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3,511,683

METHOD OF ELECTROLESSLY DEPOSITING
METALS ON PARTICLESWilton F. Espenscheid and Israel J. Heilwell, Princeton,
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24 Claims

ABSTRACT OF THE DISCLOSURE

This specification discloses a method for depositing a metal on a high surface area colloidal substrate. The substrate particles may consist entirely of, or may be a nonmetal having a surface coating of, a metal which is, in the electromotive series, above the metal to be deposited on them. The method involves dissolving a compound on the metal to be deposited on the substrate in a nonaqueous anhydrous solvent and adding the substrate to the resulting solution. In a specific embodiment, there is first deposited electrolessly on the substrate particles a reactive metal which is, in the electromotive series, above the metal to be deposited on them from the nonaqueous anhydrous solvent.

CROSS-REFERENCE TO RELATED APPLICATION

The operation of electroless deposition, as described herein, is also disclosed in copending application, Ser. No. 647,344, filed June 20, 1967, and certain products of the method of said application are useful as substrates for the present invention.

BACKGROUND OF THE INVENTION

(1) The field of the invention comprises metal deposition, including a method for the same and the resulting product.

(2) So far as is known, the deposition of metals like platinum, either electrolessly or electrolytically, on a substrate comprising particles in the colloid size range, is not described in the literature, patent or otherwise. The method disclosed herein, comprising the immersion deposition of these metals in a nonaqueous solution, provides a novel means of obtaining colloidal particles coated with the metals.

SUMMARY OF THE INVENTION

Platinum and similar metals are deposited on colloidal particles composed entirely or partly of metal by immersion deposition in nonaqueous solutions. The substrate particles have outer surfaces comprising a reactive metal which is above platinum in the EMF series, and on immersion of the same in a nonaqueous solution of a suitable platinum compound, they become coated by replacement of the reactive metal by platinum.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

The invention is of particular value in providing for the deposition of platinum on high surface area colloidal particles for, as indicated, the published literature does not disclose a way which accomplishes this result. The product is contemplated as having considerable importance in, among other applications, fuel cell and zinc-air battery technologies by permitting a decrease in platinum concentration presently required for air electrodes. In the field of catalysis, the avoidance of the aqueous phase in the preparation of the metal-coated particles enables active metals to be deposited, such as the alkali and alkaline earth metals, and at the same time decrease the effects of any adverse surface chemistry of the substrate

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or of the deposit itself during deposition of metal thereon.

Platinum is one of a group of metals that either cannot be deposited on high surface area substrate particles, or can be deposited only with difficulty. Other metals of this group include palladium, ruthenium, rhodium, iridium, and osmium, which together with platinum are sometimes referred to as the platinum series of metals. Also included are Group VIII metals generally. Although depositable with more ease, metals like silver, gold, and Group I-B metals are useful in the invention. For these, the invention offers a way of depositing them on the described substrates. Other suitable metals are the alkali and alkaline earth metals which are too active to be deposited from aqueous solutions. Also contemplated are the less active metals like titanium, molybdenum, zirconium, tungsten, lead, tin, hafnium vanadium and germanium, which, although thermodynamically capable of depositing from aqueous solutions, do not do so because of solvation effects and the nonreactivity of their ions. In general, the depositable metals are those which form compounds soluble in the nonaqueous solvent and which, in the EMF series of metals, lie below the reactive metal of which the surfaces of the substrate are composed. Preferred metals to be deposited are platinum, and the other members of the platinum series. It should be understood that more than one metal may be deposited; thus two or more metals may be deposited together or one after another to form layered deposits.

Compounds of the metal to be deposited include inorganic salts like platinum tetrachloride, palladium dichloride, silver perchlorate, ferric chloride, stannic chloride, stannous chloride, gold chloride, etc. Also suitable are organometallic compounds conventionally used as petroleum additives, comprising metal salts of alkyl, aryl, and alkyl-aryl dithiophosphates, sulfonates, sulfates, carboxylates, phosphonates, phosphates, phenates, etc., the metal moiety of which is a metal of the groups described. Other useful metal compounds are coordinated metal derivatives of olefins, acetylenes, and aromatics, as may be illustrated by such compounds as octadiene complexes of gold; silver acetylide; bis-acrylonitrile-metal derivatives; tris (pi-allyl)iridium; (arene)tungsten(CO)₃ complexes where arene may be benzene, toluene, p-xylene, mesitylene, etc. The metal compound may be used alone or in admixture with one or more other such compounds. It will be understood that the metal compound selected from the foregoing is soluble in the non-aqueous solvents contemplated herein.

