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COPPER-MANGANESE ALLOYS AND ARTICLES MADE THEREFROM

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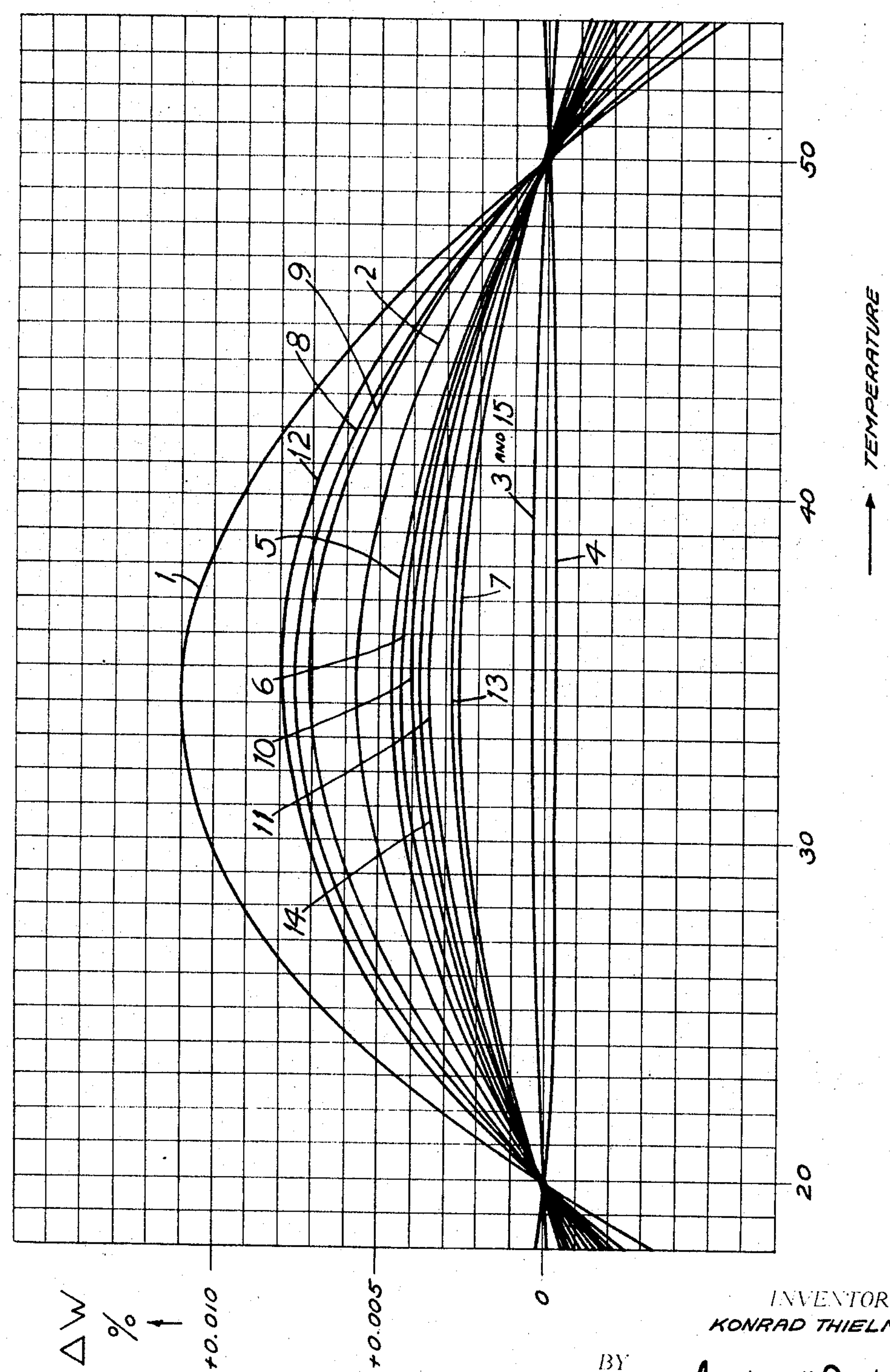

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COPPER-MANGANESE ALLOYS AND ARTICLES MADE THEREFROM

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ABSTRACT OF THE DISCLOSURE

An alloy especially useful for high precision resistor material consisting essentially of about 6 to about 11% manganese, about 0.1 to about 8% germanium and the balance being a metal from the group consisting of copper and silver. The alloy is characterized by having a temperature-resistance curve considerably more flattened than the temperature-resistance curve of "Manganin."

