

F. A. FAHRENWALD.
COMPOSITION OF MATTER FOR PLATINUM SUBSTITUTE.
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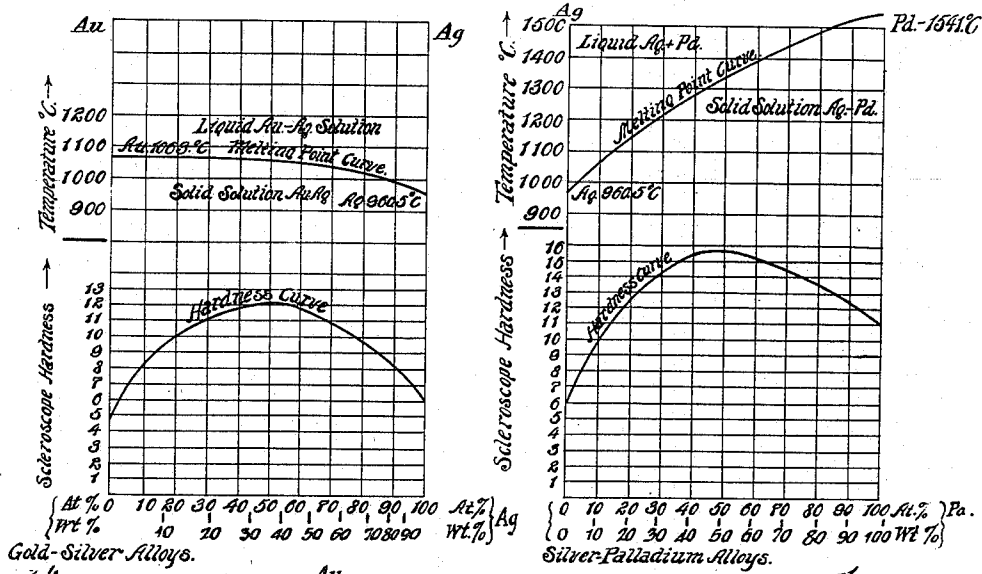


Fig. 1

Fig. 2



Fig. 4

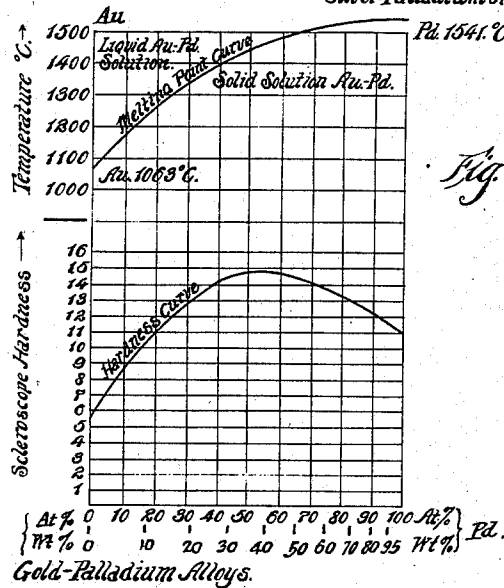


Fig. 3



Fig. 5

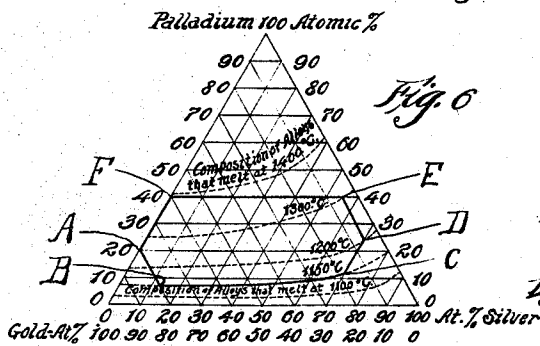


Fig. 6

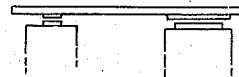


Fig. 7

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COMPOSITION OF MATTER FOR PLATINUM SUBSTITUTE.

