

1

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METHOD FOR THE PRODUCTION OF FINELY DIVIDED METALS

Lewis C. Hoffman, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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17 Claims. (Cl. 75-108)

This application is a continuation-in-part of my co-pending application, Ser. No. 258,607, filed Feb. 14, 1963 now abandoned.

This invention relates to the production of noble metal alloys consisting essentially of two of the following metals: silver, gold, platinum and palladium. More particularly, it relates to the production of such alloys in finely divided form.

The noble metal alloys produced by this invention are palladium-gold, platinum-gold, silver-gold, silver-palladium, silver-platinum and palladium-platinum alloys. Each of the above metal combinations form continuous series of solid solutions over the entire range of alloy compositions with no eutectics or compounds of the metals being formed.

Noble metal alloys in very finely divided form, e.g., an average particle size of no larger than 40 microns with no more than about 5% of the particles larger than 42 microns, and preferably with a particle size not exceeding about 5 microns and most preferably of an average size in the range of 0.1 to 0.5 micron; are highly desired for the production of electric current conducting layers on dielectric surfaces, e.g., in the production of capacitors, resistors and conductors. Such finely divided noble metal alloys are virtually impossible to obtain by the comminution of such alloys produced in massive form in the usual manner, by melting together the metal constituents of the alloys.

It is therefore an object of this invention to provide a new method of obtaining finely divided noble metal alloys consisting essentially of two of the metals; silver, gold, platinum and palladium.

It is another object of this invention to provide a method of obtaining finely divided noble metal alloys consisting essentially of two of the metals; silver, gold, platinum or palladium, where the average particle sizes of the alloys are of the order of 0.1 to 0.5 micron.

Other objects will become apparent from the following detailed description of the invention.

The above objects may be accomplished, in general, by preparing a solution of the metal constituents of the alloy powder in a ratio approximately equal to the compositions of the alloy desired, followed by simultaneously coprecipitating both dissolved metals to provide the desired alloy through the use of a reducing agent or mixture of reducing agents. In the preparation of, for example, gold alloys devoid of silver, platinum alloys devoid of silver, and palladium alloys devoid of silver; chloride compounds (which are the most convenient form of these metals available) can be employed in the preparation of solutions from which the alloys are precipitated. Other soluble compounds of these metals, e.g., cyanides, bromides, nitrates, etc. can be employed equally as well. In the preparation of silver alloys, soluble salts of silver, such as the nitrates of this metal, obtained as such or formed by dissolving silver in nitric acid, can be employed. The other noble metal to be alloyed with silver must not, when placed in solution with the silver,

2

effect precipitation of the silver as an insoluble salt. Accordingly, chlorides of noble metals are to be avoided in making silver alloys and the nitrates and cyanides of these noble metals can conveniently be employed.

In the preparation of solutions of palladium and silver, both the silver and palladium may be simultaneously dissolved in nitric acid or the palladium may first be dissolved in the acid and the silver subsequently dissolved therein. If desired, the given amount of palladium and silver may be dissolved in separate quantities of nitric acid and the two solutions mixed. Palladium will only dissolve in nitric acid containing at least 3% excess NO_2 and having a specific gravity of at least 1.5 g./cc. and, therefore, if the two metals are dissolved in a single quantity of acid, it will be most convenient to first dissolve the palladium and then the silver in the nitric acid. Alternately, the palladium can be dissolved in nitric acid and crystalline silver nitrate in the proper ratio can be dissolved in the palladium nitrate solution.

The solvent employed with the noble metal compounds used to make the solution from which the alloy powders are precipitated is conveniently water. Other polar solvents can be used as desired. Chlorinated hydrocarbon solvents can satisfactorily be used to dissolve noble metal halide salts. Concentrations of the dissolved metals of from about 5 to 25% by weight have proven satisfactory in this process, but all concentrations of ingredients from the most dilute up to saturated solutions can be employed as desired. It has been observed that the fineness of alloy powders precipitated is influenced by the concentrations of metals, with finer powders being produced from the lower concentrations. When employing water as a solvent, the pH thereof should be maintained acidic to avoid precipitation of metal noble bases and can be varied between pH values of from about 1 to 6. It has been found that the speed of precipitation increases with increased temperature and pH values. Generally, the coarseness of the alloy powder formed is directly proportional to the speed of precipitation. High quality alloy powders have been obtained using the combination of room temperature and pH values of from 4.5 to 6.5.

