United States Patent [19]

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[11] **3,725,308**

[45] **Apr. 3, 1973**

[54] ELECTRICALLY CONDUCTIVE MASS

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[22] Filed: **Dec. 10, 1968**

[21] Appl. No.: **782,758**

[52] **U.S. Cl.**.....**252/513,** 117/100 M, 117/130 E, 252/514

[51] **Int. Cl.**.....**H01b 1/02**

[58] **Field of Search**.....29/182.5; 75/212; 252/512, 252/513, 514; 117/100 M, 130 E

[56] **References Cited**

UNITED STATES PATENTS

3,598,761	8/1971	Woulbroun et al.	252/514
3,583,930	6/1971	Ehrreich et al.	252/514
3,171,817	3/1965	Lambert et al.	252/513
3,031,344	4/1962	Sher et al.	252/514
2,771,380	11/1956	Coleman et al.	252/514
2,470,352	5/1949	Holmes	252/514
1,820,591	8/1931	Andre	252/514
3,120,699	2/1964	Russo	29/182.5
2,418,812	4/1947	Girvin	29/182.5
2,358,326	9/1944	Hensel et al.	75/212
1,986,197	1/1935	Harshaw	75/212
1,051,814	1/1913	Lowendahl	29/182.5

FOREIGN PATENTS OR APPLICATIONS

710,371	5/1965	Canada	252/514

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[57] **ABSTRACT**

There is described a mass comprising finely divided particles of nickel or cobalt coated with gold or silver or platinum, and binder or matrix of organic or inorganic materials for holding the particles in contact with each other to provide a mass which is electrically conductive or semi-conductive and has properties approximating those of true gold or silver or platinum.

7 Claims, No Drawings

ELECTRICALLY CONDUCTIVE MASS

BACKGROUND OF THE INVENTION

The present invention relates to an electrically conductive mass as just described and, more particularly, to such a mass wherein the base metal particles are coated with the noble metal by electroless plating.

SUMMATION OF THE INVENTION

Accordingly, an object of the present invention is to provide an improved mass of the class described.

Another object is to provide such a mass wherein the particlescan be coated in an economical, efficient and rapid manner.

Another object is to provide such a mass which functions substantially like solid gold or silver or platinum but effects a considerable saving of these noble metals.

A further object is to provide such a mass wherein the particles have the electrically conductive properties of the noble metals and have the magnetic properties of nickel.

A still further object is to provide such a mass which can be produced as an adhesive, dispersion, paint, conductor or wire for printed circuits and a material for joining members by soldering or welding.

Other and further objects and advantages will become apparent from the description about to follow.

In accordance with the present invention, the foregoing objects are generally accomplished by coating nickel or cobalt particles with silver or gold or platinum in accordance with the processes about to be described, and binding the coated particles with an organic or inorganic material to produce the electrically conductive mass.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that gold can be electroless plated onto particles of nickel and cobalt or alloys of nickel or cobalt containing at least 50 percent of nickel or cobalt respectively by heating aqueous compositions containing potassium gold cyanide and ammonium chloride with or without sodium citrate and sodium hypophosphite.

Potassium, gold cyanide, $KAu(CN)_2$, has a solubility of 25 grams in 100 C.C. of water at 20°C. and 100 grams at 100°C.

Ammonium chloride NH_4Cl, has a solubility of 29.7 grams in 100 C.C. of water at 0°C. and 75.8 grams at 100°C.

Sodium citrate, $N_{a3}C_6H_5O_7.2H_2O$, has a solubility of 72 grams in 10 C.C. of water at 25°C.and 167 grams at 100°C.

Sodium hypophosphite, $N_aH_2PO_2H_2O$, has a solubility of 1.49 grams in 100 C.C. of water at 25°C. and 5.46 grams at 60°C.

Thus, these compounds possess more than adequate solubility in one liter of water.