The present invention relates to valuable alloys and more particularly to alloys which are especially useful as high precision resistor material.

Heretofore, precision resistors as used for electrical measurement purposes are usually made of an alloy composed of 86% of copper, 12% of manganese, and 2% of nickel. This alloy was developed in 1889 by the Physikalisch-Technische Reichsanstalt of Berlin and has been manufactured and marketed by the Isabellen-Huette of Dillenburg under the trademark "Manganin." Such an alloy has proved to be of special value as resistor material because of the following properties:

(1) Its temperature coefficient of resistance is very low.

(2) Its thermal electromotive force versus copper is low.

(3) Its resistivity remains constant over a prolonged period of time.

The first mentioned property of said alloy is due to the fact that its resistance-temperature curve is parabolically curved at or about room temperature so that the resistance passes through a maximum between 20° C. and 40° C. The temperature coefficient becomes slightly positive below said maximum and slightly negative above said maximum. Thus due to the parabolic curvature of the resistance-temperature curve the temperature coefficient of resistance of "Manganin" is sufficiently low only at or near its resistance maximum so that this material can be used for precision measurements only at or about room temperature. The temperature range within which this alloy will give satisfactory results will decrease with increasing demands for exact measurements.

Therefore, many attempts have been made to produce an alloy with a resistance-temperature curve of a larger radius than that of the "Manganin" resistance-temperature curve in order to increase the temperature range at which maximum precision measurements can be carried out. A slight improvement was achieved by replacing the nickel in said alloy by tin or aluminum. But even such an improved resistor material did not meet all the requirements and, furthermore, the improvement was achieved while certain disadvantages had to be put up with.

It is one object of the present invention to provide an improved alloy which is especially useful as resistor material and which has a flattened resistance-temperature curve; i.e. has a low temperature coefficient within a relatively wide temperature range and which, therefore, meets the highest requirements of precision measurements.

Other objects of the present invention and advantageous features thereof will become apparent as the description proceeds.

Surprisingly it has been found according to the present invention that replacement of part or all of the nickel in said copper-managanese alloys by germanium in an amount between about 0.1% and about 8.0% and preferably between 1% and 6% and reduction of the manganese content of the alloy to between about 6% and about 11% yields alloys, the resistance-temperature curve of which is considerably more flattened than that of "Manganin."

According to another embodiment of the present invention the copper in such new alloys can be replaced by silver.

A copper alloy with 7% of manganese and 6% of germanium shows a resistance-temperature curve which is flattened to a straight line within the temperature range of room temperature and 50° C. When increasing the germanium content to more than 6% said curve is even slightly negatively curved.

It is clearly evident that such a flattening of the resistance-temperature curve is of considerable importance especially in electrical precision measurements. The new alloys do not possess any noteworthy disadvantageous properties except that the thermal electromotive force of an alloy with a high germanium content versus copper is slightly higher than that of "Manganin." But this disadvantage is more than compensated for by the fact that the constancy in time of the resistivity is markedly improved over that of "Manganin." The technological properties and the workability of the new alloys are excellent. They can be hot rolled and be drawn to the finest kind of wires without difficulty.

The alloys according to the present invention which are composed of copper and/or silver as the main component, of 6% to 11% manganese, and of 0.1% to 8.0%, and preferably of 1% to 6% germanium, may contain additional metal components which may be called hereinafter and in the claims secondary alloying metals, namely:

	Percent
Tin	0 to 3
Antimony	0 to 1
Arsenic	0 to 0.5
Gallium	0 to 5
Indium	0 to 1
Aluminum	0 to 5
Zinc	0 to 5
Nickel	0 to 5

whereby, however, these other components together should not exceed about 10% of the alloy. Addition of these other components permits to reduce the amount of germanium present in the alloy considerably to the lower amounts given hereinabove. Thus, for instance, only about 1% of germanium need be present in the alloy without any substantial impairment of its properties, if the amount of these other secondary alloying metals is between about 4% and about 6% or even more.

Of course, each one of these secondary alloying metals, tin, antimony, arsenic, gallium, indium, aluminum, zinc, and/or nickel may be the sole additional alloying component or, respectively, the alloy may contain several of said metals provided that their total amount does not exceed about 10% and that the homogeneity of the final alloy is preserved. Care is also to be taken that the upper limits as given for arsenic and antimony which are rather low, and are not exceeded.

