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METHOD OF PRODUCING FINELY DIVIDED METALLIC PRODUCTS

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This invention relates to a method of obtaining metals in a pulverized or finely divided condition, and more specifically to a method of obtaining metals in a finely divided condition such as is suitable for use as a paint pigment or other purpose for which a fine state of division is required or advantageous.

The method of this invention is particularly useful for the production of copper in finely divided or pulverized condition for use as a paint pigment.

The invention may also be utilized for the production of alloys of copper and other metals such as zinc, and it will be understood that references to the use or treatment of copper, in the following general description and in the appended claims, are intended to include either copper alone or copper in conjunction with another metal, and that references to the formation of a metallic product comprising copper are intended to include either copper alone or an alloy containing copper.

The principal object of the invention is to provide a novel and advantageous method for producing finely divided metallic products comprising copper, and particularly for the production of such finely divided metallic products adapted for use as paint pigments.

A particular object of the invention is to provide a simple and economical process for the above purpose, in which a relatively small expenditure of power is required for reducing the metal to the desired state of division for use.

A further object of the invention is to provide a method for obtaining such finely divided metallic products of a high state of purity and freedom from oxidation.

A further object of the invention is to provide for the production of a finely divided metallic pigment material in pure condition, either alone or in suspension in a liquid paint vehicle.

A further object of the invention is to provide for the production of copper alloys in pulverized or finely divided condition.

Other objects of this invention will be either pointed out hereinafter or will be apparent from the following description of the invention and of certain specific embodiments thereof.

In carrying out the invention, I form an amalgam of copper (or copper and another metal) with mercury, by any suitable amalgamating method; then heat the amalgam to distil off the mercury, leaving a metallic residue containing the copper (either alone or alloyed with said other metal) in a spongy or more or less loosely coherent and easily disintegrated form; and then mechanically break up said metallic residue to reduce it to the desired finely divided condition, as by grinding or pulverizing in any suitable manner.

The physical structure of the metallic residue remaining after distillation of the mercury is quite porous or spongy, comprising, a thin-walled metallic skeleton penetrated throughout by fine voids or pores, and has relatively little mechanical strength, so that only a relatively light grinding or pulverizing action is required to reduce this residue to the form of finely divided metallic particles.

The formation of a copper amalgam may be carried out in any suitable or well-known manner, such as by electrolytic deposition from solution containing a copper salt, using metallic mercury as a cathode, or by chemical reduction and precipitation of the copper from such a solution in the presence of mercury, or by bringing the copper, preferably in divided condition, into contact with mercury in any desired manner.

The proportion of copper introduced into the amalgam may be varied between wide limits. As the concentration of amalgamated metal in the mercury amalgam increases, the fluidity of the amalgam decreases, and I have carried out the process using amalgams of various concentrations, ranging from fluid to substantially solid amalgams. In general, however, I have found that the best results are obtained by using an amalgam of a plastic, pasty, or semi-fluid consistency, and I therefore prefer to use an amalgam of such a consistency, particularly where the amalgam is apt to be contaminated by impurities, since an amalgam of this concentration is susceptible to purification by washing, puddling, or working the same, as hereinafter described. It will be appreciated, however, that the amount of metal recovered in an actual embodiment of the process is dependent upon the concentration of the metal in the amalgam, and I therefore prefer to use as high a concentration as is consistent with other requirements of the process. In the case of copper alone, I have found that the optimum proportions are about eleven parts of copper to eighty-nine parts of mercury by weight, at which concentration the amalgam may be puddled or worked for removal of impurities, although it is to be understood that the invention is by no means limited to these proportions.

The amalgam formed as above described may, if desired, be purified, as by washing with

water or other solvent, or by puddling, working, or agitating the same, either alone or in the presence of water or other liquid or fluent medium. In some cases, the impurities present may be agglomerated as a scum or sludge at the surface of the amalgam by simply puddling or working the amalgam, and the sludge thus formed may be separated. The addition of a suitable viscous material, such as a heavy grease, during the puddling operation, is in some cases advantageous, to assist in the elimination of impurities from the amalgam. The amalgam may, if desired, be ground or otherwise worked to break up crusts of solidified amalgam which may have been formed, as in cases where the mercury is not thoroughly agitated during the amalgamation, and a suitable inert liquid may be added during this grinding or working operation, to prevent oxidation of the amalgam.

After preparation of the amalgam, and after any necessary or desirable treatment thereof to remove impurities or to produce an amalgam of uniform consistency, the amalgam is introduced into a retort or other vessel and heated to distil off the mercury, the varporized mercury being preferably recovered by condensation.

The temperature during the distillation operation should be held below the point at which the residual copper might fuse sufficiently to impair subsequent reduction of the metallic mass to a pulverized condition. The distillation may be carried out under atmospheric pressure, or under any desired higher or lower pressure. In order to provide complete vaporization of the mercury, the mass may be heated to a temperature considerably above the boiling point of mercury at the pressure employed, during the later stages of the operation. Also, a suitable inert gas may be introduced into the retort, particularly toward the end of the distilling operation, to facilitate the removal of the mercury vapor and to displace or expel the last traces of mercury remaining in the retort.