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To all whom it may concern:

Be it known that I, FRANK A. FAHRENWALD, a citizen of the United States, residing at Cleveland, in the county of Cuyahoga and State of Ohio, have invented a certain new and useful Improvement in Compositions of Matter for Platinum Substitute, of which the following is a full, clear, and exact description, reference being had to the accompanying drawings.

My invention relates to an improvement in alloys, and has for its object to provide a composition of metal which may be employed in many cases as a metallic substitute for platinum and expensive platinum alloys in various types of electrical construction, (as spark devices, resistance elements, thermo-couple elements, etc.) and in articles of jewelry, chemical containers, and the like, thus effectively conserving this scarce and valuable metal for those scientific purposes in which its use is at present imperative.

The physical and chemical properties that I have developed in my alloy are the result of scientific investigations covering a period of years, and the selection of the components of my alloy, and the adjustment of the proportions of these components, are based upon a study of the relations of each metal to the other, and to the alloy body as a whole.

In view of this fact, I consider it advisable to describe in some detail the methods and principles that I have discovered and used in working out my invention. Before undertaking the development of a new material that would serve instead of platinum in its various applications, it was necessary to adopt certain criteria which should serve as specifications for physical and chemical properties of any material that would be satisfactory.

The requirements of a material suitable for chemical ware, electrical construction, and the like are in general, well known. Exact specifications cannot be drawn, but from a long study of this subject and from countless observations of the behavior of many types of metals and alloys, under varying conditions of use I have concluded that chemical and physical stability at relatively high temperatures are the prime requisites.

These requirements in a platinum substitute may be detailed as follows:

1. Its melting point should be higher than pure gold. (This would not be necessary in articles of jewelry and the like but for general chemical ware and units of electrical construction high melting-point is imperative.)

2. It must not be affected by chemicals or gases encountered in its application.

3. It must not oxidize at any temperature up to and including that necessary to melt it. (This is very necessary in chemical applications and of great importance in the case of spark devices. I have observed that the arcing produced in many breaker designs is sufficient to melt the surface of even pure platinum. A careful microscopical examination of the surface of a used point reveals many minute globules of material that have been melted by arcing across terminals. Even when platinum points are employed, the surface of the support surrounding each point is usually covered with a deposit of fine platinum black, a condensed metallic vapor. Should an oxid film be produced on the contact surface of the points themselves by this condition of local high temperature, the circuit would be broken, or at least it would be most difficult to start the device after it had once been stopped, due to the insulating effect of this oxid film. This is the chief objection to the use of tungsten contacts.)

4. It must possess sufficient strength and hardness to withstand stresses tending to change its form while in place. (Even pure platinum is deficient in this property, but this is often overcome by adding up to 30% of iridium, which, however, greatly increases the cost. In my experiments with contact devices it was observed that soft metals such as gold, were battered out of shape by the continued hammering effect. Strength is very valuable in chemical and other electrical construction also.)

5. The electrical resistance should preferably be greater than that for platinum. (A material of this nature often finds application in electrical heating units. I have found that low electrical conductivity is not disadvantageous in contact devices, for the

amount of current carried is very small for the large cross section employed, while the thermal and electrical resistance across surfaces of contact formed in fastening are very great when compared with that of the metal itself.)

6. It must be sufficiently malleable and ductile to permit of rolling, drawing, stamping, or otherwise working, to a desired shape.

7. Its cost of production must be low as compared with that of platinum.

It will be seen at once that the above requirements of physical and chemical stability at high temperatures form a set of specifications of a very exacting nature, and at once exclude from consideration all metals of a readily fusible or oxidizable nature.

A consideration of all materials at present available, using the above specifications as criteria, proved that no single metal was suitable. It was evident, therefore, that any search for the desired material must be in the field of alloys, since experience has shown that the physical and chemical properties of a metal may be radically changed by the addition of varying amounts of another element, or of several elements.