The useful non-aqueous solvents for dissolving the metal compounds include both cyclic and aliphatic compounds. The cyclics comprise aromatics like benzene, toluene, the xylenes, ethylbenzene, propylbenzene, the trimethylbenzenes, cymene, etc.; cycloalkanes like cyclohexane, methylcyclohexane, cyclopentane, etc.; heterocyclics like pyridine, furan, the picolines, etc. Aliphatics preferably include such polar compounds as hydrazine; the alkyl formamides; alkyl sulfones and sulfoxides; alkyl halides; and various organic derivatives of carbonic acid like ethylene or propylene carbonates, etc. These solvents, which are normally liquid, may be used singly or in combinations of two or more. Also useful are liquefied sulfur dioxide, ammonia, hydrogen sulfide, phosgene, etc. The presence of conventional auxiliary agents in the solution is frequently helpful, such as a mixture of acetic acid and acetic acid anhydride, or the latter alone, which helps to maintain anhydrous conditions and to insure uniform adhering films of deposited metal. Other useful conventional auxiliary agents or modifiers for promoting deposition are phosphorodithioic acid; alkyl and aryl sulfonic acids and mixed alkyl-aryl sulfonic acids; and ethylenediamine and derivatives.

The high surface area substrate particles may, as noted, be entirely or partly of metal; in any event they have outer surfaces composed of a reactive metal which, in the EMF series, is above the metal of the metal compound dissolved in the nonaqueous solvent. Particles entirely of metal may be chosen from any suitable metal that is obtainable in the colloid size range, including metals from Groups I-A, I-B, II-A, II-B, III-B, IV-B, V-B, VI-B, VII-B, VIII, III-A, IV-A, and V-A of the Periodic Table. In this connection, the colloid size range is considered to include particles having a diameter of 1 to 1000 millimicrons, or 10 to 10,000 angstrom units. A preferred size range is 25 to 500, more preferably 50 to 200, angstrom units. As the substrate, when coated with metal, comprises the product, the latter may determine the choice of such substrate characteristics as size, material, shape, etc.

Particles made partly of a nonmetal and partly of a metal may be obtained in accordance with the electroless deposition method described and claimed in said copending application Ser. No. 647,344, filed June 20, 1967, and as illustrated in Examples 2, 3 and 4 below. According to this method, colloid size particles of material like alumina are brought in contact with a sensitizing agent like stannous chloride to sensitize the particle surfaces; the particles are removed and freed of excess agent and then contacted with an activating agent such as palladium dichloride which forms palladium on the surfaces. Such palladium functions as a catalyst for the next step, wherein the particles, after removal of excess activating agent, are mixed with a reducible salt of a metal of Groups I-B, II-B, VI-B, and VIII and with a reducing agent therefor, such as a mixture of nickel sulfate and sodium hypophosphite, thereby to reduce such salt to form free nickel and to deposit such nickel on the particle surfaces. The resulting particles, which comprise a core of alumina and an outer shell of nickel, may then be subjected to immersion deposition as described herein. Besides alumina, other inorganic oxides, particularly refractory oxides, may serve as the substrate or core, such as silica, silica-alumina, titania, thoria, zinc oxide, vanadia, chromia, zirconia, molybdena, etc.; also materials like carbon black, graphite, cellulose, glass, etc.; crystalline aluminosilicate molecular sieves, natural and synthetic; polymers like the polyolefins, fluorinated hydrocarbon polymers, polyethers, polyamides, polysulfones, polystyrenes, vinyl polymers, acrylic polymers, and various natural and synthetic resins. Particularly suitable are monodisperse particles like those of rutile and polystyrene latexes, i.e., particles that are very uniform, with the ratio of the diameters of the largest to the smallest particles not being larger than about 2:1. Instead of using a sensitizing agent like stannous chloride, it is feasible, as disclosed in the aforementioned copending application, to use a vaporous agent like hydrazine, thereby to avoid an excess. Furthermore, suitable metal-coated particles may be produced according to a modification, also disclosed in said copending application, wherein the substrate particles, after treatment with the activating agent such as the palladium salt, are taken as the product; they thus comprise a core of nonmetallic material having a thin shell of palladium or other activating metal.

