

[54] POWDERS OF METAL, SILVER AND GOLD
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[57] ABSTRACT

A substantially homogeneous, finely divided powder, substantially free of silver chloride or cyanide comprising at least one metal other than silver or gold, and silver and gold, and an anti-agglomerating agent substantially homogeneously dispersed throughout said powder. The powders are particularly useful in the electronic arts.

9 Claims, No Drawings

POWDERS OF METAL, SILVER AND GOLD

This is a division, of application Ser. No. 141,006, filed May 6, 1971 now U.S. Pat. No. 3,717,453.

This invention relates to processes for making metal-silver-gold powder systems and the resulting powders made therefrom. More particularly, this invention relates to processes for making metal-silver-gold powders and the powders resulting therefrom which are extremely homogeneous in nature and thus find a wide variety of uses particularly in the electronic arts, such as those uses disclosed in concurrently filed, commonly owned copending application Ser. No. 140,988, filed May 6, 1971 in the name of Bernard Greenstein and entitled RESISTOR COMPOSITIONS AND METHODS.

The value of metal oxides such as palladium oxide and the like as electronically active materials has long been known. For example, as set forth in the above-cited commonly owned copending application, it is known, that in the microelectronic circuitry art, a resistive metal such as palladium may be admixed with a glass binder and an organic vehicle to form a printing paste. The paste is then printed onto a dielectric substrate such as aluminum oxide or the like by the use of a screen or mask of the desired mesh and formed to provide the desired pattern. The desired pattern is then fired in air to oxidize the palladium to palladium oxide and form an electronically active device (e.g. resistor).

Unfortunately, many resistive metal oxides (including palladium oxide) have relatively large and negative temperature coefficients of resistivity (hereinafter referred to as TCR) which must usually be adjusted if the resistor is to be operative for its intended purposes. In order to regulate this TCR, (and in effect to increase it to a tolerable level somewhere about ± 0 ppm/ $^{\circ}$ C) certain metals such as silver or gold have been alloyed with the resistive metal. In addition to regulating TCR, these additive metals have also been found to dilute the system and thereby control resistivity and increase the "stability" of the resistor.

The term "stability" is well-understood in the art and is used herein in accordance with this well-known meaning. That is to say, stability defines that characteristic of an electronic system which enables it to maintain its resistivity value within tolerable limits over extended periods of time and use.

As further disclosed in the aforementioned copending application and as disclosed in commonly owned, copending application Ser. No. 58,740 filed July 26, 1970, now U.S. Pat. No. 3,681,261 one of the major problems attendant resistive metal systems is their great sensitivity to the firing process used to formulate the ultimate device from its printing paste. Slight fluctuations and/or variations in temperature during the firing cycle, for example, greatly change the resistivity of the resulting product. Air flow and firing times are further variables to which the characteristics of the final product are extremely sensitive. Such sensitivity, of course, renders these oxide systems extremely difficult to reproduce. Not only is reproducibility low, but for some reason, not entirely understood, stability is also very low.

While the additive metals used in admixture with the resistive metal oxide generally provide commercially tolerable stability to the system, they are generally

found to detrimentally increase TCR, usually far above the desirable ± 0 ppm/ $^{\circ}$ C, when used in amounts sufficient to obtain tolerable stability. In this respect, and especially when silver is used as the stabilizing metal, stability must be sacrificed for acceptable TCR; while, on the other hand, TCR must be sacrificed for acceptable stability. In almost all instances, reproducibility, regardless of the metal stabilizers used, is detrimentally low.

The aforementioned commonly owned, copending application, Ser. No. 58,740, filed July 27, 1970, discloses a unique and valuable solution to the above-described problems attendant these resistive metal oxide systems, especially when these systems are used to form microelectronic resistors. The entire disclosure of this copending application is incorporated herein by reference.

In this copending application, the problems of stability, sensitivity, and reproducibility are eliminated by a unique process which, when effected, produces extremely homogeneous alloys of palladium or other resistive metals with at least one stabilizing metal. By achieving high homogeneity, reproducibility is increased because sensitivity of the system to later processing such as firing and the like is materially decreased. In this respect, while one stabilizing metal alone can be employed, it was found to be preferred to use at least two of these metals together in amounts which were found to synergistically reduce their affect upon TCR. Thus, by using two metals in combination, excellent stability is attained without unduly increasing TCR. One of the most important of these combinations is a combination of silver and gold, usually in alloy form.

