

[72] Inventor **Oliver A. Short**
Wilmington, Del.
 [21] Appl. No. **14,630**
 [22] Filed **Feb. 26, 1970**
 [45] Patented **Nov. 16, 1971**
 [73] Assignee **E. I. du Pont de Nemours and Company**
Wilmington, Del.
Continuation-in-part of application Ser. No. 873,055, Oct. 31, 1969, now abandoned, which is a continuation-in-part of application Ser. No. 705,305, Feb. 14, 1968, now abandoned, which is a continuation-in-part of application Ser. No. 626,394, Mar. 28, 1967, now abandoned. This application Feb. 26, 1970, Ser. No. 014,630

[51] Int. Cl. **B22f 9/00,**
C22b 11/04
 [50] Field of Search **75/0.5 A,**
108, 118, 121

[56] **References Cited**

UNITED STATES PATENTS

3,385,799	5/1968	Hoffman	75/0.5 A X
3,390,981	7/1968	Hoffman	75/0.5 A X
3,427,153	2/1969	Venkatesan et al.	75/108
3,443,933	5/1969	Boyhan et al.	75/108

Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—G. K. White
Attorney—John J. Klocko, III

[54] **PROCESS OF PREPARING NOBLE METAL ALLOY POWDERS**
6 Claims, No Drawings
 [52] U.S. Cl. **75/0.5 A,**
75/108, 75/118, 75/121

ABSTRACT: A method of preparing alloy powders which exhibit low, if any, catalytic activity. Acid chloride solutions of noble metals are prepared; the metal alloy is precipitated as an alloy-ammonia complex and then reduced to yield a relatively coarse noble metal alloy precipitate powder. The important process parameters include the particular chemical reagents utilized, pH control and the rates of precipitation and reduction.

PROCESS OF PREPARING NOBLE METAL ALLOY POWDERS

CROSS-REFERENCES TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Pat. application Ser. No. 873,055 filed Oct. 31, 1969, which is a continuation-in-part of U.S. Pat. application Ser. No. 705,305, filed Feb. 14, 1968, now abandoned, which is a continuation-in-part of U.S. Pat. application Ser. No. 626,394, filed Mar. 28, 1967, now abandoned.

BACKGROUND OF THE INVENTION

Commercially available noble metal powders, particularly platinum powders, prepared by conventional precipitation techniques are extremely fine (i.e., greater than 40 m.²/gm.) and catalytically active. As such, they are not extremely useful for use in printed circuits unless the powders are mixed with other metals or otherwise modified to (1) reduced catalytic activity during early stages of firing when organic vapors are present and (2) to prevent agglomeration of the very fine powders at the high temperatures of firing.

In general a new type of noble metal powder is needed which is fine enough to use in printed circuit inks but still coarse enough to inhibit catalytic activity and to production of printed circuits.

SUMMARY OF THE INVENTION.

This invention relates to a highly useful process for preparing noble metal alloy powders which are used in the formulation of metallizing compositions and to printed circuit components therefrom.

Accordingly, the process of this invention comprises (1) preparing an aqueous solution of at least two noble metal chlorides, (2) forming a coprecipitate from solution as a noble metal-ammonia complex by adding ammonium hydroxide to the solution until the pH of the solution is in the range of 9-11, and (3) reducing the noble metal-ammonia complex by adding a reducing agent from the group consisting of monohydrazine sulfate, dihydrazine sulfate, hydrazine hydrochloride, hydrazine hydrate and mixtures thereof, to the complex to yield noble metal alloy powder having an average surface area within the range of 0.1-20 m.²/gm.

The noble metal alloy powders produced by the process are used in metallizing compositions which can be printed and fired to form various electrical components. As is well known, the noble metals include gold, silver, platinum, palladium, ruthenium, rhodium, osmium and iridium

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The alloy powders may be prepared as follows:

sufficient metal compounds, preferably in the form of acidic chloride solutions, are mixed to produce the desired ratio of metals in the alloy to be formed. The metals are precipitated as hydroxides and ammonia complexes by adding diluted ammonium hydroxide until the pH is between 9 and 11. This complex is then reduced with a reducing agent from the group of monohydrazine sulfate, dihydrazine sulfate, hydrazine hydrochloride, hydrazine hydrate and mixtures thereof, to the complex to yield noble metal alloy powder having an average surface area within the range of 0.1-20 m.²/gm. The powder thus formed is filtered, washed free of ammonium hydroxide and ammonium chloride, and dried to yield the alloy powder.