After the distillation of the mercury is completed, the spongy metallic copper residue may be removed from the retort, cooled, and ground in any suitable manner, for example, in a pebble mill. The grinding should preferably be so conducted as to avoid contamination or damaging of the metallic product. The grinding may be carried out either dry or in the presence of a liquid medium, preferably an organic liquid, for the purpose of preventing oxidation, or facilitating the grinding, or for the purpose of forming a suspension or mixture of the finely divided product in said liquid medium for some certain use. For example, in preparing the metal for use as a paint pigment, the metallic residue from the retort may be ground with suitable oils or materials known to the art as paint vehicles, such as lacquer, varnish, linseed oil, so-called banana oil, etc. As an example of a substance other than a paint vehicle which may advantageously be employed during the grinding of the metal for protection from oxidation, a volatile liquid hydrocarbon such as gasoline has been found to be very satisfactory. After grinding in the presence of gasoline or the like, the metal may be separated therefrom in any suitable manner, as by allowing the same to settle, removing the clear liquid from above and exhausting the remainder of the gasoline by evaporation, leaving the metal in substantially pure and finely divided form.

In applying the process for the production of an alloy, such as an alloy of copper and zinc, or copper and any other amalgamable metal or metals adapted to form an alloy with copper, the procedure is similar to that above described, except that an amalgam, containing the two or more desired metals in proper proportions, is prepared and subjected to distillation to drive off the mercury. Such an amalgam may be prepared in various ways. For example, the different metals may be brought successively or simultaneously into contact with a body of mercury to form an amalgam containing said metals in the desired proportions, either by electrolytic deposition using a mercury cathode, by chemical reduction and precipitation, or by other known means. Alternatively, I may form separate amalgams of the different metals with mercury in any of the ways above mentioned, and then combine these amalgams in the desired proportions. The remaining steps of the process, including any necessary purification or other treatment of the amalgam, the distillation of the mercury, and the reduction of the spongy metallic residue to finely divided condition, may be carried out in substantially the same manner as above described. It is thus seen that various copper alloys, containing different proportions of the two or more constituent metals, in finely divided condition, may be produced by the method of this invention, the composition of the final metallic product being controlled by the relative amounts of the different metals introduced into the amalgam. Products formed in this manner have the characteristics of true alloys. Alloys of copper and zinc so formed were examined under the miscroscope and showed a homogeneous combination of the two metals.

In one particular laboratory operation, a copper amalgam was formed by electrolytic deposition of copper upon a mercury cathode, using a liter beaker having a diameter of about four inches as the electrolytic cell. Metallic mercury was placed in the bottom of the cell to a depth of about one quarter inch, and a heavy copper plate suspended parallel to and about two inches above the surface of the mercury. A nearly saturated solution of copper sulphate and water containing some free sulphuric acid was placed in the cell to a depth of about four inches. The mercury was employed as the cathode, connecting same to the negative terminal of a six volt battery by a copper wire in contact with the mercury but insulated from the electrolyte by means of a glass tube. The suspended copper plate served as the anode, being connected to the positive terminal of the battery. The deposition of copper with the mercury was effected by maintaining a current density at the rate of about eight amperes per square foot of exposed mercury surface. The copper deposition was continued with intermittent stirring of the amalgam until the amalgam became fairly stiff. The copper amalgam was then removed from the electroyltic cell and ground to break up crusts of amalgam that former at the upper surface of the mercury between periods of stirring. A small amount of butyl alcohol was added to the mill charge during grinding to protect the amalgam against oxidation. After grinding, the amalgam was placed in a retort and heated sufficiently to expel the mercury. The mercury was recovered by condensing the vapor from the retort. After cooling, the metallic residue was removed from the retort and ground in a pebble mill in the presence of gasoline. The pulverized metal was removed from the mill and separated from the

major portion of the gasoline by allowing the metal to settle and removing the clear gasoline from above. Part of the pulverized metal was mixed with a clear lacquer and used as paint. The product from this particular operation appeared to be in the form of crystalline or flaky masses averaging about .02 mm. in size.

In another laboratory operation, an alloy of zinc and copper was obtained. In this operation, the two metals were deposited electrolytically with the mercury separately; the copper being deposited from a copper sulphate solution and the zinc from a zinc sulphate solution. After depositing the desired amounts of the metals, the amalgam was separated from the aqueous solution, washed and puddled to remove certain impurities and then subjected to distillation in a retort for removal of the mercury. The metallic spongy residue from the retort, having a characteristic color of dull light yellow brass, was broken up by grinding in a pebble mill in the presence of just sufficient gasoline to form a metallic paste. After grinding, the pulverized metal was removed from the mill by flushing out with gasoline. The metal was removed from the gasoline by the procedure described in the foregoing example.