Generally speaking, this aforementioned copending application obtained the necessary degree of homogeneity for nonsensitivity of the palladium (or other resistive metal) with the stabilizing metal systems, by initially forming an admixture of the resistive metals and stabilizer metals in the form of organometallic compounds and adding thereto an anti-agglomerating agent. Upon heating of the admixture of a sufficient temperature and for a sufficient period of time, the organo constituents are driven off and the admixture is concentrated to an extremely homogeneous powder. Such powders were found to be extremely useful when alloyed and employed with glass binders as resistor compositions for microelectronic circuitry.

While the technique hereinabove described relative to this copending application is extremely valuable, it has a few drawbacks attendant with it which make the finding of an alternative method of forming an extremely homogeneous powder of a resistive metal with a silver and gold system most desirable. Examples of such drawbacks include the relatively high expense of the organometallic compounds used as starting materials and the pollution and danger caused by the volatilization of the organo constituents during heating to powder form. It has also been found that many of the commercially available organometallics useful in the practice of the invention disclosed in the copending application contain chlorine-bearing solvents. During the concentration step, the chloride ions have a tendency to react with the silver metal and thereby form silver chloride precipitate which contaminates the resulting powder. As discussed more fully hereinafter, silver

chloride cannot be tolerated in any substantial amounts in resistor compositions.

It is a purpose of this invention to provide the art with an alternative process for forming extremely homogeneous, finely divided powders of resistive metals in combination with silver and gold, which process does not employ organometallic compounds and thereby overcomes the above-described problems relative thereto. In this respect, it is a further purpose of this invention to provide the art with a starting material powder and a process for forming this starting material powder from which the unique resistors of the above-cited concurrently filed copending application Ser. No. 140,988, filed May 6, 1971 in the name of Bernard

Greenstein entitled RESISTOR COMPOSITIONS AND METHODS, can be formed and the other teachings of the invention disclosed therein carried forth. The entire disclosure of this copending application is incorporated herein by reference.

Generally speaking the subject invention accomplishes these purposes by, in part, relying upon a coprecipitation technique wherein at least some of the metals employed are precipitated by the use of a reducing agent from solution to thereby aid in the formation of the homogeneous, finely divided powders of this invention. In this respect, the homogeneity achieved in this invention is to an extent greater than that achievable by mere mechanical comminution or comminution and metal alloying. Thus, the term "homogeneous" is used herein to define a dispersion of materials which goes beyond that achievable by these mechanical or partially mechanical techniques.

As exemplified by U.S. Pat. Nos. 3,390,981 and 3,385,799 and British Pat. No. 1,004,652, the basic concept of coprecipitating two electronically active noble metals to thereby form a finely divided alloy of the two metals is known. Generally speaking, such a known process comprises dissolving each of the metals in a common inorganic solvent such as, for example, nitric acid, so as to form a solution of soluble salts (e.g. nitrates) of the two metals. Thereafter, the solution is contacted with a reducing agent which simultaneously reduces the dissolved metal salts and precipitates them as pure metal alloy powders.

The prior art coprecipitation techniques, as represented by the patents cited above, have several serious drawbacks. Firstly, they never contemplate the use of a system having more than two metals therein. Secondly, although they do make mention of the use of silver and gold as a coprecipitate, the application of the disclosed techniques to the formation of such a coprecipitate has many problems and detriments attached thereto. For example, there are only a very limited number of inorganic media in which both silver and gold are soluble. Of these, aqua regia (e.g. 3 parts HCl to 1 part HNO₃) and the various inorganic cyanide solutions are, generally speaking, the only ones which feasibly could be employed. While aqua regia may generally be safely employed, insoluble silver chloride is formed simultaneously with the silver and gold soluble salts, thus forming a contaminant in the ultimately precipitated metal alloy powder. Silver cyanide is somewhat more soluble than silver chloride. However, cyanide salt contamination often does occur to a limited extent and may become a material problem especially when a high degree of silver is required to be present in the system. In addition, the use of cyanides is danger-

ous and to be avoided. In summary, then, the art, by its prior techniques is unable to safely form a noncontaminated coprecipitate of silver and gold.