The method of immersion deposition comprises dissolving the metal compound in the solvent, adding one or more auxiliary agents of the type described, and dispersing the substrate particles in the solution. Deposition of the metal of the metal compound on the substrate usually begins immediately, and at room temperatures, although higher temperatures, going up to refluxing, and even lower temperatures are suitable. Times of deposition are variable, depending on the desired thickness of deposit; thus they may extend for a minute or two to 1, 2, or 24 hours or more. Concentrations of metal compound in the solution are preferably saturation concentrations but it will be understood that lower concentrations are useful, going down to 1%, or less, by weight. Concentrations of the auxiliary agents are usually only 1 to 5% of that of the

metal compound. The substrate surfaces should, of course, be clean, and it may be observed that an advantage of using nonaqueous solutions is that a separate degreasing step is not generally required as the solvent can accomplish this operation during the deposition.

It will be understood that the action of depositing a metal on the substrate by immersion deposition involves a replacement of the metal of the metal compound by the metal of the substrate surfaces, provided of course that the metal of the compound is below that of the substrate surfaces in the EMF series. In the immersion deposition solution a potential difference exists between the two metals which increases as the metals are more and more removed from each other in the EMF series. The metal higher up in the series is frequently described as more active, or less noble, or anodic, while the metal lower in the series is characterized as less active, or more noble, or cathodic.

At the end of the deposition, the coated particles are separated from the solution, as by centrifugation or filtration through a fine filter, washed and dried, and taken as product. It has a strongly adhering deposit of less active or more noble metal, the thickness of which may vary from a monolayer or two, or even a partial monolayer, up to several microns, depending on the time of contact of the substrate with the solution, the temperature, the concentration of metal compound, and the porosity of the substrate particle surfaces. Generally, thickness increases with time of contact, increases with increasing temperature and concentration, and increases with increasing porosity of the substrate. Adherence may be varied by use of different modifiers and substrates, and by varying the thickness, the adherence increasing as the thickness decreases. The amount of deposit may range from less than 0.001 to 5 or 10%, or even to 50%, preferably 0.001 to 1 or 2%, by weight of the coated particle. The product particles do not exhibit any substantial irreversible coagulation; especially is this the case when monodisperse substrate particles, like polystyrene, are used. The color of the product particles varies, depending on the deposited metal. It may be added that the particles are conveniently handled in the form of suspensions.

As described, the product is particularly useful as a catalyst, it being understood that the deposited metal is one known to be catalytic for a desired reaction. This property is enhanced by the form of the product, i.e., by the fact that the metal may be in the form of very thin films, including monolayers, and partial monolayers, and because of the extremely large surface area which the product particles may exhibit. Where the product particles have a core of nonmetallic material, particularly a refractory inorganic oxide, it is pertinent to note that the surfaces of this core, by virtue of using a nonaqueous immersion deposition solution, are not affected as they might be in the presence of aqueous solutions; thus with aqueous solutions such surfaces are modified by hydrolysis, hydration, and/or ion adsorption, with consequent adverse effects on a metal deposited thereover, particularly on its catalytic activity, adhesion, and the like.

The factors of thin films and high surface area are also of significance in other applications like fuel cell electrodes, filter material, deposition material for photographic films, paint pigments, inks, conducting plastics and magnetic microstructures for magnetic tapes or drums or discs.

Metal alloys may be deposited on a substrate by using two or more suitable metal compounds in the immersion deposition solution; for example, by using a mixture of platinum chloride and palladium chloride, an alloy of platinum and palladium may be deposited; a mixture of silver perchlorate and palladium chloride gives an alloy of silver and palladium; a mixture of stannic chloride and silver perchlorate gives an alloy of tin and silver; a mixture of stannic chloride and a zinc dithiophosphate gives an alloy of tin and zinc; a mixture of silver perchlorate, platinum chloride, and palladium chloride gives an alloy of silver, platinum, and palladium.

If desired, the outermost metal layer of the product may be coated over by immersion deposition, using a different metal compound in the deposition solution than the previous compound; or such product may be subjected to electroless deposition, followed or not by immersion deposition. In other words, the product is reusable in the invention like other substrates.

The invention is illustrated by the following examples.

EXAMPLE 1

Colloidal copper powder in an amount of 0.2 g. was dispersed in 15 ml. benzene that had been previously dried over a 5-angstrom crystalline aluminosilicate molecular sieve. Then 0.2 g. silver perchlorate was added, with agitation. The copper powder turned black, indicating a deposition of silver, in about 3 minutes.

EXAMPLE 2

Platinum was deposited on colloidal carbon black using electroless deposition followed by immersion deposition. First, 10 g. carbon black of 125 sq. m./g. surface area was sensitized by treatment with 1 liter of an aqueous solution containing 5 g. stannous chloride and 40 ml. concentrated HCl. The resulting suspension was filtered through a 0.45 micron millipore membrane filter and then washed carefully, with filtration between washings, with 3 liters distilled water. The wet particles were dispersed in 1 liter of an aqueous solution containing 0.5 ml. of a 10% palladium dichloride solution and 1 ml. concentrated HCl, and after separation of the particles, they were washed in the manner described. The wet particles were next dispersed in 1 liter of an aqueous solution containing 5 g. copper sulfate, 7 g. caustic soda, 10 g. of a 37% w./v. solution of formaldehyde, and 25 g. of sodium potassium tartrate (Rochelle salt). The particles were separated and carefully washed with 4 liters distilled water followed by 500 ml. acetone and finally air dried. Then 1 g. of the resulting copper-coated carbon black particles was placed in 10 ml. benzene containing 0.4 ml. acetic acid and 0.4 ml. acetic acid anhydride and 0.1 g. platinum tetrachloride and left overnight. The particles were separated, washed with distilled water, then with acetone, and dried. Based on emission spectroscopic analysis, the particles had a metal content of 2% platinum and 0.8% copper.

EXAMPLE 3

Platinum was deposited on high surface area graphite particles by using the procedure of Example 2 except that graphite of surface area 235 sq. m./g., corresponding to a particle size of less than 130 angstroms, was employed instead of carbon black. Analysis showed the presence of 2.5% platinum and 0.7% copper by weight.

EXAMPLE 4

Platinum was deposited on high surface area alumina particles using the procedure of Example 2 except that colloidal alumina of 275 sq. m./g. surface area was used instead of carbon black, and high speed centrifugation instead of filtration. Analysis showed the presence of 1% platinum and 3% copper by weight on the particles.

EXAMPLE 5

Chemically pure mossy zinc was immersed in 10 ml. of benzene containing 0.2 ml. concentrated acetic acid, 0.2 ml. acetic acid anhydride, and enough platinum tetrachloride to saturate. A modifier, 0.1 g. of triethylenediamine, was also present. A black strongly adhering deposit of platinum was obtained.

EXAMPLE 6

Mossy zinc as in the preceding example was immersed in 10 ml. benzene containing 0.2 ml. acetic acid anhydride, 0.1 g. di-dodecyl-naphthalene sulfonic acid, and 0.1 g. lead diisopropylphosphorodithioate. After 24 hours a strongly adhering lead deposit formed on the zinc.

EXAMPLE 7

A small piece of sodium was cut under dry benzene to expose a fresh surface and to remove any excess moisture. Then 0.2 g. of silver perchlorate was dissolved in dry benzene and added to the first-mentioned benzene. Deposition of silver on the sodium took place immediately.

The periodic table classifications used herein are based on the arrangement distributed by E. H. Sargent & Co. and further identified by the legend "Copyright 1962 Dyna-Slide Co."

In forming the solution for immersion deposition, the sequence of addition of the metal compound, solvent, and substrate is not material.

In the light of the foregoing description, the following is claimed.

1. Method for depositing a metal on high surface area colloidal substrate particles comprising dissolving a compound of said metal in a nonaqueous anhydrous solvent in which said metal compound is soluble, adding to the resulting nonaqueous anhydrous solution said substrate particles, said substrate particles having at least the outer surfaces thereof comprised of a reactive metal which is above said first mentioned metal in the electromotive series, and thereby depositing said first mentioned metal on said substrate particles.

2. Method of claim 1 wherein said first metal mentioned is a platinum metal.

3. Method of claim 1 wherein said substrate particles are comprised entirely of said reactive metal.

4. Method of claim 1 wherein each substrate particle is comprised of a core of a nonmetal and an outer shell of said reactive metal.

5. Method of claim 4 wherein said particles are made by electrolessly depositing on said core a shell of said reactive metal.

6. Method of claim 5 wherein said substrate particles are monodisperse.

7. Method of claim 1 wherein said reactive metal is an alkali metal.

8. Method of claim 1 wherein said reactive metal is an alkaline earth metal.

9. Method of claim 1 wherein said reactive metal is selected from the group comprising titanium, zirconium, molybdenum, tungsten, germanium, lead, tin, hafnium, and vanadium.

10. Method for depositing platinum on high surface area colloidal substrate particles comprising electrolessly depositing on the particles a reactive metal which is above platinum in the electromotive series, then adding the particles to an anhydrous solution of a platinum compound dissolved in a non-aqueous solvent, and thereby depositing platinum on the particles.

11. Method of claim 10 wherein said electroless deposition comprises the steps of sensitizing the substrate, then activating the same, then treating the same with a reducible salt of a reactive metal, reducing said salt to form free reactive metal, and depositing said reactive metal on the substrate.

12. Method of claim 11 wherein said sensitizing step is carried out with a vaporous sensitizing agent.

13. Method for depositing a metal on high surface area colloidal substrate particles comprising electrolessly depositing on the particles a reactive metal which is above said first mentioned metal in the electromotive series, then bringing the particles into contact with a solution of a compound of said first mentioned metal dissolved in a nonaqueous anhydrous solvent, and thereby depositing said first mentioned metal on the particles.

14. Method of claim 13 wherein said substrate particles are monodisperse.

15. Method of claim 14 wherein said substrate particles are comprised of a nonmetal.

16. Method of claim 15 wherein said substrate particles are comprised of carbon black.

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17. Method of claim 16 wherein said reactive metal is copper.

18. Method of claim 17 wherein said first mentioned metal is platinum.

19. Method of claim 15 wherein said substrate particles are comprised of graphite.

20. Method of claim 19 wherein said reactive metal is copper.

21. Method of claim 20 wherein said first mentioned metal is platinum.

22. Method of claim 15 wherein said substrate particles are comprised of alumina.

23. Method of claim 22 wherein said reactive metal is copper.

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24. Method of claim 23 wherein said first mentioned metal is platinum.

References Cited

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WILLIAM D. MARTIN, Primary Examiner

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U.S. Cl. X.R.

117—71, 100, 113, 124, 138.8, 130

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,511,683

Dated May 12, 1970

Inventor(s) Wilton F. Espenscheid and Israel J. Heilweil

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

Column 1, line 4, "Heilwell" should read --Heilweil--.

Column 2, line 35, "dithiophoesphates" should read

--dithiophosphates--.

Column 4, line 17, "in" should read --is--.

Column 5, line 74, "diisocpropylphosphorodithioate" should read --diisopropylphosphorodithioate--.

Column 6, line 27 (claim 2), "first metal mentioned" should read --first mentioned metal--;

line 47 (claim 10), "depositiing" should read --depositing--;

line 72 (claim 15), "Method of claim 14" should read --Method of claim 13--.

Column 8, the following References should be cited:

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2,898,228	8/59	Kelley	117-47
3,148,072	9/64	West et al	117-130X
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3,420,680	1/69	Gulla	117-71

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