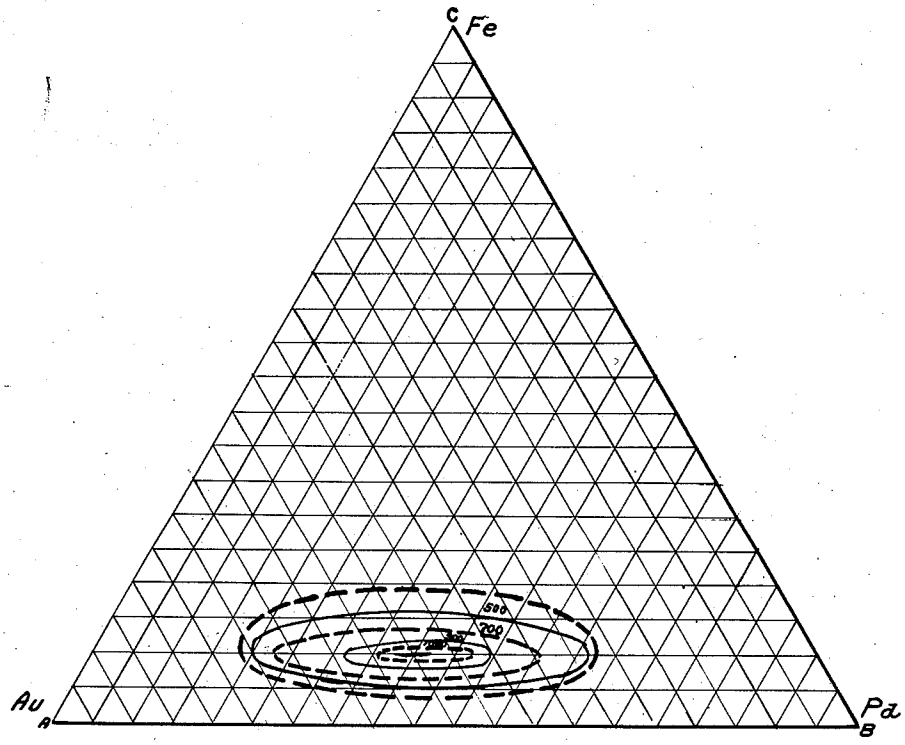
Feb. 5, 1957 J. F. SCHNEIDER ET AL 2,780,543

HIGH RESISTIVITY ALLOY

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Fig. 1.



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Fig. 2.

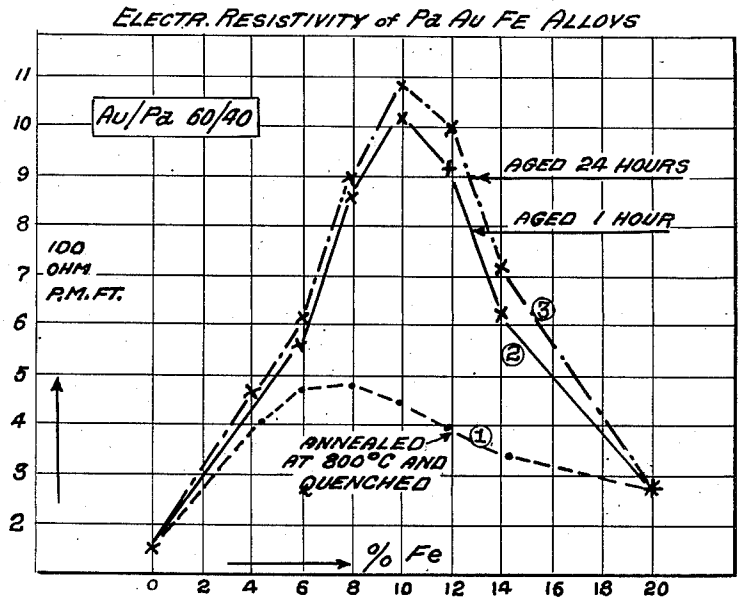
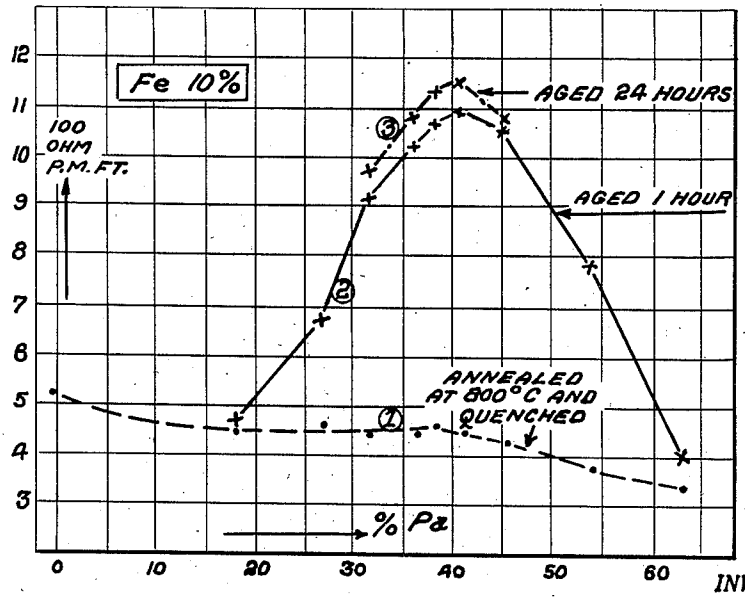