The problem of contamination of coprecipitated powders, particularly of silver and gold, is an especially acute problem in many arts such as where the powder is to be used, for example, in microelectronic devices such as conductors, resistors and the like. In microelectronic resistors, for example, substantially no contaminating silver chloride or cyanide can be tolerated. Since, therefore, the prior art coprecipitation techniques cannot provide a safely formed, noncontaminated powder comprised of silver and gold, they are incapable of satisfying a specific but important need in the art. Therefore, in addition to the above-explained need relative to a new technique for forming homogeneous, finely divided powders which do not employ organometallic compounds, there also exists a definite need in the art for a new technique for forming homogeneous, finely divided metal powders which include both silver and gold in their composition makeup, which is safe to conduct and which eliminates or substantially reduces the contamination problem.

It is the purpose of this invention not only to fulfill the first above-described need, but also to fulfill this latter need relative to a new technique wherein silver and gold may both be present in the powder composition but without the degree of metal salt contamination experienced when employing the prior art techniques.

In fulfilling the above-described needs, this invention generally envisions two alternative techniques for forming homogeneous, finely divided powders of one or more metals in combination with silver and gold (or two other metals which give rise to similar problems of contaminated coprecipitation as silver and gold).

The first alternative technique of this invention generally comprises forming a soluble salt solution of a metal other than silver or gold, and silver and thereafter reducing the solution in accordance with prior art techniques similar to those described in the aforementioned patents. Such a reduction reaction with agitation forms a metal-silver slurry. To this metal-silver slurry is then added gold in the form of a gold salt solution generally of the chloride type. The slurry solution now containing gold is then contacted with a reducing agent either already present or additionally added, to precipitate the gold into the metal-silver slurry and thereby form the trimembered powder of metal, silver and gold.

It is quite true that, in this technique, some small amount of insoluble silver chloride may form. However, the amount of silver chloride formed is substantially below that which would form if the prior art concepts were carried out by dissolving gold, silver and metal in, for example, an aqua regia medium which would serve as a medium for all three of these metals. This is because the initial reduction of the metal and silver into a powdered slurry renders the metal and silver less sensitive to chlorination.

The second alternative method contemplated by this invention provides for the total elimination of the formation of any insoluble silver chloride or cyanide in the system and thus is preferred where noncontaminated powders are required to be used such as in the microelectronics art, particularly for making resistors and the like. This second alternative method generally com-

prises initially forming a soluble salt solution of the metal or metals other than silver or gold, and silver in a manner similar to the first alternative method. To this silver-metal salt solution there is then added a finely divided gold powder usually having a particle size less than about 5 microns, preferably less than about 2 microns, and most preferably substantially submicron in size. The solution containing the gold powder, which is not soluble in the salt solution, is then thoroughly mixed as by agitation, to form a slurry of the gold and there is then added thereto a reducing agent for the metal and silver. While some small amount of homogeneity is sacrificed because the gold powder is not precipitated, precipitation of the metal and silver into the slurried gold powder effects a substantial amount of homogeneity to the extent that excellent products can be made therefrom for the purposes of microelectronic circuitry, particularly in the resistor area.

In view of this second alternative technique, this invention for the first time provides the art with a unique powder also considered a part of this invention. Such a powder generally comprises a substantially homogeneous admixture of at least one metal other than silver or gold, with silver and gold, which admixture is substantially free of silver chloride or cyanide. As stated above, the homogeneity achieved and contemplated is beyond that achievable by known mechanical comminution and/or alloying techniques and is usually to the point where the silver and other metal are actually alloyed together according to X-ray diffraction indications with the gold highly dispersed therethroughout. The particle size of the powder, without comminution is generally less than about 5 microns and usually submicron in size and thus the powder is said to be "finely divided."

Regardless of which of the above two alternative methods is employed to make the finely divided homogeneous powders of this invention, this invention relates generally to all systems wherein at least one finely divided metallic powder other than silver and gold must be formulated in admixture with both silver and gold. In this respect silver and gold will be referred to hereinafter since they are the preferred combination with which this invention deals. However, it is understood, as stated, above that this invention, as an equivalent, contemplates other metal combinations which experience the difficulty of contamination by coprecipitation similar to that of silver and gold.

The metal used in admixture with the silver and gold must be capable of forming a soluble salt in a liquid reaction medium in which a silver salt is also soluble. In addition, the soluble salt of the metal as well as that of the silver must be capable of being coprecipitated in metallic form by the addition of an appropriate reducing agent thereto.