These compounds therefore can be dissolved in one liter of water within the following ranges:

0.01 gram to saturation of gold cyanide
zero to saturation of ammonium chloride
zero to saturation of sodium citrate
zero to 15 grams of sodium hypophosphite

In the electrochemical potential series gold, nickel and cobalt have the following values:

Element	Absolute Standard Sign of Solution	Hydrogen Standard Sign of Electrode
Cobalt	−0.04	−0.23
Nickel	−0.05	−0.22
Gold	−1.35	+1.08

Thus, there is a substantial difference in potential between gold and nickel and gold and cobalt in an electrolytic solution to assure a good driving force through the electrolyte to deposit the gold on the nickel and cobalt.

EXAMPLE I

As already indicated, the proportions of the materials in the compositions may be varied considerably while still achieving electroless deposition of gold on nickel and cobalt. However, the following formula was found to be most efficient:

Water	1 liter
Potassium gold cyanide	6 grams
Ammonium chloride	30 grams
Sodium citrate	50 grams
Sodium hypophosphite	5 grams

After dissolving the compounds in the water in a receptacle with agitation, the solution is heated to between 94°C. and 98°C. At this temperature, 40 grams of about 20 micron average particle size nickel powder is stirred into the hot solution. Care must be taken that the solution is not boiling, because upon the addition of the nickel powder the volume of a boiling solution increases 250 percent due to excessive frothing.

As soon as all the nickel power is dispersed, the solution is brought to a boil and is agitated vigorously. After boiling for about 6 minutes, the solution turns greenish and the nickel powder turns goldish. The green color is an indication of spent solution. The heat then is removed and the gold-coated nickel powder is allowed to settle on the bottom of the receptacle.

The spent solution is decanted and the gold-coated nickel powder is rinsed with tap water by pouring the water on the powder and agitating the mixture vigorously for about one minute. The powder is allowed to settle and the rinse water is decanted. The rinsing operation is repeated in the same manner. The powder is then rinsed in alcohol, and is dried. After drying, the gold-coated nickel powder has the appearance of pure gold powder.

The dried gold-coated powder weighed 42.6 grams. In a more sophisticated procedure of separating the liquid phase and gold-coated powder, filtering can be employed, whereby the loss of powder that is washed away with water can be reduced to practically zero. Thus, if the procedure is operated at 100 percent efficiency with no powder lost in the decanting operations, the weight of the gold-coated powder should be 44.1 grams.

EXAMPLE II

The procedure described in Example I was repeated by adding to one liter of the solution 20 grams of nickel powder having a particle size of between 0.5 and 3.5 microns. The dried gold-coated powder weighed 22.7 grams. The weight of the powder to be coated is in inverse proportion to its surface area, that is, the finer powders have a greater surface area.

EXAMPLE III

The procedure described in Example I was repeated by adding to one liter of the solution 8 grams of cobalt powder having a particle size of between 0.5 and 3.5 microns. Upon boiling, the solution turns pinkish-brown, and the cobalt powder turns goldish. The dried gold-coated cobalt powder weighed 9.6 grams. At 100 percent efficiency, the weight of the gold-coated cobalt powder should have been 12.04 grams. Here again, if no gold-coated powder is lost in the decanting operations the efficiency would have been higher.

It has also been found that silver can be electroless plated onto particles of nickel and cobalt or alloys of nickel or cobalt containing at least 50 percent of nickel or cobalt respectively by heating aqueous compositions containing silver cyanide, potassium cyanide and potassium carbonate.

Silver cyanide, AgCN, is practically insoluble in water but, when complexed with potassium cyanide, becomes readily soluble.

Potassium cyanide, KCN, is very soluble both in cold and hot water.

Potassium carbonate, K_2CO_3, has a solubility of 112 grams in 100 cc of water at 20°C. and 156 grams at 100°C.

Thus, these compounds, when mixed, in the amounts specified herein, possess more than adequate solubility in one liter of water.

In the electrochemical potential series silver, nickel and cobalt have the following values:

Element	Absolute Standard Sign of Solution	Hydrogen Standard Sign of Electrode
Cobalt	−0.04	−0.23
Nickel	−0.05	−0.22
Silver	−1.04	+0.77

Thus, there is a substantial difference in potential between silver and nickel and silver and cobalt in an electrolytic solution to assure a good driving force through the electrolyte to deposit the silver on the nickel and cobalt.

