6	.46	140	18	6	−.14
J	8	9	.53	140	18	55	−.28
K	10	0	.51	140	18	20	−.58
L	10	3	.46	140	12	−13	−.22
M	10	6	.56	140	18	−15	−.22
P	11	0	.56	140	48	22	−.54
Q	12	2	.48	140	18	−21	−.42
R	12	4	.48	140	18	−33	−.26
S	12	6	.56	140	18	−24	−.30
T	14	2	.48	140	18	−24	−.42
U	15	0	.56	140	18	30	−.90

separated with silk thread, and the coils were shellacked, and all but two were baked for 18 hours at 140° C. The coils were then adjusted to have a resistance of 10 ohms, and their resistances were measured in oil baths at 20, 25, and 30° C. For these measurements a bridge was used with which a precision of a part in a million was easily attained for the resistance measurements. The results are given in table 1.

The values of α, in parts per million per degree centigrade, (ppm/°C) are marked on the 3-phase composition diagram shown in figure 3.

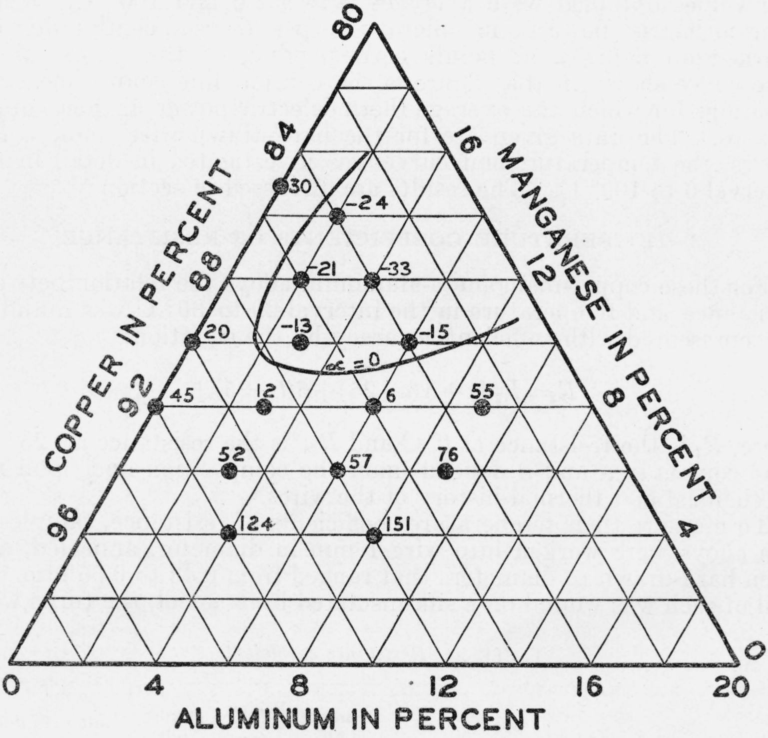

FIGURE 3.—*Values of* α *at* 25° C *for hard-drawn wire after baking at* 140° C *for 18 hours, in parts per million per degree* C.

The contour line shows a series of alloys for which the value of α, that is, the slope of the resistance-temperature curve at 25° C, is zero. As pointed out above, these values of α were determined after the wires were baked at 140° C. This baking produced a considerable decrease in the resistance, and at the same time an increase in the temperature coefficient. The decrease in resistance amounted to as much as 8 percent for coils baked at 140° C, and was roughly proportional to the aluminum content. The change in the value of α was of the order of 2 or 3 ppm/°C for each 1-percent change in resistance. The baking of the coils was intended primarily to increase the stability of their electrical resistance.

The values of β in parts per million per °C per °C are shown in figure 4. Contour lines for equal values of β are shown, but their locations are somewhat uncertain as the data were not entirely consistent. No values of β were obtained for the unbaked wire, so it is not known how its value depends upon the baking. However, all but one of several coils annealed at about 500° C had larger numerical values for β than did coils of the same material baked at 140° C. This was not necessarily a result of the difference in heat treatment, as the wires annealed at the higher temperature were of a larger diameter.

