

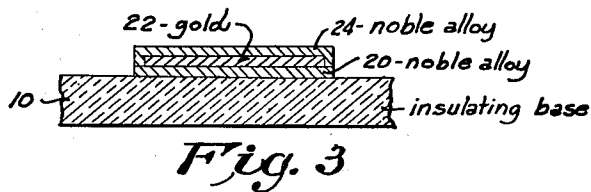
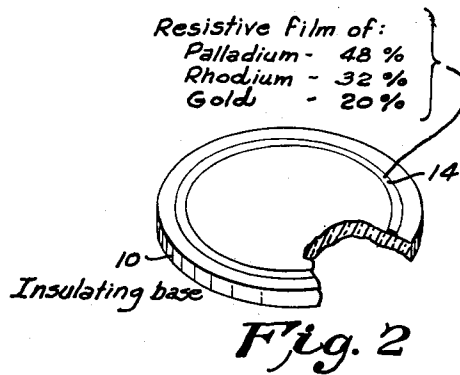
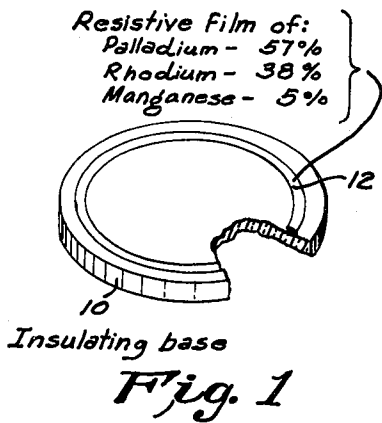
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COMPOSITIONS FOR ELECTRICAL RESISTANCE FILMS

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COMPOSITIONS FOR ELECTRICAL RESISTANCE FILMS

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This invention pertains to electrical resistance materials, and more particularly to materials and compositions for the formation of precision electrical resistors of the deposited film type.

It is a principal object of the invention to provide improved compositions for the production of evaporated metallic film resistances which are characterized by freedom from staining and oxidation at all temperatures and by relatively high stability or consistence of resistance value over long periods of use. The compositions of the invention also provide good mechanical hardness, which is of importance where the resistance element is subject to the rubbing friction of a movable contact or the like.

A further object of the invention is to provide a film resistance functionally integral with an insulating base such as a disc of glass, ceramic or the like, which shall have the above-noted characteristics by reason of the fact that the deposited resistance involves a homogeneous deposit of the proper relative quantities of different ingredients.

A brief review of the problems encountered by prior workers in this field will assist in a clear understanding of the invention. In the manufacture of small or miniature high precision resistors and potentiometers, the technique utilizing a wire winding has been found entirely unsatisfactory. To obtain high or even moderately high total resistance in a small space, suitable materials available in wire form do not have the required combination of mechanical properties and resistivity. Also, the wire wound type of device, especially in small sizes, requires a resistance increment between steps or turns which results in very coarse resolution when the resistance is to be picked off by a sliding contact. For these and other reasons, the continuous film resistance element is much to be preferred. While the adoption of such a form overcomes the necessity for forming the resistance material itself into a wire, it raises other problems such as the difficulty of obtaining homogeneous films free from pinholes and other discontinuities; also the accurate control of final resistance has been difficult to achieve. Recent improvements in vacuum deposition technique have alleviated this situation to a great extent, but certain problems associated with the electrical and thermal characteristics of the film materials have so far found no satisfactory solution. The requirements for materials suitable for vacuum deposited resistors include the so-called "noble" characteristics of freedom from staining and oxidation especially at higher temperatures, stability of resistance value over long periods of use under varied conditions, an adequate range of total resistance within a limited dimensional configuration, and good surface hardness for resistance to abrasion in the case of a sliding contact.

It is to be noted that the problem is not purely a metallurgical one, because even when a suitable mixture or alloy has been found which satisfies these conditions, it is not in general possible by conventional means to achieve vacuum deposition thereof upon a suitable insulating

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base. This is because of the fact that the selected components will not ordinarily, if ever, have evaporation rates such that the mixture will result in a deposited film of the desired composition. In a patent application filed concurrently herewith in the name of the present inventor, Serial No. 569,351, now abandoned, and assigned to the owner of this application, a technique and apparatus have been disclosed by which multi-component films having the desired characteristics can be deposited upon suitable base elements. Reference may be made to that application for such disclosure and details, the present invention being directed solely to novel compositions whose special properties result in resistive films having all of the necessary electrical and mechanical characteristics, and in such form that they can be deposited as controlled films by the techniques of said other application.