EXAMPLE IV

An aqueous composition of the following formula was prepared from:

Water	1 liter
Silver Cyanide	56 grams
Potassium Cyanide	80 grams
Potassium Carbonate	15 grams

The potassium cyanide is dissolved first, then the potassium carbonate, and finally the silver cyanide is slowly stirred in.

The solution is heated in a receptacle to between 94°C. and 98°C. At this temperature, 40 grams of nickel powder having an average particle size of about 20 microns were stirred into the hot solution. Care must be taken that the solution is not boiling, because upon the addition of the nickel powder the volume of a boiling solution increases 250 percent due to excessive frothing.

As soon as all the nickel powder is dispersed with agitation, the solution is raised to a boil and begins to turn brownish in color, while the nickel powder turns silverish. After boiling and agitating for 7 minutes the solution is brown in color, and the nickel powder is coated with silver by electroless self-catalytic reduction.

At this point, the heat is withdrawn and the silver-coated nickel powder is allowed to settle. The spent solution is decanted and the silver-coated powder is rinsed with tap water with vigorous agitation for about one minute. The powder is allowed to settle and the rinse water is decanted. The rinsing operation is repeated in the same manner. The powder is then rinsed in alcohol, and is dried. After drying, the silver coated nickel powder has the appearance of pure silver powder.

The dried silver-coated nickel powder weighed 64.0 grams. In a more sophisticated procedure of separating the liquid phase and powder, filtering can be employed, whereby the loss of silver-coated powder that is washed away can be reduced to practically zero. Thus, if the procedure is operated at 100 percent efficiency with no powder lost in the decanting operations, the weight of the silver-coated powder should be 85.0 grams.

EXAMPLE V

The procedure described in Example I was repeated by adding to one liter of the solution 40 grams of cobalt powder having an average particle size of about 20 microns. Upon boiling, the solution turns blackish-green. As deposition of silver takes place, the solution turns olive green and the cobalt powder turns silverish. Boiling is continued for six minutes, whereupon the silver-coated cobalt powder has the appearance of pure silver.

The dried silver-coated cobalt powder weighed 64.12 grams. If there is no loss of powder during decanting, and the solution operates at 100 percent efficiency, the weight of the silver-coated cobalt powder should be 85.0 grams.

It further has been found that platinum can be electroless plated onto particles of nickel and cobalt or alloys of nickel or cobalt containing at least 50 percent of nickel or cobalt respectively by heating aqueous compositions containing platinum tetrachloride, ammonium chloride, sodium citrate and sodium hypophosphite.

Platinum tetrachloride, $PtCl_4$, is very soluble in cold water and hot water.

Ammonium chloride, NH_4Cl, has a solubility of 29.7 grams in 100 cc of water at 0°C. and 75.8 grams at 100°C.

Sodium citrate, $Na_3C_6H_5O_7.2H_2O$, has a solubility of 72 grams in 100 cc of water at 25°C. and 167 grams at 100°C.

Sodium hypophosphite, $N_aH_2PO_2H_2O$, has a solubility of 1.49 grams in 100 cc of water at 25°C. and 5.46 grams at 60°C.

Thus, these compounds possess more than adequate solubility in one liter of water.

In the electrochemical series, platinum, nickel and cobalt have the following values:

Element	Absolute Standard Sign of Solution	Hydrogen Standard Sign of Electrode
Cobalt	−0.04	−0.23
Nickel	−0.05	−0.22
Platinum	−1.13	+0.86

Thus, there is a substantial difference in potential between platinum and nickel and platinum and cobalt in an electrolyte to assure a good driving force through the electrolyte to deposit the platinum on the nickel and cobalt.

EXAMPLE VI

An aqueous composition of the following formula was prepared from:

Water	1 liter
Platinum tetrachloride	5 grams
Ammonium chloride	30 grams
Sodium citrate	50 grams
Sodium hypophosphite	5 grams

After dissolving the compounds in the water in a receptacle with agitation, the solution is heated to between 94°C. and 98°C. At this temperature 30 grams of nickel powder is dispersed in the solution. The solution is then heated to boil and is boiled for about three minutes. During this boiling period, the solution changes from yellowish green to black.