To produce the desired alloy, pairs of reducing agents, one of which precipitates one of the metal constituents from the solution and the other of which precipitates the other metal constituent, can be used in combination. In addition, a single reducing agent for both of the metal constituents of the desired alloys can be used. It is only necessary in forming the metal alloy that the metal constituents thereof be simultaneously precipitated from the same solution.

While, generally, any reducing agents for the alloy constituents which coprecipitate the alloy constituents and any soluble compounds of the alloy constituents can be employed, it will be appreciated that care must be exercised to avoid competitive reactions including interreaction of the soluble compounds, undesired reactions of the metal compounds with the reducing agents, and undesired interreactions between the reducing agents employed.

Hereinafter, are set forth examples of reducing agents and combinations thereof which can be used in the process of the invention.

Hydrazine hydrate, $\text{H}_2\text{N}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$, functions to reduce gold and palladium from their solution to produce gold-palladium alloy powders and is equally usable with a gold-platinum solution to precipitate a gold-platinum alloy powder.

Pairs of reducing agents may be selected from the following Table I to precipitate palladium and gold alloy powders.

TABLE I

For Pd:	For Au:
hypophosphorous acid	hydroquinone
sodium hydrosulfite	hydrazine sulfate
	sulfurous acid
	sodium sulfite
	zinc dust
	ferrous sulfate

Pairs of reducing agents may be selected from Table II to precipitate platinum-gold alloy powder.

TABLE II

For Pt:	For Au:
sodium borohydride	hydroquinone
sodium hydrosulfite	hydrazine sulfate
	sulfurous acid
	sodium sulfite
	zinc dust
	ferrous sulfate

It was found that the sodium borohydride liberates hydrogen in acid solution and that the metal powders formed therefrom are saturated with hydrogen after filtration and drying. This hydrogen is evolved rapidly in the heating-up stage of the firing of electrical devices which contain alloy powders made by this method with disruptive consequences in those instances where it is desired to produce fired-on coatings having fine, or small dimensions. Accordingly, its use only for large cross-sectioned fired-on coatings is recommended. When employing sodium hydrosulfite and/or ferrous sulfate as reducing agents for the metals indicated above, the pH of the solution for which they are used must be adjusted to a value of from 4.5 to 6.5 or above. While hydrazine hydrate is the preferred reducing agent for the solutions of palladium-gold and platinum-gold, the pairs of reducing agents set forth above also provide excellent results.

Hypophosphorous acid functions to reduce silver and palladium from nitrate solutions thereof. Pairs of reducing agents may be selected from the following Table III to precipitate silver and palladium alloy powders.

TABLE III

For Ag:	For Pd:
sodium formate	sodium borohydride
ammonium formate	hypophosphorous acid
hydroxylamine	hydroquinone
formic acid	
hydrazine sulfate	
tartaric acid	

The pH of the solutions may be adjusted to a pH of between about 4.5 and 6.5 by the addition thereto of concentrated NH_4OH , NaOH , KOH , Na_2CO_3 , K_2CO_3 , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$ or the like. Of these neutralizing agents, NH_4OH is particularly preferred especially when the solution contains dissolved palladium, since it forms a complex with Pd and prevents the formation of small quantities of $\text{Pd}(\text{OH})_2$.

The reduction of the nitrates and precipitation of the palladium-silver alloy from such solutions produces an average particle size of alloy particles slightly larger (probably 0.3–0.5 micron) than from nitrate solutions in which the pH has not first been adjusted to between 4.5 and 6.5. The alloy particles produced by reduction of pH-adjusted solutions are not quite as subject to shrinkage during firing for the production of an electrically conducting film.