The preferred metals for the purposes of this invention are the known resistive metals such as, for example, palladium, rhodium, iridium, ruthenium, indium, and mixtures thereof. Of these, palladium is the most preferred for the preferred environmental use of microelectronic resistors because of its excellent resistive properties. Examples of other metals useful in combination with silver and gold include platinum, copper, nickel, and mixtures thereof.

The metal or metals employed may be formed into any of their known salts which are soluble in a liquid medium in which a silver salt is also soluble. Therefore,

the formation of the metal salt and silver salt may be independent or simultaneous. In addition, the metal and silver anion may be the same or different, the only criteria being that both salts are soluble in a common liquid medium and capable of being precipitated in metallic form from the medium by the addition of a reducing agent thereto, preferably without the formation of any insoluble salt occurring which cannot easily be removed from the powdered solution.

In the preferred embodiments of this invention, the liquid reaction medium employed is water. In still more preferred embodiments, at least one of the metals is palladium, and the soluble salts formed are, at least in part, the soluble nitrates of palladium and silver. Nitrate salts, of palladium and silver are simply formed by reacting the silver and palladium with nitric acid. In this respect, and because of the ready commercial availability of silver nitrate solutions, it is preferred to form the metal-silver nitrate salt solutions of this invention by separately forming a nitrate solution of the metal and thereafter add a commercially prepared silver nitrate solution thereto.

Examples of anions other than the nitrates which may be employed to form, in a known way, the soluble salts of one or more of the metals and/or of the silver include: sulfates, sulfites, bromates, chlorites, fluorides, permanganates, nitrites, and the like.

Salts formed of the nitrate anion are generally soluble in water of room temperature or below as are some of the salts of the other exemplary anions listed above. In other instances, the anion salt may be of limited solubility and thus the liquid medium may have to be heated or cooled in order to form and/or maintain a truly soluble solution prior to and during formation of the powders according to this invention if contamination with the anion or salt thereof is to be avoided or limited.

The reducing agents which cause the precipitation of metal and silver from their medium may be any of the well-known reducing agents or combinations thereof commonly employed in the art. Examples of such reducing agents include hypophosphorous acid (H_3PO_2), a mixture of sodium formate and sodium borohydride, a mixture of hydroxylamine and sodium borohydride, a mixture of formic acid and hypophosphorous acid, a mixture of hydrazine sulfate and hypophosphorous acid, a mixture of formic acid and hydroquinone or a mixture of tartaric acid and hydroquinone, or sodium bisulfite. H_3PO_2 is preferred especially with silver and palladium since minimal side reactions and substantially no insoluble contaminating salts are formed when it is used.

The reducing agents added to effect gold precipitation in the first alternative technique may be any of the well-known reducing agents for gold such as sodium sulfite, hydroquinone, hydrazine sulfate, sulfurous acid, zinc dust, ferrous sulfate, and the like. Sodium sulfate is preferred because it is readily available and causes the formation of an excellent particle of gold upon its precipitation.

In order to insure homogeneity and obtain powders in their best possible form, especially for use in the microelectronic circuitry art, an anti-agglomerating agent is preferably added to the salt solution prior to any coprecipitation so as to be a part of the ultimately formed, homogeneous, finely divided powder, regardless of the alternative technique employed. Such anti-agglomerating agents are inert to the system and form

a slurry therein. The anti-agglomerating agents usually employed are of a fine particle size, i.e., less than about 5 microns and usually submicron in size. Examples of these agents include ultra-fine alumina, an ultra-fine TiO_2 , and other ultra-fine refractories. Preferred for the purposes of this invention is ultra-fine silica (submicron in size) which is purchasable under the trademark CAB-O-SIL.

The percentages of the various ingredients employed will vary over a wide range depending upon the ultimate use to which the powder may be put. It is an aspect of this invention that the percentages attainable are quite flexible in nature. Thus, for example, homogeneous, finely divided powders are attainable which contain less than 1% of any given metal and more than 99% of another metal. In the preferred uses, as disclosed in the aforementioned copending Greenstein application, the metal other than silver and gold is a resistive metal such as palladium or the like which may constitute from about 5-95% by weight of the powder. Preferably the resistive metal constitutes 15-75% by weight of the powder, and most preferably 20-65% by weight thereof.