The platinum-coated nickel powder is rinsed and dried in the manner described in Example I.

EXAMPLE VII

The procedure described in Example II was repeated by adding to one liter of the solution 20 grams of cobalt powder.

After boiling for about three minutes the solution changes from yellowish green to black.

The examples about to follow illustrate specific conductive masses made with organic binders which have particular utilities. All parts are by weight.

EXAMPLE VIII

A compound was prepared consisting of nickel powder coated with gold and an epoxy resin made by the Glass Plastic Corporation of Linden, New Jersey. The trade name of this epoxy resin is "TITAN-TITE" clear epoxy resin.

High conductivity was achieved in a formulation of five parts of gold-coated nickel powder and one part of the epoxy resin; and six parts of nickel powder coated with gold and one part of the epoxy resin.

Similar compounds were prepared by using four parts of nickel powder coated with silver and one part of the above described epoxy resin; five parts of nickel powder coated with silver and one part of the epoxy resin; and six parts of nickel powder coated with silver and one part of the epoxy resin. The results in electrical conductivity were from good to excellent.

EXAMPLE IX

A copolymer was prepared for a conductive pressure responding adhesive having the composition about to be described:

a. From two to six parts chlorinated triphenyl made by the Monsanto Co., Organic Chemicals Div. of St. Louis, Missouri. The trade name of this plastic is "ARCHLOR 5442".

b. From three to seven parts chlorinated biphenyl made by the Monsanto Co., Organic Chemicals Div. of St. Louis, Missouri. The trade name of this compound is "ARCHLOR 1254".

c. From one to six parts amorphous polypropylene made by Eastman Chemical Products Inc. of Kingsport, Tenn. The trade name for this plastic is "EASTOBOND M-5H".

The components were placed in a pyrex glass dish and heat was applied. As the components began to liquify, they were agitated constantly. Finally all components liquified and stirring was continued until a homogeneous clear liquid appeared. One part of copolymer and from 3½ parts to 6½ parts of silver-coated nickel powder were compounded by mixing in the metal powder while the copolymer was in liquid state. On cooling, the copolymers solidify. A good to excellent conductive adhesive was obtained.

The same procedure was repeated with gold-coated nickel powder, one part of the above copolymer being compounded with from four and one-half parts to seven parts of nickel powder coated with gold.

EXAMPLE X

As it will be further demonstrated, varying proportions of components will produce copolymers of somewhat different properties. A procedure for formulating conductive adhesive paint is as follows:

Three parts of the above described copolymer (Example IX) and four parts of trichloroethylene are heated and stirred until a clear solution appears. Then twelve parts of coated metal powder are mixed in, such as nickel powder coated with gold or silver. When highly volatile trichloroethylene vaporizes, a thin conductive pressure-sensitive film remains. This conductive pressure-sensitive film may be very helpful in the simplification of assembly of very small electronic components, namely in microcircuitry.

EXAMPLE XI

The following copolymers were found to be good for formulating the organic matrices of soldering compounds:

a. Copolymer comprising:

Archlor 5442	employing	3 – 8 parts
Archlor 1254	"	1 – 5 parts
Eastobond M-5H	"	1 – 6 parts

b. Copolymer comprising 67 percent of ethylene and 33 percent of vinyl acetate made by E. I. duPont de Nemours Electrochemical Dept. of Wilmington, Del. The trade name is "ELVAX 150".

Elvax 150	employing	1.5 – 6 parts
Eastobond M-5H	"	1.5 – 5 parts
Archlor 5442	"	2 – 7 parts
Archlor 1254	"	2 – 6 parts

c. Copolymer comprising phenolic resin which is actually copolymer of phenol, formaldehyde, terpine made by Reichhold Chemicals, Inc. of White Plains, N.Y. The trade name for this compound is "SUPER BECKACITE 2100".