Fig. 3.



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Fig. 3.

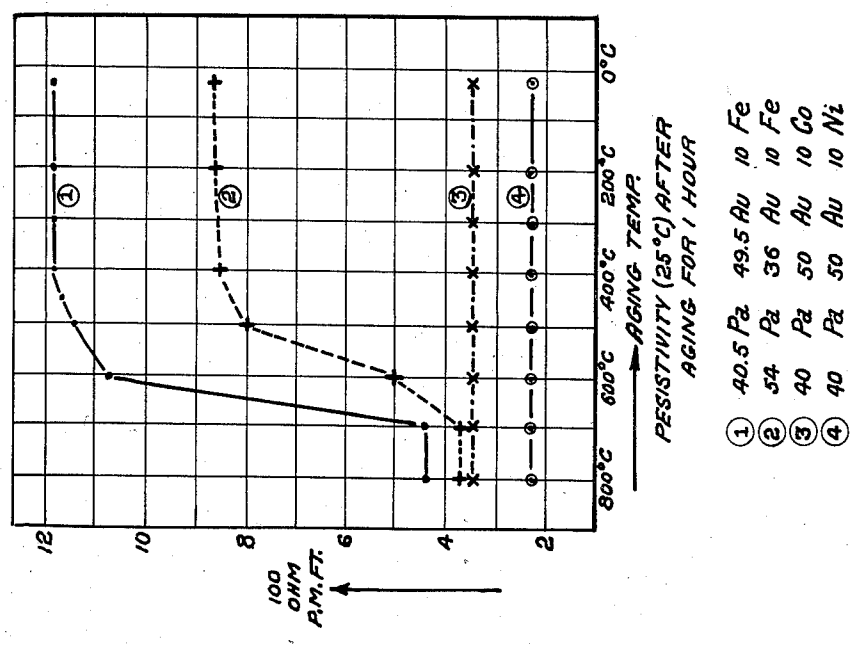
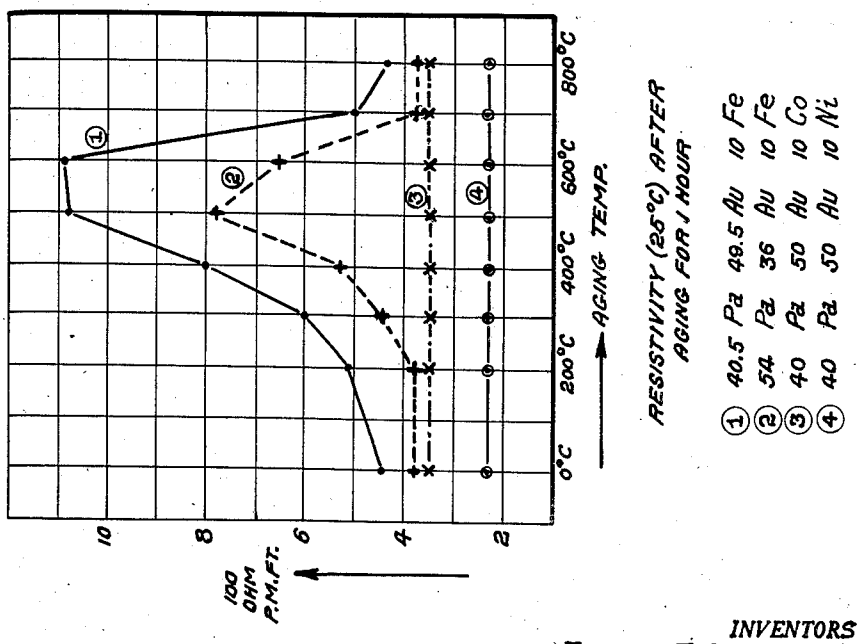


Fig. 4.



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2,780,543

HIGH RESISTIVITY ALLOY

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Application May 17, 1955, Serial No. 508,942

5 Claims. (Cl. 75—165)

The present invention deals with a high resistivity alloy for electrical application and, more particularly, with an alloy of high electrical resistivity and high tensile strength.

While high resistivity alloys for electrical application may be chosen from numerous conventional alloy compositions, such alloys constitute a compromise between the desirable high resistivity and the sacrifice of tensile strength, susceptibility to corrosion, and ductility.

Base metal alloys which have been generally employed for electrical resistance applications have been found inadequate for employment as potentiometer wire in precision potentiometers because of susceptibility to corrosion, which causes imperfect contact with the slider resulting in electrical noise.

Precious metal alloys, for example gold alloys, such as 98% Au–2% Cr, exhibit low resistivity of about 200 ohms per mil foot. Alloys such as 90% Au and up to 10% of at least one of Fe, Mn, Ni exhibit resistivity of about 300 to 426 ohms per mil foot. Also, gold alloys of high gold content such as 91%–93% Au with a balance of vanadium, iron, nickel, and manganese give resistivity values of about 456 to 696 ohms per mil foot.

All these gold alloys containing chromium or vanadium are difficult to produce, and special care must be exercised to avoid oxidation when introducing these base metals into the molten gold since chromium and vanadium have a strong affinity to both oxygen and nitrogen at their melting points. Furthermore, such conventional gold alloys do not possess the desired hardness and tensile strength.

It is an object of the present invention to provide high resistivity alloys for electrical application and which are characterized by high electrical resistivity, good ductility, high tensile strength, and resistance to corrosion. It is a further object of this invention to provide a potentiometer wire composed of an alloy having high electrical resistivity combined with high tensile strength, good workability, and resistance to corrosion. Other objects and advantages of this invention will become apparent from the description hereinafter following, and the drawings forming a part hereof, in which:

Figure 1 is a graphic representation of the critical composition range of the ternary alloy Au–Pd–Fe according to this invention.

Figure 2 is a graphic representation of the resistivities obtained in one group of Au–Pd–Fe alloys. Curve 1 is the representation of the values obtained after annealing at 800° C. and quenching in water. Curve 2 is a plot of the values obtained when wires treated as for curve 1 are aged for 1 hour at the optimum aging temperature, while curve 3 shows the effect of 24 hours' heating at the optimum aging temperature after the 800° C. solution anneal.

Figure 3 is a graphic representation of the resistivities of another group of Au–Pd–Fe alloys, the values being obtained by the heat treatments described for Figure 2.

Figure 4 is a graphic comparison of the resistivity of Pd–Au–Fe alloys and that of similar alloys where nickel or cobalt has been substituted for the iron. All alloys were solution annealed at 800° C. and quenched and were then aged for 1 hour at the desired temperature and quenched.

Figure 5 is a graphic comparison of the resistivity of Pd–Au–Fe alloys and that of similar alloys where nickel or cobalt has been substituted for the iron. In this series of tests the heat treatment varied from that described for Figure 4 in that the alloys were annealed at 800° C. and then cooled to the desired aging temperature, and maintained at that temperature for one hour and quenched.

The present invention deals with an alloy of gold, palladium, and iron, comprising a critical composition range which is essential for high electrical resistivity in combination with high tensile strength and good ductility, wherein the resistivity reaches values up to 1100 and 1200 ohms per mil foot and the tensile strength is of the order 120,000 p. s. i. while elongation is as high as 20% to 25%.

The composition of the alloys herein contemplated is in the range of 28% to 70% Au, at least 4% and not higher than 18% Fe, and from 20% to 62% Pd. This group of Au–Pd–Fe alloys covers a rather limited area of elliptical shape in the alloy range above set forth and identified by triangular co-ordination of the Au–Pd–Fe system as illustrated by Figure 1, which also shows the approximate electrical resistivity in ohms per mil foot for various alloy ranges within the alloy range above identified.

Alloys of the ternary Au–Pd–Fe system outside the range above set forth have low or medium high resistivity at room temperature which is not changed by aging at medium high temperatures, e. g. temperatures between 300° C. and 600° C. However, alloys of the ternary Au–Pd–Fe system within the range herein established have a high resistivity up to 1100 and 1200 ohms per mil foot at room temperatures, and which resistivity is developed and stabilized by aging at the medium high temperatures. The high resistivity at room temperatures is retained whether the alloy, or a wire made therefrom, is quenched or slowly cooled after the heat treatment. In fact, the high resistivity is stable at room temperatures and is not changed by heat treatment at lower temperaures, e. g. temperatures between about 100° C. to 150° C.

These alloys, when quenched from an annealing temperature of about 750° C. and higher, show a medium high resistivity of about 450 ohms per mil foot, but this medium high resistivity does not represent the stabilized state and the resistivity tends to increase slowly with time under room temperature conditions unless stabilized by proper aging to the increased optimum resistivity which represents the stabilized condition, i. e. the increase in resistivity is accelerated as the aging temperature is increased and is very rapid at the optimum aging temperature between 300° C. and 600° C. Slow cooling after high temperature annealing has the same effect as aging after quenching, and after such slow cooling the resistivity is also high. In short, the condition of high resistivity after aging or slow cooling represents the stable state at lower temperatures, and the quenched state after annealing represents the unstable state from which the resistivity of the materials tends to creep toward the higher resistivity and toward the stable state.

The following Table I illustrates the aging effect on resistivity of various alloys of the Au–Pd–Fe system after annealing, said aging being effected at 1 hour and 24 hours aging time at 500° C. It is apparent that the effect of the aging depends upon the alloy composition.

For example, alloys No. 1 and No. 8 do not respond to aging. Others, such as alloys No. 10 and No. 17, respond slightly. However, a maximum increase in resistivity is illustrated by alloys No. 5, No. 13, No. 14, and No. 15, which represent alloys within the critical range specified.

Table I

ELECTR. RESISTIVITY OF PD–AU–FE ALLOYS

	No.	Fe, Percent	Au/Pd Ratio	Pd, Percent	Soft annealed	Ohms per mil foot	
						Aged 1 Hr.	Aged 24 Hrs.
Group I	1	0	60/40	40	159	160	--------
	2	4	60/40	38.5	390	470	--------
	3	6	60/40	38	475	561	600
	4	8	60/40	37	480	865	915
	5	10	60/40	36	445	1,020	1,080
	6	12	60/40	35	390	915	1,000
	7	14	60/40	34	342	617	710
	8	20	60/40	32	275	275	275
Group II	9	10	100/0	0	525	--------	--------
	10	10	80/20	18	452	460	--------
	11	10	70/30	27	460	675	--------
	12	10	65/35	31.5	445	914	964
	5	10	60/40	36	445	1,020	1,080
	13	10	58/42	37.8	455	1,065	1,131
	14	10	55/45	40.5	445	1,095	1,149
	15	10	50/50	45	430	1,055	1,069
	16	10	40/60	54	375	780	--------
	17	10	30/70	63	340	392	--------

The above table shows group I and group II alloys. Figures 2 and 3 further illustrate, graphically, the resistivity of both alloy groups upon aging. Group I includes Au–Pd–Fe alloys with the Au–Pd ratio constant and the Fe content varying. Group II includes Au–Pd–Fe alloys with the Fe content constant and the Au–Pd content varying.

The values of resistivity given in Table I can be increased by prolonging the time of aging, e. g. at 500° C. for longer periods, such as two or three days, the resistivity may increase to 1100 to 1200 ohms per mil foot. Alternatively, the higher resistivity values are attained by very slow cooling from an appropriate aging temperature, or from the solution annealing temperature.

Simultaneously with the increase in resistivity, the alloys also exhibit an increase in tensile strength as evidenced, for example, by the following Table II.

Table II

RESISTIVITY, TENSILE STRENGTH, AND ELONGATION

Alloy			State	Ohms p. m. ft.	UTS, p. s. i.	Elong., percent
Pd	Au	Fe				
37	55	8	annealed	480	90,000	24
			aged	915	120,000	23
36	54	10	annealed	450	96,000	26
			aged	1,050	111,000	22
40.5	49.5	10	annealed	445	95,000	26
			aged	1,150	122,000	24

The temperature coefficient of resistance of some of those alloys are very low. In some cases even negative values as low as minus 0.00005 ohm per ° C. were measured.

The effect of the limited iron content, producing high resistivity in Pd–Au alloys, is a surprising discovery. It was still less expected since the other elements of the iron group, nickel and cobalt, do not display a similar influence. This is evidenced by the behaviour of the alloys containing iron and alloys containing nickel or cobalt instead of iron when heat treated at different temperatures, as illustrated by Figure 4 and Figure 5.

Figure 4 shows the resistivities obtained by solution annealing at 800° C. and quenching in water, and then reheating at chosen temperatures for 1 hour. Figure 5 shows the resistivities obtained by annealing at 800° C. and cooling to the chosen aging temperature and maintaining at this temperature per 1 hour and then quenching in water.

It is clear that in the Au–Pd–Fe system, we have discovered a reversible transformation which is not present in either the Au–Pd–Ni or Au–Pd–Co alloys. This transformation results in a low resistivity state at high temperatures and a high resistivity state at low temperatures. The high resisitivity is stable below a temperature of about 700° C. and the low resistivity state is stable above this temperature. By quenching from annealing temperature above 700° C., the transformation from the low resistivity state to the high resistivity state can be suppressed but the alloys are in a metastable state and tend to revert to the high resistivity state. This tendency becomes stronger as the temperature is raised up to a maximum of 600° C. The time needed for development of the high resistivity decreases as the temperature is thus raised.

In the case of a nickel or cobalt content instead of iron there is only one resistivity condition and that is the state of low resistivity. Although the effect of high electric resistivity is given by the ternary alloys Pd–Au–Fe in the described area of composition, it may be understood that an addition of small amounts of other metals, for instance Pt, Rh, Cr, Mn, Ni, Co, Cu, up to 10% to the basic ternary alloy, in order to vary some physical or chemical properties may be made without departing from the scope of this invention.

What we claim is:

1. A high resistance alloy composed of 20%–62% palladium, 4%–18% iron, and 28%–70% gold.

2. A high resistance alloy composed of 30%–50% palladium, 7%–12% iron, and the balance gold.

3. Electrical resistance wire composed of an alloy of 20%–62% palladium, 4%–18% iron, and 28%–70% gold.

4. A high resistance alloy, according to claim 1, having a resistivity between 450–1200 ohms per mil foot.

5. The method of manufacturing a high resistance alloy comprising forming an alloy of 20%–62% palladium, 4%–18% iron, 28%–70% gold, heat aging said alloy between 300° C. and 600° C. and stabilizing the resistivity of said alloy at between 450–1200 ohms per mil foot.

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