In preferred embodiments the remainder, i.e. 95-5% by weight, of the metal content is a combination of silver and gold in a weight ratio of 4:1 to 1:4 with respect to each other. In those instances where an anti-agglomerating agent is employed, such usually need only be employed in amounts of about 0.5-15% by weight of the total powder, preferably 2-10% by weight and as where ultra-fine silica is employed, usually about 5% by weight.

The concentrations employed for making the soluble salt solutions of the metal, silver and gold, and the amount of gold powder employed in the second alternative technique are matters generally of convenience and may vary widely in order to insure the requisite amounts of the various ingredients in the final powder and at the same time be workable in the manufacturing system devised. Generally speaking, the upper limit of concentration is the saturation point of the solution for the salt while the lower limit is a practical volume consideration. In this respect, concentrations of the salt solutions lower than about 10% are normally not employed. In the preferred instances where palladium and silver are first formed into a soluble nitrate solution by reaction with nitric acid, the solution containing the two salts may have a concentration on the order of about 20-60% of the combined salts. Similar concentrations for the gold solutions in the first alternative technique may also be employed. The relative concentrations of each metal within these solutions are then, of course, adjusted in a known manner to achieve the desired powder upon reduction and precipitation.

The gold solutions employed in the first alternative technique may be any well-known soluble salt solution of gold. Generally speaking, such soluble salt solutions include the various chloride and cyanide salts of gold. A particularly preferred gold solution for the purposes of this invention is a solution of hydrochloroauric acid formed in a conventional manner by dissolving the requisite amount of gold in aqua-regia (e.g. 3-4 parts HCl to 1 part HNO_3).

The gold powder employed in the second alternative technique may be any commercially available gold powder preferably having a particle size of less than about 5 microns. A preferred gold powder, because of

its uniform and ultra-fine nature, for the purposes of this invention, is pure gold powder produced in accordance with my copending application Ser. No. 124,558 filed Mar. 15, 1971 and entitled GOLD POWDER, but washed free of emulsifier or particle size inhibitor prior to addition to the soluble salt solution. The entire disclosure of this copending application is incorporated herein by reference.

Generally speaking, this copending application discloses a method for forming a gold powder, usually having a bulk density greater than about 5.0 gms./cc and a particle size of less than about 5 microns, which comprises initially dissolving a gold-bearing material in a HCl-HNO_3 acid. Thereafter, there is added to the solution an effective amount of an emulsifying agent capable of coating freshly formed gold particles and preventing coalescence and cold-welding thereof and keeping the particle size of said gold particles less than about 5 microns. To this solution there is then added a precipitating agent, which precipitates gold powder from solution substantially free of contaminating chloride or other salts. The so-formed gold particles are encapsulated with the emulsifier which is removed, usually by washing the powder in a solvent such as acetone or water and then drying the powder prior to using it in this invention. The powder so formed is substantially pure, uncontaminated, gold powder of the indicated particle size.

A typical operating procedure for conducting the first alternative technique described hereinabove is to initially prepare a metal-soluble, salt solution by dissolving the metal in an inorganic acid. For example, palladium in commercial sponge, powder or other form may be dissolved in a 70% solution of HNO_3 to form a solution preferably of about 300-400 gms./l. of Pd. A separate silver nitrate solution may be prepared with nitric acid or commercially obtained. Alternatively, silver sponge, powder, etc. may be added with the palladium in the requisite amounts to the 70% HNO_3 solution. The gold solution is prepared by dissolving gold sponge, powder, etc. in aqua regia and removing excess HNO_3 by heating the solution. A typical concentration of the resulting hydrochloroauric acid is about 20-60%.

The nitrate solutions of silver and metal (e.g. palladium) are then admixed if not simultaneously formed and an antiagglomerating agent is added thereto. The solution is agitated to slurry the antiagglomerating agent and a reducing agent such as H_3PO_2 or sodium bisulfite is added to precipitate the metal and silver in their metallic form. Generally speaking, it is desirable to precipitate substantially all metal and silver from the solution, the ratio of metal to silver being controlled by the concentrations and amounts of solutions formed. For this reason, at least a stoichiometric amount of reducing agent and preferably about 2 or 3 times in excess of this amount, is employed to insure substantially complete precipitation of the metal and silver.

