Patented May 8, 1945 2,375,506

UNITED STATES PATENT OFFICE

2,375,506

PROCESS FOR PRODUCING METAL COMPOSITIONS OF LOW APPARENT DENSITY

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No Drawing. Application December 13, 1941, Serial No. 422,882

14 Claims. (Cl. 75—0.5)

The present invention relates to metals and metallic alloys of low apparent density, and, more particularly, to such metals and metallic alloys in a novel form suitable for various uses wherein a large surface area is desirable, such as in catalysis, and to a process for producing the same.

The value of various metals and metallic alloys in catalyzing certain chemical reactions has long been known. In general, metals are used as contact catalysts, so that it is desirable to have as large a surface available as possible. For this reason, it is common practice to employ metals in the form of metal gauzes, powders, wire, beads, grains, and small lumps. It is also known to deposit these metals upon porous carriers, such as silica gel, thoria, diatomaceous earth, kieselguhr, etc. While these carriers provide a greatly increased surface of metal for catalytic purposes, it is apparent that at least that surface of each metal particle which is adjacent the carrier surface at any given point is unexposed and so less efficient as a catalyst.

It is an object of the present invention to provide a process for producing metals and metallic alloys and preparations in such form that greatly increased areas of surface are available.

It is another object of the invention to provide a process for producing rigid metallic catalysts having an apparent density as low as about 2% to about 10% of the true density of the metals in solid form.

It is also an object of the invention to provide a novel process for producing metals and metallic alloys and preparations of low apparent density, high surface area and relatively high mechanical strength suitable for use as catalysts.

Other objects and advantages of this invention will be apparent to those skilled in the art from the following description.

According to the present invention, reducible metallic compounds which give bulky flocculent or gelatinous precipitates are employed to produce metallic catalysts having extremely low apparent density. The preparation of these metallic catalysts in a very porous state is preferably accomplished by precipitating the metal hydroxide, where the hydroxide of the particular metal is flocculent, in a suitable liquid protective and supporting medium. The liquid medium is then transposed to a gaseous medium. The metal hydroxide (or oxide, where the hydroxide suffers dehydration), still in its original highly expanded form, is reduced in situ to the metal, and the metal retains the expanded form. The metallic hydroxides can be precipitated in an aqueous medium, and, although water can be used as a supporting medium during the entire time that a liquid medium is employed, it is rather preferred to replace the aqueous medium by an organic solvent having a lower critical temperature, such as acetone, methyl alcohol, ethyl alcohol, benzene, pentane, heptane, ether, etc.

As reducing agents, various materials may be used, depending upon the ease of reduction of the particular metallic hydroxide or oxide concerned. Thus, hydroquinone, pyrocatechin, decahydronaphthalene and other organic reductants can be used. Hydrogen, hydrazine, ammonia or ammonium chloride at high temperatures can also be used for this purpose. With certain of the metallic oxides which are relatively easily reduced, it has been found that at high temperatures the lower aliphatic alcohols, having from 1 to about 5 carbon atoms per molecule, are satisfactory reducing agents, and in this case said alcohols may serve both as liquid media and as reductants, if desired.

In going from the liquid medium to a gaseous medium, the flocculent or gelatinous precipitate of the metallic compound suspended in the liquid medium is introduced into an autoclave. The interior of the autoclave is evacuated to remove substantially all of the air therein, and it is preferred to flush the autoclave with an inert gas to insure the removal of all oxidizing gases. A suitable pressure of the inert gas can be built up within the autoclave, and the autoclave is then slowly heated to a temperature above the critical temperature of the liquid medium employed, the pressure within the autoclave rising during this increase in temperature. As is well known to those skilled in the art, all of the medium will be in the vapor phase above the critical temperature, irrespective of the pressure within the autoclave. At this point, therefore, the liquid medium has been entirely displaced by a gas. Since, at the critical temperature and critical pressure, the medium goes from the liquid to the vapor phase without substantial change in density, the agitation normally associated with boiling is not produced to any undesirable extent, and the bulkiness of the solid material or residue is not substantially affected.

During this temperature rise or at or above the critical temperature, the reducing agent reduces the metallic compound to the metal, and the fluid in the pores and cavities of the metal is in the gaseous state. The vapors are with-

drawn, the system being preferably evacuated, and the autoclave is allowed to cool.

In general, it is preferred not to have a metal catalyst exposed to an oxidizing medium at any time, and it is therefore desirable to run an inert or non-oxidizing gas, preferably nitrogen, into the autoclave before it is opened. The metal is then transferred, after cooling, to a storage container having an inert atmosphere, say, of nitrogen. However, where such precautions are not required, the metal may alternatively be cooled to a sufficiently low temperature so that there is no danger of substantial oxidation if exposed to air, and air can then be admitted to the autoclave, or the autoclave can be opened.

The metal produced in this manner is rigid and in extremely porous form and may have an apparent density as low as about 2% or less, in the case of some of the metals, of the true density of the solid or compact metals. In general, it will be found that the apparent density of metals produced in this manner will run as low as 10 to 15% of the apparent density of the precipitated metal powders which have heretofore commonly been used as catalysts. The enormously increased surface area of metallic catalysts produced in accordance with the process herein disclosed is of great advantage in the catalysis of many reactions.