The surface area of the alloy powder is a critical feature of this invention. As indicated above, the average surface area must be within the range of 0.1-20 m.²/gm. Alloy particles having a surface area less than 0.1 m.²/gm. produce either low capacitance, poor reproducibility and/or open circuits. On the other hand, alloy powders having a surface area greater than 20 m.²/gm. produce high viscosity dispersions (pastes) which cannot be screen printed. Powders finer than 20 m.²/gm. also have a tendency to "cake" and catalytically react with the vehicle and/or substrate. Therefore, the surface area of the

alloy powders must be within the critical range set forth above in order to be within the scope of this invention.

The important process parameters of this invention are the particular chemical reagents utilized (precipitating agent and reducing agent) the pH control of the precipitation step and the rates at which the precipitation and reduction are performed. While generally speaking, various other hydroxides, such as sodium hydroxide or potassium hydroxide, would precipitate the noble metal alloys from solution, it has been found that ammonium hydroxide is necessary to produce alloy particles having the desired surface area. In the reduction step, various other reducing agents such as ferrous sulfate would reduce the platinum. However, it has been found to be critical that only monohydrazine sulfate, dihydrazine sulfate, hydrazine hydrochloride, hydrazine hydrate, and mixtures thereof will produce noble metal alloys having the desired surface area.

One of the most important aspects of this invention is the pH control in the precipitation step. As previously stated, the pH must be within the range of 9-11 at the start of the reduction reaction; a preferred range is pH 10-11. If the pH is dropped to 8.5, little or no precipitate is obtained and, if a precipitate is obtained, the particle sizes (surface areas) are not within the desired range. When the pH is raised above 11, the precipitation and reduction reactions proceed very slowly, if at all, and the yield of noble metal is less than 50 percent in addition to producing particle sizes not within the desired range. After the reduction step it is also preferable, although not necessary, to add a sufficient quantity of ammonium hydroxide to the solution to return the pH to 10-11. This additional pH adjustment provides adequate settling of the precipitate and eases the decantation and washing procedures.

It is also important to control the rate at which the ammonium hydroxide is added to the noble metal chloride solution. Care must be taken to rapidly add the ammonium hydroxide. Generally, there appears to be a measure of control over the surface area (particle size) of the noble metal alloy; faster addition rates appear to produce coarser particles (in combination with the pH control), whereas slower addition rates produce finer, catalytic particles.

The following examples are given to illustrate in detail the preferred method of preparing noble metal alloy powders in accordance with the teachings of this invention; it is pointed out that these details are not to be taken as limitations of this invention.

EXAMPLE 1

Acidic chloride solutions of platinum, palladium and gold were prepared by dissolving platinum, palladium and gold metal in a mixture of nitric and hydrochloric acids (aqua regia) and subsequently decomposing the nitric acid by continued boiling and repeated additions of hydrochloric acid. A platinum-palladium-gold alloy was prepared from 40.4 grams of a 29.7 percent acidic platinum chloride solution, 24 grams of a 25 percent acidic palladium chloride, and 32.4 grams of a 37 percent acidic gold chloride solution. These were mixed and diluted to 200 ml. with water; Then 100 ml. of concentrated ammonia (28 percent), which was previously diluted with 150 ml. of water, was added to the solution of metals. At this point a precipitate was formed and the pH of the solution was 9.5. A solution of 25 grams dihydrazine sulfate in 500 ml. water was added to the metal hydroxide precipitate to effect reduction. The precipitate formed was washed free of chloride, filtered and dried to yield an alloy powder. The alloy contained 40 percent platinum, 20 percent palladium and 40 percent gold. An X-ray examination indicated alloy formation. The average particle size of the powders was about 3 m.²/gm.

By varying the relative amounts of the solution of the metal compounds used in example 1, above, alloy powders can be prepared by the method of this example having any desired metal ratios.