After this reduction and precipitation, the resulting mixture is vigorously agitated to slurry the particles of anti-agglomerating agent, silver, and metal in a highly dispersed fashion throughout the liquid reaction medium. To this slurried solution is then added the hydrochloroauric acid solution. In those instances where the reducing agent initially employed for the metal and silver is also a reducing agent for gold, gold precipitate will form upon mere addition of the gold solution to the

slurry. In such an event, sufficient reducing agent is added initially to insure that substantially all of the gold is precipitated from solution. In those instances where a different reducing agent is employed or the reducing agent initially added is insufficient to precipitate gold, a reducing agent is added with continued vigorous agitation until the precipitation of the gold is substantially complete. The reduction reaction of gold does result in some reaction occurring between the slurried silver and the chloride ions in the decomposed hydrochloroauric acid. However, as stated above, because the silver is previously precipitated, a reduction in the amount of insoluble AgCl normally formed by common-coprecipitation of gold and silver from a common aqua-regia solution is obtained.

The homogeneously dispersed finely divided powder of metal, silver, gold, anti-agglomerating agent, and reduced amounts of AgCl is now separated, as by filtration, from the liquid medium and dried. As previously stated, the powder is of particles less than about 5 microns and usually less than about 1 micron. In addition, the homogeneity of dispersion of the individual ingredients is far beyond that achievable by simple comminution and/or alloying. Furthermore, it has been found that in most instances, as indicated by X-ray defraction techniques, the silver is alloyed with the metal.

In a typical procedure for conducting the second alternative technique described hereinabove the solutions of metal and silver, preferably in nitrate form, are formed and admixed in a manner similarly as described in the first alternative technique. Gold powder having a particle size of less than about 5 microns is then added to the common solution. Preferably, as stated, the gold powder is that as produced by my afore-cited copending application. The anti-agglomerating agent is added either prior to, simultaneously with, or after the gold powder is added and the particles of this agent and gold are slurried in the solution with vigorous agitation.

A reducing agent in the before-described amounts is then added to precipitate the metal and silver and the homogeneous powder is obtained and processed similarly as described with respect to the first alternative technique. The product of the second alternative technique differs markedly from the first alternative technique because no chloride (or cyanide) is used to dissolve the gold and thus no chloride (or cyanide) is present to form a contaminating insoluble salt in the powder. As previously stated, this is of significant value in the microelectronic resistor art.

The following examples are presented as illustrative of this invention.

EXAMPLE 1

FIRST ALTERNATIVE TECHNIQUE

A gold reactant solution (HAuCl_4) was prepared from pure gold sponge. This was accomplished by reacting 20 gms. of Au in an aqua-regia solution and diluting the solution to 160 ml. with H_2O . A palladium nitrate solution was prepared by dissolving 53.8 grams of the metal in 150 ml (70%) HNO_3 . The resultant Pd (NO_3)₂ solution had a volume of 160 ml. A silver nitrate solution was formed by dissolving 115.3 grams of silver nitrate crystals in 150 ml. of distilled water. The total volume of the resultant solution was 175 ml.

To start the process 80 ml. of the Pd (NO_3)₂ solution, 87 ml. of the AgNO_3 solution, and 100 ml. of H_2O were

charged into a reactor. The reactor employed was a 1 liter baffled glass kettle provided with a pitched marine-type propeller agitator capable of operating at up to 500 rpm. A cooling bath surrounded the kettle and reaction temperature was measured by a thermometer immersed in the reaction solution.

After mixing the initial charge thoroughly, an admixture containing 3.75 gms. of CAB-O-SIL (ultrafine silica) in 50 ml. of H_2O was added and slurried. With continued agitation the reduction reaction was carried out by adding 170 ml. of a solution containing 75 grams of NaHSO_3 to the reactor. The NaHSO_3 addition took place over a 14 minute time interval and the reaction media was maintained at 38° C.

Agitation was continued to slurry the precipitated silver and palladium metals with the anti-agglomerant and the slurry was prepared for HAuCl_4 addition and reduction by the addition thereto of 15 grams of Na_2SO_3 in 100 ml. of H_2O . This was followed by rapid addition of 80 ml. of the HAuCl_4 solution. An additional 100 ml. of the Na_2SO_3 solution was added to insure complete reduction of the gold. After 5 minutes of further mixing, the agitator was shut off.