These secondary alloying metals have also a flattening effect upon the resistance-temperature curve which in some cases is even more pronounced than when using small amounts of germanium alone.

Thereby, the flattening effect of the added secondary alloying metals is the stronger, the higher the valency of said metals is. Most effective are the two five-valent metals arsenic and antimony. However, these metals can be added to the alloy only in a small amount because they cause brittleness and, when added in larger amounts, render impossible processing and working of the alloys by rolling and drawing.

All the alloying additives mentioned hereinabove have only a minor effect upon the thermal electromotive force of the alloy versus copper, with the exception of nickel. Said metal causes a noteworthy displacement of the thermal electromotive force values towards negative values. Therefore, the nickel content should not be too high if it is desired to maintain the thermal electromotive force at a low value.

Germanium also displaces the thermal electromotive force curve towards negative values but the displacement in only two fifth of that caused by nickel addition.

The constancy of the resistivity of the alloys according to the present invention over a prolonged period of time is largely dependent on the preceding thermal and mechanical working of the alloy wires, strips, ribbons, or the like shapes of which the precision resistors are made. In principle the same working conditions are involved as they are known from and used in working "Manganin" although there are certain variations and differences in procedure. Rapid cooling especially as encountered on strand-annealing, causes the alloys to be converted into an unstable state and to be subject to stresses accompanied by time-dependent, slight variations of their resistivity. Cold working and elastic distorting stretching (coiling stretching) have the same effect. All these instabilities and strains can be eliminated by an artificial aging process as this is known for "Manganin." When aging the wound alloy wires or strips by baking at 120° C. to 155° C. as employed in aging of "Manganin," most of the alloys according to the present invention achieve constancy of their resistivity many times more rapidly than "Manganin." This is quite surprising and represents an additional technical advantage of the new alloys.

The figure of the attached drawing clearly demonstrates the flattening effect of germanium and, if added, of the secondary alloying metals upon the resistance-temperature curve. In said figure the ordinate represents the changes in resistivity in percent in dependence upon the temperature which is given as abiscissa. Curve 1 illustrates the resistance-temperature curve of "Manganin" while the curves 2 to 14 represent the resistance-temperature curves of the various alloys given as examples in the lollowing table.

To facilitate an understanding of the figure of the drawing the maximum of all curves has been assumed to be attained at 35° C. Actually this position of the maximum is obtained only with a specific, exactly predetermined manganese content. If the manganese content is higher, the maximum is displaced towards the lower temperatures while, if it is lower, the displacement proceeds towards the higher temperatures. Or, if the curve is flattened considerably, higher manganese contents cause the curve to slope off at increasing temperature towards lower resistance values, i.e. the temperature coefficient becomes more negative while a higher manganese content has the effect that the curve ascends to higher resistance values, i.e. the temperature coefficient becomes more positive.

Thus, in order to achieve as small a temperature coefficient as possible, it is necessary to maintain the manganese content of the alloy within very narrow limits. It is, however, readily possible to compensate for small variations in the manganese content by varying the thermal treatment of the alloy. It has been found, for instance, that rapid cooling after annealing has the effect produced by an increase in the manganese content while cooling at a slower rate acts in the same way as a decrease in the manganese content.

The following table with examples serve to illustrate alloys according to the present invention without, however, limiting the same thereto. In this table there are also given the values of the resistivity as well as of the thermal electromotive force versus copper of said alloys.

TABLE

No.	Percent											Resistivity, ohm/m./sq. mm.	Thermal electromotive force vs. copper, μ/° C
	Cu	Mn	Ge	Sn	Sb	As	Ga	In	Al	Zn	Ni		
1	86	12									2	0.43	−0.7
2	91.5	8	0.5									0.31	+0.4
3	87	7	6									0.44	−1.7
4	85.1	6.9	8									0.49	−1.7
5	90.7	8.0	0.1	1.2								0.31	+0.3
6	90.4	8.7	0.1		0.8							0.33	+0.4
7	92.4	7.0	0.1			0.5						0.29	−0.1
8	90.3	8.6	0.1				1.0					0.33	+0.7
9	89.9	9.0	0.1					1.0				0.34	+1.0
10	87.6	8.3	0.1						4.0			0.40	+0.3
11	87.4	8.5	0.1							4.0		0.31	+0.8
12	88.4	9.5	0.1								2.0	0.37	−0.6
13	81.5	8.5	1	2					2	4	1	0.43	−0.7
14	84.9	8.6	1	2					2.5		1	0.43	−0.8
	Ag												
15	92.5	6.9	0.6									0.24	+1.7

The new alloys are useful not only as resistor material in Wheatstone bridges, decade boxes, potentiometers, and the like precision measuring instruments but also, for instance, as shunts in direct current ampere meters, and for other purposes for which copper alloys have proved to be useful.