It may be pointed out, also by way of general background, that the well-known resistance material consisting essentially of 80% nickel and 20% chromium by weight ("Nichrome") is an example of a composition which can be fabricated either in the form of fine wires or in the form of a deposited film. The fact that this alloy can be filmed by conventional methods results from the fact that the boiling points of nickel and chromium are sufficiently close that vacuum deposition thereof produces a film having nearly the same composition as the original alloy. However, this material is not suitable for the objects of the present invention because it forms stable films only when the films are extremely thick, and such thick films have resistances which are too low for most purposes. While stability against oxidation could be obtained by a protective coating or varnish, this would prevent electrical contact and make the film useless for variable resistors. Moreover, films of these metals undergo slow continuous oxidation in use which causes their resistance to alter considerably with age, and produces surface discontinuities which are intolerable when they are used with sliding contacts.

The invention itself will best be understood by referring now to the following detailed disclosure of certain preferred examples of novel compositions, and which are illustrated in the accompanying drawings, in which:

Fig. 1 is a fragmentary perspective view of a part of a film resistance having one preferred composition.

Fig. 2 is a similar view showing an alternative composition, and

Fig. 3 is a transverse sectional view, with greatly exaggerated vertical scale, showing a combination film used to obtain a desired resistance range.

Briefly, the compositions of the invention have as their major components the elements palladium and rhodium, together with minor but significant quantities of the elements manganese, gold and/or germanium. For the purposes of the present invention, the physical form of these ingredients is of the essence of the invention, in that the listed ingredients must be in finely divided form, the same being mixed before use so that the actual product is a uniform and finely divided mixture of all of the ingredients. Special mention will be made below of precautions which must be taken as to the form and relationship of certain of the components; for example, where the metal gold enters into the formulation.

In the description which follows, a resistance unit expressed as "ohms per square" is used to designate the relative resistance values obtained. This unit is convenient where the resistance element is a deposit of known or constant thickness and has constant width, as is the case of an annular constant-width pattern or ring deposited on a base element, whether or not intended

to cooperate with a contact movable lengthwise of the pattern. Since the effective resistance will be proportional to the length and inversely as the width (the cross-sectional area for constant film thickness is proportional to width), the unit is rational as to dimensions. The "square" may be thought of as representing an element of length of the annular or linear deposit whose elemental length dimension is equal to the width of the deposit. For purposes of establishing a scale related to actual resistance values, it is mentioned that in the set-up (as to dimensions and film thickness) used herein, the actual resistance of the element in ohms is forty times the resistance in ohms per square. This value depends, of course, upon the selected dimensions of the pattern as to width and thickness.

A first preferred formulation which is suitable for forming resistance films in the general total resistance range from 500 to 50,000 ohms per square (e.g., in the form of an annular deposit upon a base of the order of $\frac{3}{4}$ inch in diameter or less) is as follows (in Fig. 1, 10 designates the insulating disc base and 12 the resistive film):

Formula A

	Percent By Weight	Atomic Percent
Palladium.....	57	59.3
Rhodium.....	33	38.1
Manganese.....	5	2.6

It will be seen that the proportions listed represent a mixture (by weight) of 5% manganese and the balance a mixture consisting of 60% palladium and 40% rhodium. In forming the finely divided product to be used in the evaporation process, either the indicated 60/40 alloy of palladium and rhodium, or the metallic elements themselves, are first ground or otherwise finely divided so that a major portion of the divided material will pass a 400 mesh screen. The manganese is also divided to the same fineness, and after sieving through a 400 mesh screen, the proper proportions indicated above are thoroughly mixed together. This finely divided and admixed composition is then evaporated in the manner disclosed in the copending application above, that is, by continuously feeding the finely ground mixture to a superheated element or crucible, at such a rate that the fed material is constantly evaporated without selective distillation of any of the components.

Films formed with the material of Formula A provide final stabilized resistance values which are within $\pm 10\%$ of the value at the time of completion of evaporation. The fixed ratio of rhodium to palladium is primarily responsible for this effect, since films composed of greater amounts of palladium show decreases in resistance from the time of evaporation to their final value, and greater amounts of rhodium produce increases in the resistance over this period. The effect of the manganese is to increase the range of final resistance on the upper end (i.e., for total resistances over 100,000 ohms) by forming thicker films and, as will be pointed out in connection with a further example, gold is preferably used to increase the final resistance range on the lower end (i.e., for total resistances under 1,000 ohms) by forming thinner films.

Since, as has been indicated, the resistance change of this composition from the time of evaporation to the completion of the post-operative aging step is constantly about $\pm 10\%$, the ultimate resistance of the film can readily be calculated and predicted, and conditions and dimensions correlated to provide very closely a desired total final resistance value. While the aging step is not a factor directly related to the present invention, in a typical case it may involve maintaining the evaporated film (and its support) at a temperature of 650° F. for

one hour in an air oven, and supplementary aging for stabilization may follow.