After permitting the reactants to settle out for 30 minutes, the solids were separated from the liquid by filtration. The solids were washed by slurrying in H_2O and filtering several times. The final wash was followed by drying at 110° C overnight. A finely divided, homogeneous powder was obtained. The powder analyzed as containing on a metal basis by weight, 47.4% Ag, 14.55% Au, and 38.05% Pd. The powder also contained 13.02% by weight chloride salt, assuming all chlorides to be silver chloride.

EXAMPLE 2

SECOND ALTERNATIVE TECHNIQUE

250 gms. of a powder consisting of by weight 52% Ag, 35% Pd, and 13% Au were prepared by the following technique.

A Pd(NO_3)₂ solution was prepared by adding 87.5 grams of palladium metal to 245 ml. of a 70% HNO_3 solution. The addition of Pd to the acid was conducted slowly and the nitrous oxide gas formed was vented. An AgNO_3 solution was prepared by adding 204.3 grams of AgNO_3 crystals to 500 ml. of distilled water with stirring. The gold powder employed had a particle size of less than 5 microns and was produced in accordance with Example 1 of my aforementioned copending application. 32.5 grams of the powder were washed free of emulsifier in acetone and thoroughly dried for use hereinafter.

The AgNO_3 solution was charged into a reaction vessel which consisted of a 5 liter glass baffled flask with a propeller type agitator. The reaction vessel was provided with a heating and cooling bath to regulate the temperature. One liter of distilled water was added and the solution mixed rapidly by the propeller agitator. At this time, 12.5 gms. of CAB-O-SIL (ultrafine SiO_2) anti-agglomerating agent was suspended in the reaction medium. Five minutes of vigorous stirring were then allowed to proceed.

Next, the Pd(NO_3)₂ solution was added and the 32.5 gms. of gold powder suspended in the combined solution with continuing agitation. An additional 375 ml. of distilled water were also added to aid in the washing in of the gold powder.

The reduction reaction was initiated, with continued vigorous agitation, by adding to the reaction mass, dropwise, 390 gms. of a 50% hypophosphorous acid solution diluted in 400 ml. of distilled water. The total time to add all of the H_3PO_2 was about ½ hour. During that time the resulting exothermic reaction was maintained at about 50° C by cooling water. After the reducing agent had been added the reaction media was held at the reaction temperature with mixing for 1 hour to insure completeness and optimum homogeneity of the metal slurry.

Thereafter, the metal slurry was filtered and washed with about two liters of distilled water and placed in a 110° C drying oven overnight.

The resulting dry powder was a microscopically homogeneous black mass having substantially no particles greater than about 5 microns. Analysis indicated the powder to consist on a metal basis of, by weight, 52% Ag, 35% Pd, and 13% Au and further indicated that no contaminating salts were present therein. This powder, as evidenced by the examples in the aforementioned copending Greenstein application, may be used as a valuable starting material for microelectronic resistor production.

Once given the above disclosure many other features, modifications, and improvements will become apparent to the skilled artisan. Such other features, modifications, and improvements are therefore considered to be a part of this invention, the scope of which is to be determined by the following claims.

I claim:

1. A substantially homogeneous, finely divided powder, substantially free of silver chloride or cyanide

comprising at least one metal other than silver or gold, and silver and gold, and an anti-agglomerating agent substantially homogeneously dispersed throughout said powder.

2. A powder according to claim 1 wherein said powder has a particle size less than about 5 microns.

3. A powder according to claim 1 wherein said at least one metal is selected from palladium, rhodium, iridium, ruthenium, indium, and mixtures thereof.

4. A powder according to claim 1 wherein said at least one metal is the single metal palladium.

5. A powder according to claim 1 wherein said anti-agglomerating agent is particulate silica submicron in size.

6. A powder according to claim 1 consisting essentially of about: 5-95% by weight palladium, 5-95% by weight of an admixture of gold and silver in a weight ratio of about 4:1 - 1:4, and about 0.5-15% by weight anti-agglomerating agent.

7. A powder according to claim 1 which consists of about 20-65% by weight palladium, about 80-35% by weight of said silver, gold admixture, and about 5% of submicron particle size silica as said anti-agglomerating agent.

8. A powder according to claim 1 consisting of by weight about: 52% Ag, 35% Pd, and 13% Au on a metal basis, the total composition including about 5% by weight of said silica.

9. A powder according to claim 1 wherein said palladium is indicated as alloyed with said silver by X-ray diffraction techniques.

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