It may be pointed out that the new alloys according to the present invention are superior to known copper-manganese-tin alloys by their excellent hot rolling properties and over the known copper-manganese-aluminum alloys by their property of being readily soft-soldered.

It may also be mentioned that when replacing copper by silver, the manganese content need not exceed about 8% and the germanium content about 2%. The advantageous properties achieved with higher amounts of manganese and germanium, when using copper as main constituent of the alloy, are obtained with the above given lower amounts of the alloying components manganese and germanium.

Of course, many changes and variations in the amounts of copper, manganese and germanium, the main components of the new alloys, and in the amounts of the secondary alloying components, in the manner of processing and working the alloys, in their use as precision resistor material and for other purposes, and the like may be made by those skilled in the art in accordance with the principles set forth herein and in the claims annexed hereto.

It may be mentioned that the new alloys can be hard soldered or soft soldered. They can also be welded. Their resistance to corrosion meets all requirements.

I claim:

1. Alloy especially useful as material for precision resistors, said alloy containing
between about 6 % and about 11% of manganese,
between about 0.1% and about 8% of germanium, and the remainder being a metal selected from the group consisting of copper and silver.

2. Alloy according to claim 1, wherein the germanium content is between about 1% and about 6%.

3. Alloy especially useful as material for precision resistors, said alloy containing between about 6% and about 11% of manganese, between about 0.1% and about 8% of germanium, at least one of the following additional secondary alloying metals in the amounts as given:

	Up to about (percent)
Tin	3
Antimony	1
Arsenic	0.5
Gallium	5
Indium	1
Aluminum	4
Zinc	5
Nickel	5

the total amounts of said secondary alloying metals not substantially exceeding 10%, and the remainder being a metal selected from the group consisting of copper and silver.

4. Alloy according to claim 3, wherein the alloy contains at least about 4% of the secondary alloying metals while its germanium content does not substantially exceed 1%.

5. Alloy according to claim 1, wherein the copper content is about 87%, the manganese content about 7%, and the germanium content about 6%, said alloy having a resistivity of about 0.44 ohm/m./sq. mm. and a thermal electromotive force versus copper of about −1.7 μv./° C., its temperature-resistance curve being substantially a straight line between 20° C. and 50° C.

6. Alloy according to claim 1, wherein the copper content is about 85%, the manganese content is about 7%, and the germanium content is about 8%, said alloy having a resistivity of about 0.49 ohm/m./sq. mm. and a thermal electromotive force versus copper of about −1.7 μv./° C., its temperature-resistance curve being substantially a straight line between 20° C. and 50° C.

7. Alloy according to claim 3, wherein the copper content is 92.4%, the manganese content is 7.0%, the germanium content is 0.1%, and the arsenic content is 0.5%, said alloy having a resistivity of about 0.29 ohm/m./sq. mm. and a thermal electromotive force versus copper of about −0.1 μv./° C.

8. Alloy according to claim 3, wherein the copper content is 81.5%, the manganese content is 8.5%, the germanium content is 1.0%, the tin content is 2.0%, the aluminum content is 2.0%, the zinc content is 4.0%, and the nickel content is 1.0%, said alloy having a resistivity of about 0.43 ohm/m./sq. mm. and a thermal electromotive force versus copper of about −0.7 μv./° C.

9. Alloy according to claim 3, wherein the copper content is 87.4%, the manganese content is 8.5%, the germanium content is 0.1%, and the zinc content is 4.0%, said alloy having a resistivity of about 0.31 ohm/m./sq. mm. and a thermal electromotive force versus copper of about +0.8 μv./° C.

10. Alloy especially useful as material for precision resistors, said alloy containing
between about 6% to about 8% of manganese,
between about 0.1% to about 2% of germanium, and the remainder being silver.

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CHARLES N. LOVELL, *Primary Examiner.*

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