Some variation in the 60-40 ratio of palladium to rhodium is possible, but carries with it an alteration in the degree to which the final stabilized resistance value departs from the initial evaporation value. The 60-40 ratio provides the minimum deviation between these values.

A second preferred formulation under the invention is as follows (see Fig. 2, in which the film is designated 14):

Formula B

	Percent By Weight	Atomic Percent
Palladium.....	48	48.4
Rhodium.....	32	26.6
Gold.....	20	32

The presence of gold in this example yields final resistance values for typical film dimensions and thicknesses in the range from 50 to 500 ohms per square. It will be noted that the proportions of palladium and rhodium are equivalent to the use of 80% of a 60/40 alloy of these metals. Special note must be taken of the dividing and mixing procedure when gold is present, because this metal is very soft and has a tendency to self-weld into agglomerates when used with a vibrating feeder, or to clog the screens through which the mixture is fed. This difficulty is readily overcome by first grinding the gold and the rhodium together, and then sieving the grind to eliminate particles which will not pass the 400 mesh screen. The loss incurred here is minute and has no material effect on the final product. The finely ground palladium is then weighed and mixed thoroughly with the ground-together particles of gold and rhodium, as in a laboratory mixer or by other conventional mixing procedures.

Films formed from Formula B exhibit a consistent drop of from 20-25% between the completion of evaporation and completion of the aging or stabilization, at 650° F. as described above. As in the case of Formula A, the resistance change is quite consistent and permits the attainment within close limits of the desired final value of resistance.

It is impractical to obtain very low resistance films merely by increasing the amount of gold in Formula B. For such low values of total resistance, it is preferable to form the film deposit in layers as indicated in Fig. 3. Here, a layer 20 of Formula A is first deposited upon the insulating base 10, and upon this is deposited an intermediate layer 22 of pure gold. Finally, another layer 24 of Formula A is applied over the gold. Since pure gold films are quite soft, this arrangement results in complete mechanical protection for the intermediate gold layer, the bottom layer of Formula B overcoming the difficulty in adhering pure gold to glass. The use of glass as the insulating base material 10 is preferred, although other ceramics and like materials can, of course, be employed. For purposes of control and calculation of the desired total composite resistor, the two films 20 and 24 of Formula A may have resistance values of 500 ohms per square, from which the resistance of the intermediate gold layer may be calculated from the following, based on ordinary parallel resistance computations:

$$(1) \quad \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}$$

where:

R=final overall resistance value in ohms per square
 R_1 =resistance in ohms per square of underlay of Formula A

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R_2 =resistance in ohms per square of gold low-resistance layer

R_3 =resistance in ohms per square of overlay of Formula A

Since the Formula A layers are both evaporated to 500 ohms per square, the calculation becomes:

$$(2) \quad R = \frac{250 R_2}{250 + R_2}$$

or

$$(3) \quad R_2 = \frac{250 R}{250 - R}$$

While gold has been mentioned hereinabove specifically as the material used for reducing the resistance of the deposit, similar resistance-modifying results could be obtained, with a sacrifice in nobility and in the minimum resistivity obtainable, by substituting for gold the other good conductivity metals of group I of the periodic table; e.g., silver and copper. To the same extent, the resistivity of the critically proportioned palladium-rhodium base mixture could be raised by adding other metals of group II of the periodic table, such as iron, chromium, nickel and cobalt. Gold and manganese are, however, greatly to be preferred, being characterized by the greatest control effects on raising or lowering the final resistivity.

As stated, the 3 to 2 proportions of palladium to rhodium can be varied with some loss in the degree to which the final stabilized value agrees with the resistance of the freshly deposited film. Thus, a range of these proportions from 5:3 to 7:5 (between 1.67 to 1 and 1.4 to 1) may be tolerated with a resistance change which is negligible for many purposes.

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Having described the invention by way of specific examples and pointed out the best mode of practicing the same, it is to be understood that variations in non-critical proportions can be accomplished without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. As a new composition of matter, an intimate physical mixture of finely divided metallic particles consisting of substantially 80 percent total weight of palladium and rhodium in the weight proportions of from 1.4 to 1.67 of palladium to 1 of rhodium, the balance of the total weight being gold.

2. As a new composition of matter, an intimate physical mixture of finely divided metallic particles consisting of substantially 95 percent total weight of palladium and rhodium in the weight proportions of from 1.4 to 1.67 of palladium to 1 of rhodium, the balance of the total weight being manganese.

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