Super Beckacite 2100	employing	1.5 – 4.5 parts
Eastobond M-5H	"	1.0 – 5 parts
Archlor 5442	"	1.5 – 7 parts
Archlor 1254	"	2 – 6 parts

d. Copolymer comprising another phenolic resin, namely polymer of terpine phenol made by Reichhold

Chemicals, Inc. of White Plains, N.Y. The trade name for this compound is "SUPER BECKACITE 2000".

Super Beckacite 2000	contributing	1.5 – 5 parts
Eastobond M-5H	"	1 – 5 parts
Archlor 5442	"	5 – 7 parts
Archlor 1254	"	2 – 6 parts

e. Copolymer comprising one more phenolic resin particularly polymer of phenol formaldehyde made by Reichhold Chemicals, Inc. of White Plains, N.Y. The trade name for resin is "SUPER BECKACITE 1050".

Super Beckacite 1050	contributing	1.5 – 5 parts
Eastobond M-5H		1 – 5 parts
Archlor 5442		1.5 – 7 parts
Archlor 1254		2 – 6 parts

In all cases of the above enumerated formulas, the process of formulating is that all components of a given formula are placed in a pyrex container. Heat is applied and, as soon as melting of some components begins, agitation is begun. The heat and agitation are continued in every case until the liquid becomes clear and homogeneous.

These above given compositions of copolymers were compounded with nickel powder coated with gold or silver in various proportions ranging from three to seven parts of nickel powder coated with gold or silver to one part of any of the above given copolymer formulas.

EXAMPLE XII

Polyureas have been formulated into a conductive thermoset plastic by combining the following materials:

a. 0.84 parts of modified polyamine made by General Mills, Chemical Div. of Kankakee, Illinois. The trade name for this component is "AMINE-100".

b. 0.43 parts of xylene solvent

c. 3.8 parts of silver-coated nickel powder

The Amine-100 was mixed with the xylene and then silver-coated nickel powder was stirred in to provide part one.

Part two is prepared from diisocyanate made by General Mills Chemical Div. of Kankakee, Ill. The trade name for this compound is "D.D.I. 1410".

The formula is:

1.26 parts of D.D.I. 1410

0.60 parts of Toulene solvent

6.3 parts of silver-coated nickel powder

These components are mixed in the same order as they are listed. It is understood that nickel powder coated with gold can be substituted for nickel powder coated with silver.

Parts one and two are kept separate until such time as it is required for thermoset conductive plastic, then they are mixed in a 1:1 ratio.

EXAMPLE XIII

Polyamide and epoxy have been formulated with nickel powder coated with gold and also nickel powder coated with silver.

The polyamide resin is a reaction product of linoleic acid and polyamine made by General Mills Chemical Div. of Kankakee, Ill. The trade name of this resin is "-VERSAMID 115".

The epoxy chemically is diglycidyl ether of bisphenol A made by General Mills Chemical Div. of Kankakee, Ill. The trade name for this particular type of epoxy is "GENEPOXY 190".

The formula is:

a. Genopoxy 190	0.5 parts
b. Versamid 115	0.5 parts
c. Gold-coated nickel powder	6 parts

EXAMPLE XIV

Tar epoxy is described by U.S. Pat. No. 2,765,288 and is manufactured by U.S. Steel Chemicals Div. U.S. Steel Corp. of Pittsburgh, Pa. The trade name for this resin is "TARSET STANDARD".

The formula is:

a. 0.84 parts of Tarset Standard

b. 0.24 parts of Tinner

c. 0.014 parts of Tarset Harmer

d. 1.8 parts of Trichloroethylene

e. 6.4 parts of nickel powder coated with silver

All components are combined in the order they are enumerated. One component is admixed at one time.

The examples about to follow illustrate specific conductive masses including inorganic binders and having particular utility. All parts are by weight.

EXAMPLE XV

Portland cement chemically is $3CaO.SiO_2$ and 2 CaO . SiO_2 with minor proportion of 3 Ca O . Al_2O3 and 4 Ca O . Al_2O_3 — Fe_2O_3 made by Atlas Cement Div. of U.S. Steel of Pittsburgh, Pa.