The neutralizing agents may be added as such or in concentrated aqueous solution. The alloy powder containing silver and palladium produced when ammonium hydroxide is used as the neutralizing agent is superior for certain uses such as capacitor or resistance electrodes to the powders formed through the use of other neutralizing agents.

The following examples are given to illustrate, in detail, several preferred embodiments of the invention, it

being understood that the details of these examples are not to be taken as limitations of the invention.

EXAMPLE 1

310 grams of palladium sponge (commercial refiner's grade) are dissolved in 5 liters of red, fuming nitric acid (Sp. gr. 1.53 g./cc.) at 50–60° C. The solution is allowed to cool. 77.5 grams of silver are then dissolved in the solution to give an 80/20 weight ratio of Pd/Ag.

With rapid stirring, one liter of 50% H_3PO_2 solution is slowly dropped into the above solution. A black precipitate forms and settles to the bottom of the reaction vessel. The precipitate is filtered off and dried to produce about 386.5 grams of alloy powder. This powder is found to have an average particle size of about 0.3 micron. The particles, when subjected to a gradual increase in temperature are found to have a melting point of about 1400° C., the known melting temperature of an 80/20 Pd/Ag alloy as shown in the liquidus curve of Pd/Ag alloys.

By contrast, a mixture of finely divided Pd and Ag in the ratio of 80/20 shows a melting point of 960° C., the melting point of silver, and samples thereof heated to 1000° C., and cooled show the presence of discrete large balls of silver in finely divided palladium.

When the precipitated alloy powder is shaken with a 7% aqueous solution of nitric acid, the solution shows no presence of silver nitrate by the usual chloride test, whereas a mixture of finely divided Pd and Ag will, under the same circumstances, show the presence of silver nitrate.

EXAMPLE 2

310 grams of palladium sponge are dissolved in 5 liters of red, fuming nitric acid (Sp. gr. 1.53 g./cc.) at 50–60° C. The solution is allowed to cool. 77.5 grams of silver are then dissolved in the solution to give an 80/20 weight ratio of Pd/Ag in the solution. 7.1 liters concentrated ammonium hydroxide (Sp. gr. 0.9) are then slowly dropped into the solution changing the solution from brown through red and yellow to yellow-green. The pH of the solution is about 5.5.

1 liter of 50% H_3PO_2 solution is next slowly dropped into the above solution. A black precipitate forms and settles to the bottom of the reaction vessel. The precipitate is filtered off and dried, yielding 386.5 grams of alloy powder.

The powder has a melting point of about 1400° C., showing that it is an alloy of Pd and Ag rather than a mixture of the two. The average particle size of this powder is about 0.4 micron.

EXAMPLE 3

Example 2 is repeated but using 1 liter of a 50–50 mixture of sodium formate and sodium borohydride, both 50% aqueous solutions, as the reducing agent to reduce the palladium and silver nitrates to finely divided metal alloy powder. The resulting precipitate, by the tests above set forth in Examples 1 and 2, shows itself to be an alloy of palladium and silver and not a mixture of palladium particles and silver particles. In a series of examples, using the procedure of Example 2, palladium and silver of proportions varying from 5 to 90 parts Pd and 95 to 10 parts Ag were dissolved in nitric acid and reduced with H_3PO_2 . The resulting alloy particles contained proportions of Pd and Ag corresponding substantially to their content in the nitric acid solutions. These alloys had melting points corresponding with the melting points of Pd-Ag alloys on the known liquidus curve of Pd-Ag alloys.

Examples of different materials and amounts thereof used to form platinum-gold alloy powders are set forth below.