When two or more metals are brought together in the liquid state, they behave exactly like two ordinary liquids. When the temperature is lowered the solidified mass may contain any one of the four following constituents: pure components; solid solutions; compounds; and eutectics—or some combination of these. While a theoretical contemplation of the properties of different metals will to some extent suggest the probable properties of an alloy thereof, still it is only by experiment and test that its mechanical and physical properties can be absolutely settled. However, if a certain application is desired as in the problem under consideration, a definite limit may be placed upon the number and amount of constituents permissible.

Fortunately, the number of fundamental conditions is limited to four, as given above. Pure metals impart their own characteristics; solid solutions are, in general, of a ductile and malleable nature (if formed of ductile metals, or of a preponderance of one ductile metal); compounds and usually, eutectics, are hard and brittle; while the latter, even when present in very small amounts, tend to solidify between the grains of the alloy, thus producing segregation and destroying its ductility.

Alloys of the solid-solution type would therefore produce the most satisfactory platinum substitute, for compounds are too brittle to permit of being worked, while the segregation produced by eutectics would produce selective erosion and corrosion. The alloying of metals serves to increase hardness, to produce resistance to corrosion,

etc., but my experiments have shown it will not prevent oxidation at or near the melting temperature. For instance more than a trace of base metal, as copper, nickel, iron, etc., in any of the precious metals will cause an oxid coating to form on the surface of the heated metal. With all of these various considerations in mind, then, it became evident that even in the alloyed condition no metal of a base-metal nature should be present in appreciable quantities, wherefore the substance sought must be a solid solution alloy of two or more of the noble metals silver, gold, palladium, platinum, rhodium, iridium, ruthenium and osmium.

In view of the fact that a substitute for platinum was the object of my researches, this metal was not to be included to more than very small amounts, in the desired alloy. Likewise the metals rhodium, ruthenium, osmium, and iridium are too rare and costly to be used at least in large amounts, in an inexpensive platinum substitute.

Thus after my researches had included the entire list of elements separately, it was found that only gold, silver, and palladium fulfilled to the greatest degree, the preliminary set of governing specifications. Not one of these, however, was suitable, when used alone. Silver is too soft and of too low melting point, and is not sufficiently chemically inert. Gold, also, is not sufficiently hard or refractory, while palladium alone is too costly.

These three metals form solid solution binary and ternary alloys in all proportions, although it is found that differences in composition have very great effects upon the hardness, melting point and electrical and chemical resistivity of the resulting alloy. Some of these effects are illustrated graphically in the drawing accompanying and forming a part of this application wherein Figure 1 represents the hardness curve and melting point curve for gold-silver alloys; Fig. 2 the similar curves for the silver palladium alloys; Fig. 3 the similar curves for the gold palladium alloys; Fig. 4 represents a photomicrograph section of the gold palladium alloy; Fig. 5 a photomicrograph section of the silver palladium alloy; Fig. 6 a diagram showing the melting points of various compositions of the ternary alloy containing gold, silver and palladium; and Fig. 7 represents one use of my improved composition of matter as a spark point or electric terminal.

The solution of one of these metals in another increases the hardness to a remarkable extent. This is shown in the curves given for the three binary series of gold-silver, silver-palladium, and gold-palladium, Figs. 1, 2 and 3, respectively. These metallic solid solutions are truly crystalline, and in the crystalline arrangement (or "space lattice"

as it is called) of two or more constituents, the lattices or units are regarded as interpenetrating. For example, in the case of the element gold to which a second element silver, or palladium, which passes into solid solution, is added, the atoms of gold in the space lattice are replaced progressively by those of the isomorphous silver or palladium, and the lattice passes imperceptibly from that of the one pure element to that of the other. This atomic replacement within the crystal reacts on the physical properties. The space volumes occupied by atoms of different elements are not the same, so that if the metals, whose atomic volumes are not equal and which possess other intrinsic differences, form symmetrical, solid-solution-space lattices, there must result a contraction of the larger atom and an expansion of the smaller, and other energy adjustments, thus producing an internal strain which increases the hardness, lowers the electrical and thermal conductivity, and variously affects other properties of the components.

It is evident also that this internal strain and the corresponding resulting properties will be a function of the number of atoms dissolved. This is shown in the case of the hardness curve, which shows a maximum at the point where equal atomic proportions prevail, *i. e.*, at 50 atomic per cent. of each component in a binary series. The curves for electrical and thermal conductivity likewise show a minimum at this composition. Experiment proves that those metals, like gold and silver, which possess the most nearly equal atomic volumes will replace each other and form solid solutions most readily and with the least amount of segregation. Their atomic volumes are: gold, 10.20; silver, 10.23. Palladium, however, with an atomic volume of 8.9 tends to segregate upon solidification of the binary alloy with either, as shown in Figs. 4 and 5 which are photo-micrographs, showing the internal structure of silver-palladium and gold-palladium alloys respectively, this tendency being particularly marked in the case of palladium silver alloys. I have discovered, however, that the addition of a quantity of gold to this palladium-silver alloy markedly decreases the segregating tendency and signally improves the character of the alloy in other respects.

I have, therefore, discovered that a ternary alloy containing gold, silver, and palladium fulfils the requirements of a platinum substitute in a remarkable degree. The proportions of these ingredients may be varied through a considerable range depending upon the price limitations and the rigidity of the requirements. The addition of silver to an alloy of gold and palladium even up to 50 atomic per cent. has comparatively small

effect upon the melting point of the composition but decreases the cost per unit volume in great degree, and in case of alloys containing a relatively low per cent. of palladium is of material service in increasing the hardness.

The addition of palladium even in small quantities to alloys of gold and silver greatly increases the melting point and hardness and chemical resistivity. The addition of gold to alloys of silver and palladium markedly decreases the segregating tendency and increases its chemical resistivity.

The portion of Fig. 6 included within the heavy line thereon indicates the area of most valuable commercial percentages, those alloys corresponding to the lower right hand portions of this area being the least expensive though sufficiently conforming to the above expressed basic requirements for many electrical purposes. Alloys corresponding to portions above and toward the left will conform to more rigid requirements. For example any alloy falling within the left hand half of this area exhibits the most perfect physical and chemical stability at high temperatures, fully comparable in most of its applications to that of platinum.

Investigation of these ternary alloys proves the following: (1) That the addition of over one per cent. of silver to any alloy containing gold and palladium increases the hardness up to a certain limit, lowers the melting point very little, and at the same time decreases the cost.

The increased hardness is very valuable, in many cases where increased silver is not objectionable and the decreased cost is of importance. By adding varying amounts of silver therefore, I obtain the same necessary hardness as would be obtained by using higher percentages of palladium, as shown on Fig. 3. For certain chemical applications of rigid requirements, however, I use the pure binary alloy of gold and palladium.

(2) The addition of more than 10 atomic % of palladium to the gold-silver series raises the melting point to a degree where the alloys can withstand high temperatures without fusing. The approximate melting point of any alloy within the diagram may be judged from its position with reference to the series of dotted lines which are drawn through points representing alloys of equal melting point. These lines are marked 1100° C., 1150° C., 1200° C., etc. The alloys decrease in degree of "nobility" from the gold end of the series, but to a very slight extent for small amounts of silver but the increased hardness, increased electrical resistance and decreased cost in many cases more than balance this.

(3) The addition of more than 5 atomic % of gold to the silver-palladium alloys reduces segregation, reduces volatilization and

increases resistance to erosion and corrosion.

- (4) Ternary alloys of these three metals are more satisfactory than a silver-palladium or gold-silver binary alloy of any composition.

Limits of palladium.

Because of the results of my experiments as outlined above, and their evident relation to the atomic proportions of these elements, I have based my descriptions and claims upon the relative number of atoms or atomic percentages of each element present. My experiments have shown that a melting point of at least 1150° C. is necessary in a platinum substitute to be used under most favorable conditions. I, therefore, have fixed the lower limit for palladium content to a line coinciding with that dotted line representing a melting temperature of 1150° C. Because of high cost and other undesirable features, as tendency to segregate, etc., I fix the upper limit of palladium at 40 atomic %.