One part of Portland cement was mixed dry with seven parts of nickel powder coated with gold. To this mix, one part of water was admixed.

Another composition comprised one part of Portland cement, seven parts of nickel powder coated with silver mixed well in a dry state. To this mixture, four partsof water were added.

EXAMPLE XVI

Soluble silicates are excellent binders.

Potassium silicate in aqueous solution is composed of potassium oxide K_2O 12.50 percent, and silicon dioxide $SiO_2$26.3 percent. Such a solution is manufactured by Philadelphia Quartz Co. of Philadelphia, Pa. under the trade name of "KASIL No. 6".

A compound was prepared by mixing one part of Kasil No. 6 with one part of water and then mixing 0.75 parts of the above solution with seven parts of nickel powder coated with gold.

Another compound was prepared by mixing one part of Kasil No. 6 with two parts of water and then adding five parts of nickel powder coated with silver.

When the above compounds are heated to 400°C. the binder becomes glass.

Still another compound was prepared by dry mixing 0.5 parts of a potassium silicate powder sold under the trade name of KASIL SS with six parts of nickel powder coated with silver. Then, three parts of boiling water were added, and the mixture was heated gently for one-half minute.

EXAMPLE XVII

One part of flowers of sulphur (U.S.P.) was mixed thoroughly dry with seven parts of nickel powder coated with gold. The mixture was heated to a temperature of between 115°C. and 120°C. in order to fuse the sulphur.

Sulphur was found to be an excellent binder.

Cursory tests demonstrated that gold, silver and platinum coated powders can be used interchangeably to produce the masses described in Examples VIII to XVII.

Gold or silver coated nickel and cobalt powder can also be prepared by the following procedures for use in the masses described in Examples VIII to XVII.

Vacuum Coating Method

The necessary amount of nickel or cobalt powder is suspended in the vacuum metalizing chamber.

The chamber pressure is reduced to 2×10^{-5} mm. of mercury. This is in order to prevent oxidation of the metallic vapors.

The gold or silver metal is evaporated from the electrically-heated tungsten coils.

The nickel or cobalt powder falls by gravity into atmosphere composed of gold or silver vapors, and since the nickel or cobalt powder has a much lower termperature, the gold or silver vapors condense on its surface, thus coating the individual powder particles with gold or silver as the case may be.

Method of Coating Using Organometallic Chemicals

The method is somewhat similar to the vacuum chamber method.

Organometallic molecules are decomposed by heat and condense on falling cobalt or nickel powder, thus coating particles with gold or silver.

Method of Coating by Electroplating

Standard gold or silver electroplating solutions are used for this purpose.

The nickel or cobalt powder is dispensed on conductive conveyor cathodes. Parallel to conveyor cathodes are placed anodes maintaining the required distance.

At the end of this cathode conveyor powder is dropped on to other conveyor and thus is turned over.

The other cathode conveyor moves in the other direction.

At the end of the second cathode conveyor powder is carried out of plating tank for cleaning and drying.

EXAMPLE XVIII

The conductivity of the mass may be increased by eliminating the binder and compressing the same. For example, coated particles of the prior examples may be compressed by a punch and die set and/or sintered in a vacuum oven to provide the required configuration for use as a contact disc.

What is claimed is:

1. An electrically conductive mass consisting essentially of 1 finely divided particles of nickel or cobalt or alloys of nickel or cobalt containing at least 50 percent nickel or cobalt electroless coated with gold or silver to capsulate the particles and 2 a binder for holding the coated particles in contact with each other to provide an electrically conductive path.

2. A mass according to claim 1, which is in solid state.

3. A mass according to claim 1, in which the binder is a liquid.

4. A mass according to claim 1, in which the binder is a contact adhesive.

5. A mass according to claim 1, in which the binder is a water glass.

6. A mass according to claim 1, wherein the binder is sulphur.

7. A mass according to claim 6, including about seven parts by weight of the particles and about one part by weight of sulphur.

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