EXAMPLE 4

To obtain a 90% gold-10% platinum alloy, 24 grams of a PtCl_4 solution containing 32.67% platinum by analysis were mixed with 176 grams of an AuCl_3 solu-

tion containing 39.09% gold. The resulting solution was diluted to 2500 ml. and a solution of 50 grams of hydrazine hydrate in 1000 ml. of deionized water was dropped in with rapid stirring. A black precipitate of the gold and platinum alloy formed which was allowed to settle, washed with water by decantation, filtered off and dried. The observed melting point of this precipitate together with the theoretical melting point of a 90% gold-10% platinum alloy is set forth opposite Example 4 in Table IV.

Table IV also lists other platinum-gold alloys of various compositions which have been prepared by the same general method as set forth for Example 4, using the metal salt solutions of Example 4, but in different relative amounts and diluted to 2500 ml. The indicated reducing agents dissolved in 1000 ml. of deionized water in the amounts shown were used to precipitate the alloys. The observed melting points were obtained by placing a thermocouple in a furnace containing the test sample of the alloy and observing the temperature at which the first liquid appeared as the temperature inside the furnace was increased. The theoretical melting points were obtained from the literature.

TABLE IV

Example Number	Wt. of Pd Solution in gms.	Wt. of Au Solution in gms.	Percent Pd in Alloy	Reducing Agent and Amount Dissolved in 100 ml. of H ₂ O	Observed Melting Point, °C.	Melting Point (theor.), °C.
4.....	24	176	10	50 g. hydrazine hydrate.....	1,080	1,080
5.....	50	150	21.4	do.....	1,121	1,129
6.....	68	132	30	do.....	1,204	1,200
7.....	110	90	50	do.....	1,330	1,330
8.....	130	70	60	do.....	1,428	1,390
9.....	148	52	70	do.....	1,398	1,425
10.....	168	32	80	do.....	1,525	1,450
11.....	184	16	90	do.....	1,700	1,680
12.....	110	90	50	25 g. hydroquinone, 25 g. sodium borohydride.....	1,332	1,330
13.....	50	150	21.4	25 g. hydrazine sulfate, 25 g. sodium borohydride.....	1,127	1,129
14.....	110	90	50	25 g. sodium borohydride, 25 g. sulfurous acid.....	1,330	1,330
15.....	110	90	50	25 g. sodium sulfite, 25 g. sodium borohydride.....	1,337	1,330
16.....	110	90	50	25 g. sodium borohydride, 25 g. zinc dust.....	1,338	1,330
17 ¹	110	90	50	25 g. sodium hydrosulfite, 25 g. ferrous sulfate.....	1,341	1,330

¹ pH adjusted to about 5.5 with NaOH before adding reducing agent.

The observed melting point values demonstrate that the powder products formed are true alloys since their

was increased. The theoretical melting points were obtained from the literature.

TABLE V

Example Number	Wt. of Pd Solution in gms.	Wt. of Au Solution in gms.	Percent Pd in Alloy	Reducing Agent and Amount Dissolved in 100 ml. of H ₂ O	Observed Melting Point, °C.	Melting Point (theor.), °C.
18.....	15	85	10	4 g. hydrazine hydrate.....	1,175	1,200
19.....	27	73	20	do.....	1,360	1,350
20.....	40	60	30	do.....	1,403	1,400
21.....	50	50	40	do.....	1,454	1,450
22.....	60	40	50	do.....	1,490	1,475
23.....	70	30	60	do.....	1,495	1,500
24.....	77	23	70	do.....	1,515	1,520
25.....	87	13	80	do.....	1,541	1,540
26.....	93	7	90	do.....	1,570	1,550
27.....	60	40	50	2 g. hypophosphorous acid, 2 g. hydroquinone.....	1,482	1,475
28.....	60	40	50	2 g. hypophosphorous acid, 2 g. hydrazine sulfate.....	1,480	1,475
29.....	60	40	50	2 g. hypophosphorous acid, 2 g. sulfurous acid.....	1,490	1,475
30.....	60	40	50	2 g. hypophosphorous acid, 2 g. sodium sulfite.....	1,481	1,475
31.....	60	40	50	2 g. hypophosphorous acid, 2 g. zinc dust.....	1,476	1,475
32 ¹	60	40	50	2 g. sodium hydrosulfite, 2 g. ferrous sulfate.....	1,468	1,475

¹ pH adjusted to about 5.5 with NaOH before adding reducing agent.

melting points are within 35° C. of the theoretical values of the alloys. The observed melting points of the alloys are higher than 1062° C., the melting point of gold, further indicating that alloy particles and not mixtures of gold particles and platinum particles are formed.