The metallizing compositions of the invention will usually, although not necessarily, be dispersed in an inert vehicle to form a paint or paste for application to ceramic dielectrics. The proportion of vehicle to solids (metal alloys, inorganic binder) may vary considerably depending upon the manner in which the paint or paste is to be applied and the kind of vehicle used. Generally, 10-90 percent by weight of vehicle will be used to produce a paint or paste of the desired consistency. Any liquid, preferably one that is inert towards the alloy powder, may be employed as the vehicle. Water or any of various organic liquids, with or without resin binders, thickening and/or stabilizing agents, and/or other common additives may be utilized as the vehicle. Examples of organic liquids that can be used are esters of higher alcohols, for example, the acetates and propionates; the terpenes such as pine oil, alpha- and beta-terpineol and the like; and solutions of resin binders such as the polymethacrylates of lower alcohols, or solutions of ethyl cellulose, and solvents such as pine oil and the monobutyl ether of ethylene glycol monoacetate (butyl-O-CH₂CH₂-OOCH₃). A preferred vehicle for use in this invention consists of: hydrogenated rosin, ethyl cellulose, beta-terpineol, and kerosene. Such vehicles are disclosed in my copending application, Ser. No 828,346, filed May 27, 1969, now U.S. Pat. No. 3,536,508. The vehicle may contain or be composed of volatile liquids to promote fast setting after applications; or it may contain waxes, thermoplastic resins or the like materials which are thermofluid so that the vehicle-containing composition may be applied at an elevated temperature to a relatively cold ceramic body upon which the composition sets immediately.

While metallizing compositions which are applied to green (unfired) dielectric substrates customarily consist essentially of metal powder and a vehicle, the metallizing compositions which are applied to prefired ceramic substrates usually contain an inorganic binder in addition to the metal powder and inert vehicle. Also, inorganic binders are used in resistor and conductor compositions. The inorganic binders used in the metallizing compositions of this invention may be composed of any glass or ceramic material which will melt at a temperature lower than the melting point of the alloy powder with which it is used and which will adhere well to the substrate onto which the metallizing composition is applied. The high melting point alloy powders used in the metallizing compositions of this invention will enable the metallizing compositions to be fired to higher temperatures than are possible when physical mixtures of the pure corresponding metals are used. It has been observed that greater adhesion to the substrate can be achieved with the higher temperatures which are made possible by the use of alloy powders. Any inorganic material which serves to bind the metals to the substrate can be used as the inorganic binder component. The inorganic binder can be any of the glass frits employed in metallizing compositions. Such frits are generally prepared by melting a glass batch composed of the desired metal oxides, or compounds which will produce the glass during melting, and pouring the melt into water. The coarse frit is then milled to a powder of the desired fineness. The patents to Larsen and Short, U.S. Pat. No. 2,822,279, and to Hoffman, U.S. Pat. No. 3,207,706, describe some frit compositions which can be employed either alone or in combination with glass wetting agents, such as bismuth oxide. Typical frit compositions usable as binders in the compositions of this invention include: lead borate, lead silicate, lead borosilicate, cadmium borate, lead-cadmium borosilicate, zinc borosilicate, and sodium-cadmium borosilicate frits. The average particle size of the inorganic binder should be no larger than 40 microns, preferably within the range of 1-5 microns.

When inorganic binders are present in the metallizing compositions, the binders should always be present in sufficient quantities to provide adequate adhesion, for example, in amounts equal to or in excess of 1 percent of the combined amount of alloy powder and inorganic binder, also known as the solids content of the metallizing composition. A desirable

range for the binder is from 1-95 percent of the combined weight of alloy powder and inorganic binder.

The present metallizing compositions which are used to form electrodes on capacitors, to form resistors or other conductors, comprise metal alloy particles which contain from 0.5-99 percent of at least three of the enumerated metals. At least 0.5 percent of each metal must be utilized to produce an excellent overall combination of electrical properties and low cost electrodes in addition to overcoming the deficiencies of the prior art. Correspondingly, the use of more than 99 percent of any metal would not produce the desired results.

The present metallizing compositions can be printed and fired on various types of ceramic dielectrics including those composed of forsterite, steatite, beryllium oxide, titanium oxide, barious titanate, alumina or zircon porcelain. Any other conventional unfired (green) dielectrics or prefired dielectrics can be used. Of course, their most important utility is for use on bismuth stannate-containing dielectrics, particularly dielectrics that contain at least 0.1 percent by weight of bismuth stannate.

The invention is further illustrated by the following examples. In the examples and elsewhere in the specification all parts, ratios and percentages of material or components are by weight.