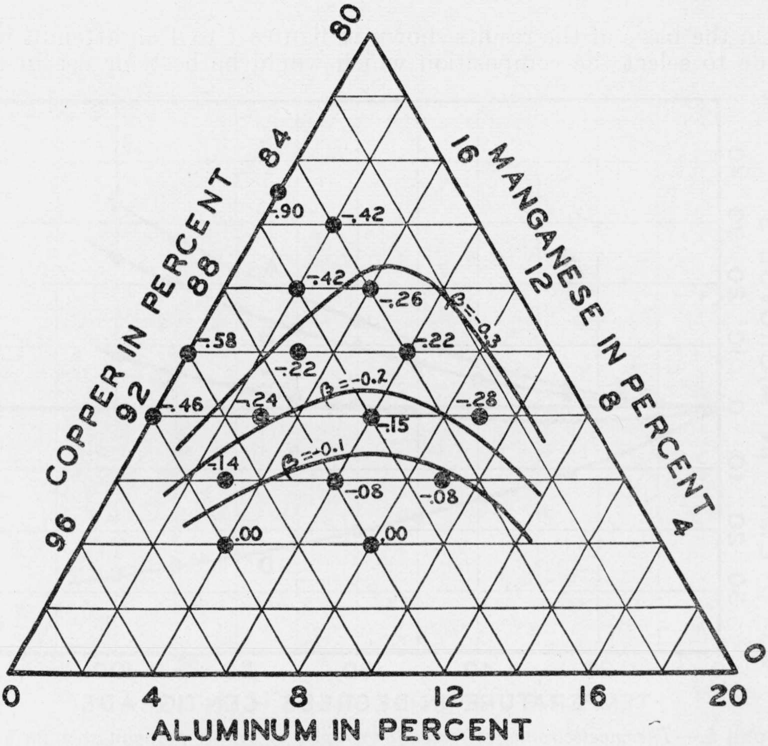

FIGURE 4.—*Values of β in parts per million per* °C *per* °C *for temperatures at or near* 25° C.

These values are for hard-drawn wire after baking for 18 hours at 140° C.

IV. EFFECT OF IMPURITIES

The principal impurity in the alloys was iron which came from the manganese used in their preparation. To test the effect of iron an alloy was prepared, containing about 9.5 percent of manganese and 5 percent of aluminum, the remainder being copper. Calculated from the manganese used, the iron amounted to 0.15 percent. Part of this alloy was remelted and electrolytic iron was added to raise the iron content to 0.30 percent. This additional iron raised the resistivity from 45 to 45.5 microhm-centimeters, and decreased the thermoelectric power against copper from +0.3 to −0.3 μv/°C.

The alloy of 90 percent of copper and 10 percent of manganese was also melted with additional iron. The iron content of this alloy was increased by about 0.3 percent, and this resulted in an increase in the resistivity from 35 to 36.5 microhm-centimeters. At the same time the thermoelectric power against copper was decreased from 1.0 to 0.2 μv/°C.

The effect of impurities other than iron was not investigated. It it assumed that their effect is less than that of iron as they are presens in considerably smaller proportions.

V. BEST COMPOSITION FOR RESISTANCE COILS

On the basis of the results shown in figures 1 to 4 an attempt was made to select the composition which would be best for use in the construction of coils for resistance standards and for measuring apparatus. When the curves of figures 2 and 3 are drawn on the same diagram they do not intersect. It was, therefore, not possible to obtain an alloy of these three ingredients having both a zero temper-

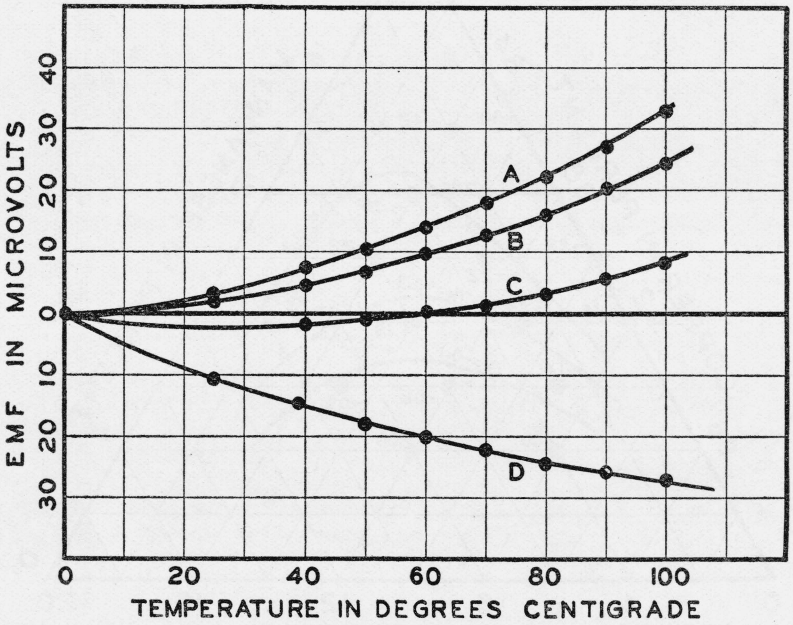

Figure 5.—*Thermoelectromotive forces for couples of copper-manganese-aluminum alloys, with and without added iron, against copper.*

These curves were obtained by keeping one junction at 0° C and bringing other junctions to temperatures as shown on plot. Curves are for alloys of following ingredients, besides copper:

Curve	Manganese	Aluminum	Iron
	%	%	%
A	9.5	5.5	0
B	9.0	5.0	0
C	9.5	5.5	0.07
D	9.5	5.0	0.15

ature coefficient of resistance at 25° C and a zero thermoelectric power against copper. Hence the composition was selected which would give an alloy with a zero temperature coefficient and the smallest obtainable thermoelectric power against copper. For this purpose the following composition was chosen: copper, 85.5 percent; manganese, 9.5 percent; and aluminum, 5 percent. This is the alloy described in section IV for which the resistivity was 45 microhm-centimeters and the average thermoelectric power against copper was $+0.3$ μv/°C for the interval 0 to 100° C. Three 10-ohm resistance standards were made of coils of this wire and baked until their temperature coefficients of resistance were nearly zero. The values of α for these coils ranged from $+0.4$ to -1.0 ppm/°C. The values of β for these standards were about half as large as for most manganin standards.

Another alloy was prepared to contain manganese, 9.5 percent; aluminum, 5.5 percent; iron, 0.07 percent in addition to that from the manganese; the remainder being copper. Four 10-ohm standards were prepared from this material, and the values of α for this group ranged from -0.1 to $+1.4$ ppm/°C. Like the 10-ohm coils of the preceding group, these coils required baking for 18 to 24 hours at 140° C to bring their α's to these small values. The added iron brought the thermoelectric power of this alloy against copper almost to zero. Its average value in the interval 0 to 100° C was 0.08 μv/° C, and its value at room temperature was somewhat smaller. Detailed data are shown in figure 5, curve C. To obtain these data, copper wires were silver-soldered to the ends of the alloy wire, one end was kept at 0° C and the other in an oil bath at temperatures up to 100° C.

In this same way data on the thermal emf against copper, in the interval 0 to 100° C, were determined for several other alloys of slightly different composition. Figure 5 shows the results obtained for alloys made from 9 and 9.5 percent of manganese and 5 or 5.5 percent of aluminum. The results of small additions of iron are shown. From these curves it is evident that the amount of iron is a very important factor in determining the thermoelectric power against copper.

VI. STABILITY OF RESISTANCE

The stability of the electrical resistance of the copper-manganese-aluminum alloys has been tested for standards prepared in two ways. In the first place, the seven 10-ohm coils described in section V were sealed in oil-filled containers of the Rosa[1] type soon after their completion, and their resistances measured from time to time. Then three 1-ohm coils and one 10-ohm coil were annealed in vacuo at 475 to 550° C, and sealed in containers of the double-walled type.[2] The data obtained for these two groups of coils are given in tables 2 and 3. In addition to these coils, some 100-ohm and some 1-ohm coils have been recently constructed and baked at 140° C. While they have been under observation for only a short time, their initial performance has been about the same as for the 10-ohm coils which were baked at the same temperature.

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[1] E. B. Rosa, Bul. BS **5**, 413 (1908) S107.

[2] J. L. Thomas, BS J. Research **5**, 295 (1930) RP201.

TABLE 2.—*Data on resistance coils baked in air at 140° C*

Items	Data for coils numbered—						
	1	2	3	4	5	6	7
Copper (%)	85.5	85.5	85.5	84.93	84.93	84.93	84.93
Manganese (%)	9.5	9.5	9.5	9.5	9.5	9.5	9.5
Aluminum (%)	5.0	5.0	5.0	5.5	5.5	5.5	5.5
Added iron (%)	0.0	0.0	0.0	0.07	0.07	0.07	0.07
Diam of wire (mm)	0.56	0.56	0.56	0.53	0.53	0.53	0.53
Baking temp (°C)	140	140	140	140	140	140	140
Baking time (hr)	18	24	18	42	18	18	24
$\alpha \cdot 10^6/°C$	0.4	−1.0	−1.0	0.0	1.4	1.3	−0.1
$\beta \cdot 10^6/°C^2$	−0.20	−0.20	−0.24	−0.24	−0.24	−0.22	−0.22

Date	Resistance at 25° C, in ohms						
1935							
March 29	9.99482	------	------	------	------	------	------
April 4	9.99484	------	------	------	------	------	------
April 18	9.99485	------	------	9.99524	------	------	------
May 2	9.99486	9.99548	9.99531	9.99528	9.99563	9.99534	9.99532
May 24	9.99487	9.99579	9.99540	9.99528	9.99564	9.99537	9.99536
June 24	9.99489	9.99582	9.99544	9.99530	9.99564	9.99540	9.99539
July 23	9.99487	9.99581	9.99545	9.99529	9.99562	9.99538	9.99539
August 23	9.99488	9.99582	9.99548	9.99529	9.99563	9.99537	9.99541
October 9	9.99487	9.99580	9.99548	9.99528	9.99563	9.99536	9.99541
November 8	9.99487	9.99581	9.99552	9.99530	9.99564	9.99537	9.99542

TABLE 3.—*Data on resistance coils annealed in vacuo at about 500° C*

Items	Coil number—			
	1	2	3	4
Copper (%)	87	87	82	86
Manganese (%)	10	10	12	9
Aluminum (%)	3	3	6	5
Diam of wire (mm)	0.65	1.25	1.7	1.4
Annealing temp (°C)	475	500	550	550
$\alpha .10^6/°C$	9.4	8.3	12.1	31.0
$\beta\ 10^6/°C^2$	−0.24	−0.30	−0.28	−0.26

Date	Resistance at 25° C, in ohms			
1935				
February 11	9.99557	------	------	------
February 25	9.99557	0.999572	------	------
March 11	9.99555	.999571	------	0.999477
March 25	9.99553	.999570	0.999548	.999475
April 22	9.99555	.999569	.999547	.999474
May 22	------	------	.999546	.999473
June 25	9.99556	.999569	.999546	.999474
August 23	9.99557	.999568	.999545	.999473
October 9	9.99557	.999566	.999546	.999473
November 8	9.99557	------	------	------

So far the coils baked at 140° C have been as stable or more stable in resistance than manganin coils prepared in the same way. The coils annealed in vacuo at 475 to 550° C have performed very much like manganin coils baked at 550° C and sealed in double-walled containers. The latter generally change by 2 or 3 ppm during the first month after sealing.

VII. MISCELLANEOUS PROPERTIES

It was hoped that the presence of aluminum in these alloys would make them nontarnishing. This, however, was found not to be the case. They discolored rather rapidly even when exposed to air at atmospheric temperatures. A very decided darkening of the surface was produced by baking at 140° C for a few hours. However, it is possible that this oxidation forms a surface coating which retards further surface action.

After being severely cold-worked the alloys were very strong and springy. However, when baked at 140° C for 18 hours, alloys containing 9.5 percent of manganese and 5 to 6 percent of aluminum were found to be very brittle, and the wire would break when it was bent sharply. The ductility could be restored by annealing in a gas flame. No tests were made of the other alloys to see if they also became brittle from baking.

The temperature coefficient of linear expansion was measured for one sample of the alloy made to contain 84.93 percent of copper, 9.4 percent of manganese, 5.5 percent of aluminum, 0.15 percent of iron from the manganese, and 0.07 percent of added iron. A piece of this material was cold-drawn from 1 mm down to 0.5 mm and baked in air at 140° C for 18 hours. Its coefficient of expansion was then determined from measurements at 20 and 100° C, and its average value in this interval was found to be 0.000 018 per degree centigrade. This value is practically the same as that reported by A. Schulze [3] for manganin, and it is also very near to that of the brass spools on which resistance coils are ordinarily mounted.

The 10-ohm coils of the alloy having the best composition were made from wire which was annealed at a diameter of 1 mm and then cold-drawn to a diameter of about 0.5 mm. Such coils required a baking of about 18 hours at 140° C to obtain the desired temperature coefficient of resistance. However, when a piece was cold-drawn from 1 to 0.2 mm, in order to obtain wire for a 100-ohm coil, a longer baking was required. Two 100-ohm standards prepared in this way had to be baked for 72 hours at 140° C in order to obtain the desired small temperature coefficients. It follows that the amount of baking required to bring the temperature coefficient to zero depends upon the amount of cold-working to which the wire has been subjected. The time of baking has not been investigated for wires of other diameters.

The author wishes to express his thanks to J. A. Scherrer for the chemical analysis of one of these alloys and to P. Hidnert for the determination of its temperature coefficient of linear expansion.

WASHINGTON, December 12, 1935.

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[3] Z. tech. Phys. **14**, 89 (1933).