I claim:

1. A method of making a finely divided metallic product which comprises forming an amalgam containing copper and mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising said copper, and grinding said spongy metallic residue to form a finely divided product.

2. A method of making a finely divided metallic product which comprises forming an amalgam containing copper and mercury by electrolytic deposition of said copper, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising said copper, and grinding said spongy metallic residue to form a finely divided product suitable for use as a paint pigment.

3. A method of making a finely divided metallic product which comprises forming an amalgam containing copper and mercury, subjecting the amalgam to a puddling operation to remove impurities, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising said copper, and grinding said spongy metallic residue to form a finely divided product.

4. A method of making a finely divided metallic product which comprises forming an amalgam containing copper and mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising said copper, and grinding said spongy metallic residue in the presence of an organic liquid to form a finely divided product.

5. In a method of making a finely divided product, the steps which comprise: subjecting an amalgam containing copper and mercury to distillation to remove the mercury under such conditions as to form a spongy and easily disintegrated metallic residue; and grinding said spongy metallic residue in the presence of an organic liquid to form a finely divided product.

6. A method of making a finely divided copper alloy which comprises forming an amalgam of copper and another metal with mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising an alloy containing said copper and said other metal, and grinding said spongy metallic residue to form a finely divided product.

7. A method of making a finely divided copper alloy which comprises: forming an amalgam of copper and another metal with mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising an alloy containing said copper and said other metal, and grinding said spongy metallic residue in the presence of an organic liquid to form a finely divided product.

8. A method of making a finely divided copper alloy which comprises successively contacting copper and another metal with mercury to form an amalgam containing copper and said other metal, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising an alloy containing said copper and said other metal, and grinding said spongy metallic residue to form a finely divided product.

9. A method of making a finely divided copper alloy which comprises forming an amalgam of copper with mercury, separately forming an amalgam of another metal with mercury, combining said amalgams to form an amalgam containing copper and said other metal, distilling the mercury from the combined amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising an alloy containing said copper and said other metal, and grinding said spongy metallic residue to form a finely divided product.

10. A method of making a finely divided copper alloy which comprises: forming an amalgam of copper and another or metal by electrolytic deposition of copper and said other metal in contact with mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising an alloy containing said copper and said other metal, and grinding said spongy metallic residue to form a finely divided product.

11. A method of making a finely divided copper alloy which comprises successively electrolytically depositing copper and another metal in contact with mercury to form an amalgam containing copper and said other metal, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising an alloy containing said copper and said other metal, and grinding said spongy metallic residue to form a finely divided product.

12. A method of making a finely divided metallic product which comprises forming separate amalgams of copper and another metal with mercury by separate electrolytic deposition of copper and said other metal in contact with mercury, combining said amalgams to form an amalgam containing copper and said other metal, distilling the mercury from the combined amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising an alloy containing said copper and said other metal, and grinding said spongy metallic residue to form a finely divided product.

13. A method of making a finely divided product which comprises: forming an amalgam containing copper and mercury, distilling the mercury from said amalgam under such conditions

as to form a spongy and easily disintegrated metallic residue comprising said copper, grinding said spongy metallic residue in the presence of a volatile organic liquid capable of preventing oxidation of said metallic residue, to form a finely divided metallic product, and separating said organic liquid from said metallic product.

14. A method of making finely divided copper which comprises forming an amalgam of copper with mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated residue of metallic copper, and grinding said spongy metallic copper residue to form a finely divided product.

15. A method of making finely divided copper which comprises electrolytically depositing copper in contact with mercury to form a copper amalgam, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated residue of metallic copper, and grinding said spongy metallic copper residue to form a finely divided product.

16. A method of making finely divided copper which comprises forming an amalgam of copper with mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated residue of metallic copper, and grinding said spongy metallic copper residue in the presence of an organic liquid to form a finely divided product.

17. A method of making a material suitable for use as a metallic pigment paint base which comprises forming an amalgam containing copper and mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising said copper, and grinding said spongy metallic residue in the presence of an organic liquid suitable for use as a paint vehicle, to form a product containing said metallic residue, in finely divided form, suspended in said liquid.

18. A method of making a material suitable for use as a metallic copper paint base which comprises forming an amalgam of copper with mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated residue of metallic copper, and grinding said spongy metallic copper residue in the presence of an organic liquid suitable for use as a paint vehicle, to form a product containing said metallic copper, in finely divided form, suspended in said liquid.

19. A method of making a material suitable for use as a metallic pigment paint base which comprises forming an amalgam of copper and another metal with mercury, distilling the mercury from said amalgam under such conditions as to form a spongy and easily disintegrated metallic residue comprising an alloy containing copper and said other metal, and grinding said spongy metallic residue in the presence of an organic liquid suitable for use as a paint vehicle, to form a product containing said metallic residue, in finely divided form, suspended in said liquid.

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