Examples of different materials and amounts thereof used to form palladium-gold alloy powders are set forth below.

EXAMPLE 18

15 grams of a PdCl₂ solution containing 26% Pd by analysis were mixed with 85 grams of an AuCl₃ solution containing 39.08% Au so that the weight of palladium in the resulting solution equaled 10% of the total weight

of palladium and gold. The resulting solution was diluted to 250 ml. and a solution of 4 grams of hydrazine hydrate in 100 ml. of deionized water was dropped in with rapid stirring. A black precipitate of the gold-palladium alloy formed which was allowed to settle, washed with water by decantation, filtered off and dried.

The melting point of this alloy powder is set forth in the Table V opposite Example 18. Table V also lists other Pd-Au alloys of various compositions which were prepared by the same general method as set forth by Example 18, using the PdCl₂ and AuCl₃ solutions of Example 18 but in different relative amounts. The solution resulting from mixing the PdCl₂ and AuCl₃ solutions was in each case diluted to 250 ml. The reducing agents and the amounts thereof indicated in Table V dissolved in 100 ml. of deionized water were used to precipitate the alloys from the solutions.

The observed melting points were obtained by placing a thermocouple in a furnace containing the test sample of the alloy and observing the temperature at which the first liquid appeared as the temperature inside the furnace

The observed melting point values demonstrate that the powder products formed are true alloys since their melting points are within 35° C. of the theoretical values of the alloys. The observed melting points of the alloys are higher than 1062° C., the melting point of gold, further indicating that alloy particles and not mixtures of gold particles and palladium particles are formed.

Tables VI and VII set forth the particle size distribution of the powders of Examples 4 and 18, respectively. These powders were typical of average particle size and particle size distribution for the powders of the examples of tables IV and V. These particle size analyses were obtained by microscopic study of enlarged electron photographs to micrographs of the respective powders.

TABLE VI
Gold-platinum alloy powder

Particle size range, microns:	Percentage of particles within indicated size range	
0-0.1 -----	-----	2
0.1-1.0 -----	-----	5
1.0-2.0 -----	80 } -----	90
2.0-5.0 -----	10 } -----	4
5.0-10.0 -----	-----	3
>10.0 -----	-----	1

The average particle size was 0.3 micron.

TABLE VII
Gold-platinum alloy powder

Particle size range, microns:	Percentage of particles within indicated size range	
0-0.1 -----	None	15
0.1-1.0 -----	75 } -----	90
1.0-2.0 -----	15 } -----	20
2.0-5.0 -----	-----	4
5.0-10.0 -----	-----	4
> 10.0 -----	-----	2

The average particle size was 0.2 micron.

The alloy powders of this invention are characterized in being irregularly shaped, and having a small average size resulting in a high surface area to mass ratio and excellent conductive properties. By reason of the fact that 90% by count of the particles are within a close small size range, between 0.1 and 5.0 microns, settling and vertical classification of the particles during application and firing of the metalizing compound are reduced. More uniform high quality fired-on coatings can accordingly be produced with the metal powders of this invention. Average particle sizes of about 40 microns and smaller are necessary to enable screen printing thereof with 325 mesh screens.

The term "reducing agent" as used throughout the specification and claims is meant to include single substances which are capable of individually precipitating all of the metal constituents of the alloy to be formed as well as combinations of substances which together precipitate all of the metal constituents of the alloy to be formed.

Parts, percentages and proportions as herein disclosed unless otherwise stated relates to parts, percentages and proportions by weight.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited thereto except as set forth in the appended claims.