Various metallizing compositions were prepared employing finely divided metal alloys (prepared in accordance with example 1) dispersed in an inert liquid vehicle. The surface areas of the metal alloys ranged from 1-5 m.²/gm. The inert liquid vehicle consisted of: 30 percent hydrogenated rosin, 6 percent ethyl cellulose, 2.5 percent beta-terpineol, and 61.5 percent kerosene. In all of the examples, the weight ratio of alloy powder to vehicle was 60 percent alloy metal: 40 percent vehicle. Capacitors, comprising at least one electrode and at least one counterelectrode having a ceramic dielectric material between the electrode and counterelectrode, wherein the electrode and counterelectrode comprise an alloy which was prepared from applying and firing the alloy metallizing compositions of this invention, were produced. The metallizing compositions were screen-printed on polymethyl methacrylate (PMA) resin bonded ceramic sheets. The sheets contained 10 percent PMA and 79.4 percent of barium strontium titanate with 10.6 percent bismuth stannate. Electrode prints were applied to all of the PMA sheets. For purposes of identification, the first electrode print is designated as the electrode; the second print is designated as counterelectrode, etc. After drying, eight printed sheets were stacked on top of each other. When the eight printed sheets had been stacked or "built up" and an unprinted top or cover sheet placed thereover, the stack was carefully compressed under a hydrolytic press at a pressure of about 10,000 p.s.i. Then the stack of sheets was fired to 2,300° F. (unless indicated otherwise) for several hours to form a monolithic capacitor structure. The particular alloys used and results obtained are described below in the examples.

EXAMPLE 2

An alloy containing 50 percent platinum, 25 percent palladium, and 25 percent gold was used. A satisfactory capacitor was produced.

EXAMPLE 3

An alloy containing 40 percent platinum, 20 percent palladium, and 40 percent gold was used. A satisfactory capacitor was produced.

EXAMPLE 4

An alloy containing 40 percent platinum, 30 percent palladium, and 30 percent gold was used. This composition performed satisfactorily and a good capacitor was produced. In comparison, an alloy powder, having the same metal constituents and proportions thereof, with an average surface area of 0.01 m.²/gm. was utilized to produce a capacitor as

described above. The capacitor had no capacitance and resulted in an open circuit. Also in contrast, a similar alloy powder having a surface area of 30 m.²/gm. was dispersed in the liquid vehicle. The paste was too viscous to screen print and caking occurred. Thus, alloy powders having surface areas outside of the critical range of this invention did not perform satisfactorily.

EXAMPLE 5

An alloy containing 94 percent gold, 5 percent mercury and 1 percent platinum was used. This alloy was applied to a PMA bonded low-fire glass-ceramic substrate and fired at 900°-1,000° C. A satisfactory capacitor was produced.

EXAMPLE 6

An alloy containing 98.5 percent gold, 1 percent platinum and 0.5 percent rhodium was used as described in example 5. A satisfactory capacitor was produced.

By using the teachings of this invention, metallizing compositions containing lower cost alloys can be printed and fired on bismuth stannate-containing dielectrics to form very satisfactory and commercially acceptable capacitors. The capacitors produced by this invention perform satisfactorily and do not undergo any blistering or other disruptions (e.g., delaminations). Of course, in addition to the preferred utility relating to capacitor electrodes, the present metallizing compositions can be used to make resistors and conductors for various electronic applications in accordance with conventional procedures, such as disclosed by D'Andrea, U.S. Pat. No. 2,924,540; Dumesnil, U.S. Pat. No. 3,052,573; and

Wagner, U.S. Pat. No 3,347,799.

I claim:

1. A process for the production of a noble metal alloy powder comprising (1) preparing an aqueous solution of at least two noble metal chlorides (2) forming a coprecipitate from solution as a noble metal-ammonia complex by adding ammonium hydroxide to the solution until the pH of the solution is in the range of 9-11, and (3) reducing the noble metal-ammonia complex by adding a reducing agent from the group consisting of monohydrazine sulfate, dihydrazine sulfate, hydrazine hydrochloride, hydrazine hydrate and mixtures thereof, to the complex to yield noble metal alloy powder having an average surface area within the range of 0.1-20 m.²/gm.

2. A process in accordance with claim 1 wherein the noble metal chlorides are gold chloride and palladium chloride, and the powder produced is a gold/palladium alloy.

3. A process in accordance with claim 1 wherein the noble metal chlorides are gold chloride, palladium chloride and platinum chloride, and the powder produced is a gold/palladium/platinum alloy.

4. A process in accordance with claim 1 wherein the noble metal chlorides are gold chloride an platinum chloride, and the powder produced is a gold/palladium alloy.

5. A process in accordance with claim 1 wherein the pH is also raised to 10-11 after the reduction step (3) by the addition of ammonium hydroxide.

6. A process in accordance with claim 5 wherein the ammonium hydroxide is rapidly added to the noble metal chloride solution.

* * * * *

35

40

45

50

55

60

65

70

75

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,620,714 Dated November 16, 1971

Inventor(s) Oliver A. Short

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 22, change "an" to -- and --; column 6, line 23, "gold/palladium" should be -- gold/platinum --.

Signed and sealed this 6th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents