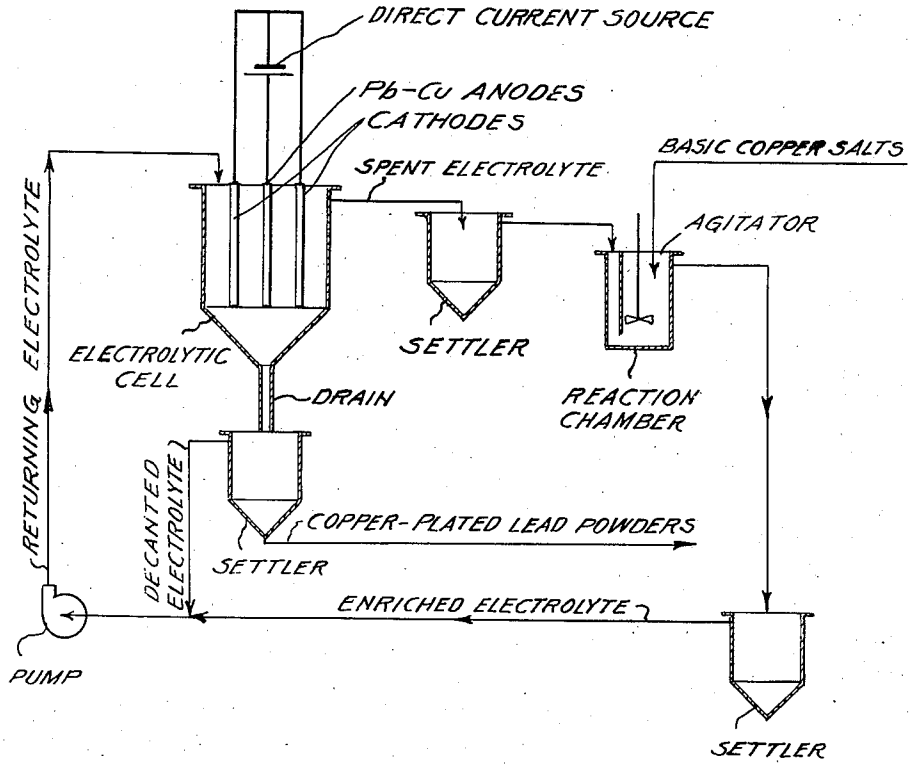
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PRODUCTION OF METAL POWDERS

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PRODUCTION OF METAL POWDERS

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This invention relates to the production of metal powders and particularly to the production of metal powder particles which have cores and coatings of dissimilar metals. The invention contemplates especially the production of copper-coated lead powders, i. e., plated metal powder particles on which the plating is of a metal standing lower than the metal of the core in an electromotive force series of metals, and the inhibition of crystal growth of the lead powders.

Any element in such a series tends to plate out of solution on a metal of the series which is less electropositive, i, e., upon a metal which stands higher in the series. For example, if metallic iron is introduced into a solution of copper sulfate the iron replaces the copper in the solution with the result that metallic copper is precipitated. A replacement reaction of this character is characterized industrially as a process of "cementation" and the precipitate is known as a cement.

The cementation processes have been employed heretofore for the production of plated metal powder particles having coatings of a metal which is lower in an electromotive series than the metal of the cores. Thus, it is proposed in United States Patent No. 2,033,240, granted March 10, 1936, to Charles Hardy, to produce copper-coated lead powders for use in the manufacture of heat-resistant bearings by stirring lead powder in a solution of a copper salt, say copper acetate. Copper-coated lead powders made by a cementation process as described in the aforementioned patent are of satisfactory quality. There is, however, a marked disadvantage of such a cementation process in that it makes as a by-product a salt of the less electropositive metal. Thus lead acetate is formed when lead powder is stirred into a solution of copper acetate. The by-product, if discarded, represents a loss of valuable material. On the other hand, the cost of recovering the by-product, especially if the recovery operation is conducted on a small scale, may be more than the value of the by-product.

As a result of my investigation I have discovered that it is possible to produce copper plated lead powder particles without making a salt of the less electropositive metal (lead) as a by-product. This is accomplished by conducting a cementation reaction in an acetate electrolyte in an electrolytic cell, and passing current through the solution in the cell so as to precipitate as a powder the less electropositive metal (lead), which thus forms nuclei upon which the more electropositive metal (copper) precipitates as a coating. In this way, the concentration of the less electropositive metal (lead) in the solution is kept from increasing, and the cores for the plated metal powders are formed in situ. The production of plated metal powders is thus greatly simplified and it becomes unnecessary to introduce the lead into the process in powder form and also unnecessary either to discard a valuble solution of a salt of the lead or to subject it to a separate recovery operation.

The density of the current introduced into the solution while cementation is taking place should be sufficiently high to cause the lead to precipitate as a powder, rather than in massive form.

My invention will be more completely understood in the light of the following detailed description of my invention with particular reference to the production of copper-coated lead powders where it is particularly useful, because of the difficulties ordinarily encountered in attempting to produce a lead powder from a cheap solution of a lead salt by electrolytic means. Efforts to obtain satisfactory lead powders by subjecting lead perchlorate electrolytes, lead acetate electrolytes, lead persulphate electrolytes, lead chloride electrolytes and alkaline lead cyanide electrolytes to electrolysis have not been markedly successful. Lead powders satisfactory for some purposes may be obtained by subjecting these solutions of these relatively cheap lead salts to electrolysis, but the powders thus produced are generally unsatisfactory as a base for making copper-plated lead powders or the like. The lead tends to precipitate as long acicular crystals or as flat plates. Particles of such shape are less satisfactory than the shapes which approach the cube or sphere. There is, moreover, a tendency for the formation of crystals which are too large to be employed successfully in powder metallurgy, where a great deal depends upon using fine powders in order to obtain a dense mass of accurate configuration with a minimum amount of heat and pressure applied to the powders. Thirdly, the lead precipitated from such electrolytes either contains a substantial quantity of oxidized lead as it is formed or becomes excessively oxidized before it can be washed and freed of the excess electrolyte. A fourth and from a commercial standpoint the greatest difficulty is that lead powders produced from the aforementioned cheap electrolytes tend to mat into an impervious mass which is difficult if not impossible to wash or to separate into its discrete particles.

However, I have discovered that when a small amount of a soluble copper salt is present in an

aqueous acetate electrolyte, satisfactory copper-coated lead powders are formed at relatively low current density, and the tendency for the formation of acicular or platy powders or powders which form impervious mats is not observed. Moreover, the lead particles are substantially evenly coated with copper and are not oxidized to an appreciable extent.

Copper salts in aqueous acetate baths in which lead powders are being formed electrolytically apparently act to restrain the crystal growth of the lead particles. It has been known previously that certain organic materials, principally colloids such as glue, may act as crystal-growth retarders or restraining agents in the electrorefining or deposition of metals. However, insofar as I am aware, it has not been known heretofore that the salt of one metal will act to restrain the crystal growth of another and less electro-positive metal during the electro-deposition of the latter.

The following example illustrates the restraining influence exerted by copper salts in acetate electrolytes upon crystal growth of lead powders during electrodeposition of the latter and also illustrates the production of copper-coated lead powders in an electrolytic cell by a process which eliminates the addition of separately formed lead powders to a copper salt solution and the subsequent discard or treatment of a lead salt solution to extract its lead content either in massive form or as lead powder to be returned.

An electrolytic cell was employed in which anodes and cathodes were hung vertically. The cathodes were of sheet nickel, although copper, lead, or other suitable materials may be employed. If contamination of the product with a small amount of iron can be tolerated, cheap sheet iron can be used for cathodes.

The anodes employed were rods of copper and of desilverized lead hung side by side between the cathodes in the proportions indicated.

A means for removing the copper-coated lead powder from the bottom of the cell was provided. The powder, after removal from the cell, was washed with distilled water to free it of entrained salts. The wash water entrained by the powder was replaced by alcohol and the powder was then dried. High drying temperatures should be avoided because of the low melting point of the lead.

EXAMPLE

Electrolyte

	Grams per liter
Lead acetate	94.8
Copper acetate	49.9
Acetic acid	15.0
Sodium chloride	2.0

Anodes

4 copper rods
1 lead rod of same size and surface as each copper rod

Anode current density—amps. per sq. ft.	8.8
Cathode current density—do	17.6
Current efficiency—percent	22.2
Power consumed, kilowatt hours per pound of metal deposited	1.5

The current density employed in this example proved to be the most satisfactory for the particular electrolyte. The copper-coated lead powder produced was of small and uniform particle size and apparently uniformly coated. The tendency for depletion of copper in the electrolyte was not very pronounced.

A series of tests conducted along the lines of the foregoing example showed that there is a tendency for copper to deposit out of the electrolyte faster than it is replenished from the soluble copper anodes and at a rate out of proportion with that at which the lead is deposited. This tendency may be overcome by employing one or more of the following four remedies.

(1) Inclusion in the electrolyte of an anode corroding agent capable of giving chloride ions in solution, such as soluble chlorides or hydrochloric acid, to increase the rate at which copper is dissolved at the anode. Sodium chloride in small amounts is beneficial. There is danger, however, in that excessive quantities of sodium chloride in the electrolyte may lead to the contamination of the deposit with insoluble lead chloride.

If there is a tendency for the copper content of the electrolyte to become depleted, this is to some extent compensated by an increase of dissolution of lead at the anode, so that in part the depleted copper content is replaced by lead. However, as the copper content of the electrolyte decreases in the cell, the acid content generally increases, so that in effect hydrogen ion is replacing the copper ion in the bath.

(2) Increasing the ratio of exposed copper anode surface to exposed lead anode surface in the bath. This has a tendency to increase the corrosion rate of the copper as compared with the corrosion rate of lead at the anode. Control by this means is, however, limited by the amount of copper which can be tolerated in the copper-coated powder. As the copper surface at the anode is increased and the lead surface decreased the proportion of copper in the powder deposited increases. To produce powder containing no more than 60% copper the ratio of copper surface to lead surface at the anodes preferably should not exceed 4 to 1.

(3) Adjusting of the current density. In general, the higher the current density at the anode the greater is the tendency for dissolution of copper to occur. This effect is accompanied, however, by an increase in the rate at which copper is deposited from the solution. Moreover, there is a limit to the current density that may be employed in any particular case which is set by the particle size desired. Increased current densities apparently operate to increase particle size.

4. Offsetting the tendency of the copper content of the electrolyte to decrease by adding soluble copper to the electrolyte from an outside source. As already indicated, the acid content of the electrolyte increases as the copper content decreases. This increased acid content may be neutralized by employing basic salts of copper. The salts most satisfactory from a commercial standpoint are the carbonates, hydroxides, and oxides of copper. These salts are cheap and do not introduce a foreign basic radical into the electrolyte. This fourth method of control is preferable in that it is more flexible than the others.

Accordingly, it is desirable to withdraw the electrolyte from the cell either periodically or continuously, and to add to the withdrawn electrolyte a basic salt of copper, whereby the acid content of the electrolyte is reduced and the copper content is replenished. Thereafter the electrolyte is separated from any excess of the basic copper salt and returned to the cell. It is possi-

ble to conduct the reaction between the basic salt of copper and the acid in the electrolyte within the cell, but preferable to conduct it elsewhere to avoid contaminating the deposit with unconsumed basic salt or disturbing the action of the cell by the evolution of reaction products such as carbon dioxide generated by the action of acid upon copper carbonate.

The following practice was found to be preferable for the production of a copper-coated lead powder containing about 60% Cu, 40% Pb by weight and of a particle size such that substantially all of the powder will pass through a screen having 200 meshes to the linear inch (Tyler scale).

An aqueous electrolyte is prepared at the inception of the operation by dissolving about 100 grams of lead acetate, 50 grams of copper acetate, 15 grams of acetic acid and at least 2 grams of sodium chloride in each liter of water. Any compound which will give chloride ions in solution may be used in place of sodium chloride.

Direct current is passed through the electrolyte in a cell equipped with soluble lead and soluble copper anodes or an anode containing both lead and copper arranged so that the exposed surface area of the copper within the electrolyte is about four times that of the exposed surface area of the lead in the electrolyte. Rods of copper and of desilverized lead hung vertically in the cell have proved to be satisfactory.

The cathode from which the plated powder migrates may be of any suitable conductive material which does not tend to corrode with deleterious contamination of the electrolyte. Copper and nickel are preferred materials. Iron may be used if contamination of the electrolyte can be tolerated.

The form of the cell should be such that anodes and cathodes may be easily inspected and, if necessary, scraped to remove deposits. A cell of the type that is employed to produce copper powders by electrodeposition is preferable. However, almost any cell may be employed provided that it permits inspection and occasional scraping of anode and cathode, and is provided with means for withdrawing the powder formed before it has had an opportunity to oxidize excessively.

A reaction chamber should be provided with means such as a pump for circulating the electrolyte from the cell to the reaction chamber and back again. The reaction chamber should be provided with an agitator so that the basic salt of copper, preferably an oxide or carbonate in finely divided form, may be caused to react quickly and thoroughly with free acid in the electrolyte thereby increasing the copper content and decreasing the free acid content of the latter. The amount of copper salt added should be such as to maintain the copper and acid content of the electrolyte in the neighborhood of its original composition.

As a safeguard against the contamination of the electrolyte in the cell with an undissolved excess of the basic salt or of insoluble impurities therein, the electrolyte from the reaction chamber should be sent through an appropriate filter, settling device or the like before it is returned to the cell.

In the event that a settling chamber or filter is employed for trapping solids from the outlet of the reaction chamber, the circulation through the cell should be gentle or a settling chamber or filter should be employed at its outlet toward the reaction chamber, to avoid losing metal powder from the cell or causing metal powder to be trapped together with other solids at the outlet of the reaction chamber.

The accompanying single figure is a diagrammatic flow sheet of the installation required for carrying out the above-described preferred practice.

I claim:

1. In the manufacture of copper-coated lead powder in which copper is plated from a solution upon particles of lead, the improvement which comprises passing a direct current through an aqueous acetate electrolyte containing acetic acid and relatively large proportions of copper and of lead in solution in an electrolytic cell containing a cathode, a lead anode, and a copper anode, maintaining the cathode current density in excess of that at which lead deposits from the electrolyte in massive form so that the lead deposits from the electrolyte as substantially non-adherent fine particles and said particles become plated with copper from the solution and controlling the ratio of copper to lead in the resulting copper-coated lead particles by varying the ratio of exposed copper anode surface in the solution to exposed lead anode surface in the solution.

2. In the manufacture of copper-coated lead particles in which copper is plated from a solution upon particles of lead, the improvement which comprises passing a direct current through an aqueous acetate electrolyte containing acetic acid and relatively large proportions of copper and of lead in solution and a relatively small proportion of a water-soluble chloride in solution in an electrolytic cell containing a cathode, a copper anode and a lead anode, maintaining the cathode current density in excess of that at which lead deposits from the electrolyte in massive form, whereby the lead deposits as substantially non-adherent fine particles and said particles become plated with copper from the electrolyte, reacting the resulting acid spent electrolyte with a basic salt of copper and thereafter returning the resulting replenished electrolyte to the electrolytic cell.

3. In the manufacture of copper-coated lead powder in which copper is plated from a solution upon particles of lead, the improvement which comprises passing a direct current through an aqueous acetate solution containing acetic acid and relatively large proportions of copper and of lead in solution and a relatively small proportion of a water-soluble chloride in solution in an electrolytic cell containing a cathode, a lead anode and a copper anode, maintaining the cathode current density in excess of that at which lead deposits from the solution in massive form so that the lead deposits as substantially non-adherent fine particles and said particles become plated with copper from the solution, and maintaining the anode current density substantially less than the cathode current density.

4. In the manufacture of copper-coated lead powder in which copper is plated from a solution upon particles of lead, the improvement which comprises passing a direct current through an aqueous acetate electrolyte containing acetic acid and relatively large proportions of copper and of lead in solution in an electrolytic cell containing a cathode and maintaining the cathode current density in excess of that at which a massive deposit is formed from the electrolyte, whereby the lead deposits as substantially non-adherent fine

particles and said particles become plated with copper from the electrolyte.

5. In the manufacture of copper-coated lead powder in which copper is plated from a solution upon particles of lead, the improvement which comprises passing a direct current through an aqueous acetate electrolyte containing copper acetate, lead acetate and acetic acid in relatively large proportions in an electrolytic cell containing a cathode and maintaining the cathode current density in excess of that at which the lead deposits in massive form at the cathode, whereby the lead deposits as substantially non-adherent fine particles and said particles become plated with copper from the electrolyte.

6. In the manufacture of copper-coated lead powder in which copper is plated from a solution on particles of lead, the improvement which comprises subjecting to electrolysis in a cell containing a cathode in aqueous acetate solution containing about 100 grams per liter of lead acetate, 50 grams per liter of copper acetate, and 15 grams per liter of acetic acid at a cathode current density in excess of that at which the lead deposits at the cathode in massive form.

7. In the manufacture of copper-coated lead powder in which copper is plated from solution on particles of lead, the improvement which comprises subjecting to electrolysis in a cell containing a cathode an aqueous acetate electrolyte containing acetic acid relatively large proportions of dissolved copper and lead, said electrolysis being conducted at a cathode current density in excess of that at which the lead deposits at the cathode in massive form, the lead depositing as particles at the cathode and passing through the electrolyte to a lower portion of the cell, the particles of lead being coated with copper, and removing the resulting copper-coated lead powder from the cell.

8. In the manufacture of copper-coated lead powders in which copper is plated from solution onto particles of lead, the improvement which comprises subjecting to electrolysis in a cell having a cathode an aqueous acetate solution containing about 100 grams per liter of lead acetate, 50 grams per liter of copper acetate, and 15 grams per liter of acetic acid at a cathode current density of about 17.6 amperes per square foot.

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