I claim:

1. The process for the production of a finely divided alloy consisting essentially of two noble metals, which metals form continuous series of solid solutions throughout their entire alloy composition range without the formation of compounds or eutectics which comprises forming a solution of compounds of the two noble metal constituents of the alloy to be formed with the two noble metal constituents present in approximately the same relative proportions that they are to be present in the alloy to be formed and with each of said two noble metal constituents constituting from 10-90% of the total amount of said two noble metal constituents, and mixing with said solution a reducing agent capable of simultaneously reducing the metal constituents of the compounds to their metals, whereby to precipitate alloy particles from the solution.

2. The process for the production of noble metal alloys consisting essentially of two noble metals selected from the group consisting of silver, gold, platinum and

palladium, which comprises preparing a solution of compounds of the two noble metal constituents of the noble metal alloy to be formed and with each of said two noble metal constituents constituting from 10-90% of the total amount of said two noble metal constituents, and mixing with said solution a reducing agent capable of simultaneously reducing the metal constituents of the compounds to their metals, whereby to precipitate alloy particles from the solution.

3. The process of claim 2 wherein the solution comprises dissolved compounds of platinum and gold.

4. The process of claim 3 wherein the reducing agent is hydrazine hydrate.

5. The process of claim 2 wherein the solution comprises dissolved compounds of palladium and gold.

6. The process of claim 5 wherein the reducing agent is hydrazine hydrate.

7. The process of claim 2 wherein the solution comprises dissolved compounds of palladium and silver.

8. The process of claim 7 wherein the reducing agent is hypophosphorous acid.

9. The process of claim 2 wherein the solution comprises dissolved compounds of silver and gold.

10. The process of claim 2 wherein the solution comprises dissolved compounds of platinum and palladium.

11. The process for the production of palladium-silver alloy which comprises preparing an acidic solution containing silver and palladium nitrates, and precipitating a finely divided alloy of Pd-Ag by the addition to said solution of a reducing agent that simultaneously reduces the silver and palladium nitrates to metal.

12. The process which comprises dissolving palladium and silver in concentrated nitric acid containing at least 3% excess NO_2 to form a solution of palladium and silver nitrates, adjusting the pH of the solution to between 4.5 and 6.5, and adding to said solution a reducing agent capable of simultaneously reducing said nitrates to their metals, whereby to precipitate Pd-Ag alloy particles from the solution.

13. The process of claim 12 in which the reducing agent is hypophosphorous acid.

14. The process for the production of palladium-silver alloy which comprises dissolving palladium in concentrated nitric acid containing at least 3% excess NO_2 , dissolving silver in said nitric acid, adding to the resulting nitric acid solution of palladium and silver nitrates a reducing agent capable of simultaneously reducing said palladium and silver nitrates to their metals.

15. The process which comprises dissolving palladium and silver in concentrated nitric acid containing at least 3% excess NO_2 to form a nitric acid solution of palladium and silver nitrates, and adding to said solution hypophosphorous acid whereby to precipitate Pd-Ag alloy particles from said solution.

16. The process of adding hypophosphorous acid to an acidic solution of palladium and silver nitrates whereby to precipitate from said solution finely divided Pd-Ag alloy particles containing palladium and silver in the same relative proportions in which they were present in said solution.

17. The process of claim 2 wherein the solution comprises dissolved compounds of platinum and silver.

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70 HYLAND BIZOT, *Primary Examiner*.

DAVID L. RECK, *Examiner*.

N. F. MARKVA, *Assistant Examiner*.

Disclaimer

3,390,981.—*Lewis C. Hoffman*, Wilmington, Del. METHOD FOR THE PRODUCTION OF FINELY DIVIDED METALS. Patent dated July 2, 1968. Disclaimer filed Apr. 30, 1976, by the assignee, *E. I. du Pont de Nemours and Company*.

Hereby enters this disclaimer to claims 1-7, 9-11, and 17 of said patent.

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