Limits of gold.

I have found that at least 5 atomic % of gold is required to produce homogeneous alloys, and to reduce excessive spark erosion and corrosion by various chemical agents. I have also found that an alloy of over 80 atomic % of gold is too soft to be of practical use in the applications herein described. The amount of gold permissible then, falls between the lines representing 5 atomic % and 80 atomic % of that element.

Limits of silver.

My experiments have shown that, for certain purposes where increased hardness or electrical resistivity is required, it is advisable to add over 1 atomic % of silver. I have found that rhodium, iridium, etc., are better than silver but too costly.

If conditions of application are not too rigid, even up to 75 atomic % of silver may be used. The limits of total variation in composition are therefore contained within the area bounded by the lines AB—BC—CD—DE—EF—FA.

By the term "palladium" as used herein I mean the commercial material which contains on the average about one-half of one per cent. of platinum as an impurity and frequently other noble metals as gold, iridium, or rhodium; it is very rarely free from these substances, especially platinum, and in exceptional instances has run as high as five per cent. of that substance. I have always ignored this noble metal impurity as not injuring the product, which from the nature of the commercial substances used will frequently contain small percentages of

these substances, in addition to which small amounts of the same may be added as heretofore suggested.

The alloys near the gold end of this area are more noble in character, are more insoluble in acids, and less affected by gases than those higher in silver. None, however, are in the least oxidized at any temperature by arcing across terminals composed of them.

Below 5 atomic % of silver these alloys are practically insoluble in boiling concentrated acids, as hydrochloric, nitric or in alkalis. Above 5 atomic % of silver, they become slightly soluble in nitric or fuming sulfuric acids, though practically insoluble in aqua regia.

It is advisable, but not necessary, to cool high palladium alloys very slowly to allow diffusion to take place.

Having thus described my invention, what I claim is:—

1. A platinum substitute containing palladium together with silver and one at least of the other noble metals immediately surrounding palladium in the periodic table, all of the constituent metals having atomic weights, between one hundred and two hundred times that of hydrogen, the palladium constituting not less than ten atomic per cent. of the whole.

2. A platinum substitute containing palladium alloyed with silver and one or more of the metals in the gold series of the periodic table, all the constituent metals having atomic weights between one hundred and two hundred times that of hydrogen, silver being preponderant, and the palladium constituting not less than about ten atomic per cent. of the whole.

3. A composition of matter for platinum substitute in electrical and chemical apparatus containing between ten and forty atomic per cent. of palladium, the remainder being gold and silver.

4. A composition of matter containing palladium from 10 at. % to 40 at. %, gold 5 at. % to 80 at. %, and silver 1 at. % to 70 at. %.

5. A composition of matter containing at least 10 atomic per cent. and not over 40 atomic per cent. of palladium, at least 10 atomic per cent. and not over eighty atomic per cent. of silver, the remainder being a metal or metals of the gold series in the periodic table having an atomic weight between one hundred and two hundred times that of hydrogen.

6. An alloy for the distribution of electric current by contact composed of gold and silver in approximately equal proportions and approximately ten per cent. of palladium.

7. An alloy for the distribution of electric

current by contact composed of gold and silver with the addition of ten per cent. of palladium.

8. An electric sparking terminal made of gold and silver in a preponderating degree with the addition of at least ten per cent. of palladium.

9. An electric current communicating element formed of an alloy consisting of approximately forty-five per cent. of gold, forty-five per cent. of silver, and ten per cent. of palladium.

10. An electric current communicating ele-

ment formed of an alloy containing palladium and silver together with one or more of the other noble metals immediately surrounding palladium in the periodic table, all of the constituent metals having atomic weights between one hundred and two hundred times that of hydrogen and the palladium constituting not less than about ten atomic per cent. of the whole.

In testimony whereof, I hereunto affix my signature.

FRANK A. FAHRENWALD.