The following examples are merely illustrative of the present invention, and it will be understood that the invention is not limited thereto.

Example I

About 25 grams of cupric nitrate trihydrate [$Cu(NO_3)_2.3H_2O$] is dissolved in about 250 cc. of water, and ammonium hydroxide is gradually added to precipitate cupric hydroxide. The precipitated slurry is permitted to settle, and the clear supernatant liquor above is then siphoned off. Acetone is added to bring the volume up to about 400 cc. The material is then agitated to mix the precipitate throughout the entire volume, and the slurry is again allowed to settle, to about 100 cc. This procedure is repeated until the amount of water present in the solution is reduced to about 1 to about 3%, and about 15 grams of isopropyl alcohol are then added as a reducing agent.

The cupric hydroxide, suspended in about 115 cc. of the acetone-isopropyl alcohol solution and held in a large test tube or glass liner, is placed inside an autoclave. The autoclave is closed and fixed in a heating chamber and is then evacuated. A stream of nitrogen is then employed to sweep all residual air out of the autoclave, and a pressure of nitrogen of about 300 pounds per square inch is built up within the autoclave, which is then sealed. The autoclave is heated to a temperature above the critical temperature of acetone, say, to about 250° C., the temperature being raised slowly over a period of about one and one-half to about two hours. During this heating, the pressure rises to about 1,700 pounds per square inch.

The acetone vapors are then bled out of the system at a rate sufficiently slow to prevent any substantial drop in the temperature within the autoclave, which is kept between about 240 and about 250° C. during such release of the vapors. The system is then evacuated and permitted to cool for some hours. Upon opening the autoclave, a sponge of red, metallic copper having an apparent density of only about 0.30 gram per cubic centimeter is obtained. In this form, the metallic copper can be cut into blocks, and its physical state is not appreciably altered on strong oxidation. The copper can be wet with water and will retain its form, porosity, large surface, rigidity, and low apparent density even after drying.

In forming the novel metallic copper body of the present invention, it has been discovered that the copper hydroxide can be precipitated in an improved manner for this purpose by first obtaining the copper-ammonia complex ion. When this complex ion is first formed, the addition of cupric nitrate to the blue solution does not immediately precipitate the cupric hydroxide, as the complex ion must have time for breaking down. Since the precipitation is not instantaneous, this method of production of the hydroxide gives time for mixing, so that an even, uniform deposition of the cupric hydroxide can be obtained. Curds and lumping caused by sudden precipitation of cupric hydroxide are thereby eliminated. Other methods of precipitation may also be employed.

Example II

About 21 grams of cupric chloride dihydrate are dissolved in about 250 cc. of water, and ammonium hydroxide is gradually added, to precipitate cupric hydroxide. The addition of ammonium hydroxide is continued until the original cupric hydroxide precipitate is completely dissolved to form the complex copper-ammonia ion. Cupric chloride in about 10% solution is then slowly added to the deep blue solution of the complex ion until the precipitate obtained and the supernatant liquor are greenish blue. The total amount of copper present, on a cupric chloride dihydrate basis, is about 30 grams, and this is made up with water to about 400 cc. The precipitated slurry is permitted to settle until it has a volume of about 150 cc., and the clear supernatant liquor above it is then decanted. Methyl alcohol is added to bring the volume to about 400 cc. again. The precipitate is then mixed throughout the entire volume by stirring, and the slurry is again allowed to settle to about 150 cc. This procedure is repeated, finally using absolute methyl alcohol, until the amount of water present in the supernatant liquor is of the order of about 1% or less.

The cupric hydroxide is suspended in about 250 cc. of methyl alcohol, and the suspension is put in an autoclave, as described in Example I. The autoclave is evacuated and swept of residual air, and a pressure of about 300 pounds per square inch of nitrogen is built up within the autoclave, whereafter it is sealed. The autoclave is heated to about 250° C., which is approximately 10° above the critical temperature of methyl alcohol, the temperature being slowly increased over a period of about two hours. The methyl alcohol vapors together with the formaldehyde that is formed are released and swept out of the system with fresh nitrogen at a rate sufficiently slow to avoid substantial decrease in temperature within the autoclave. After the autoclave has cooled for some hours, it is opened, and a red, metallic copper sponge similar to that described in Example I is obtained. A yield of about 9.8 grams of copper, which is approximately 90% of the theoretical, is produced.

It will be understood that the exchange of liquid media, such as from water to methyl alcohol, as explained in a preceding paragraph, can be carried out between more than two solvents, where successive solvents are at least partly miscible. Similarly, the precipitation can be carried out

with alkali, ammonium hydroxide, or basic salts directly in methyl alcohol.

Example III

Cupric hydroxide is precipitated by dissolving about 90 grams of cupric nitrate trihydrate in about 450 cc. of methyl alcohol, adding about 56 cc. of about 1:1 ammonium hydroxide to approximately one-third of this solution to form the deep blue copper-ammonia complex, and then adding the other two-thirds of the methyl alcohol solution with agitation. A very uniform, flocculent mass which settles very slowly is thus obtained. As there is considerable water in this liquid medium, it is desirable to siphon off the supernatant liquor after standing and to mix fresh methyl alcohol with the residue, repeating the procedure until substantially all water, ammonium nitrate and ammonium hydroxide are removed. The cupric hydroxide, thus suspended in the methyl alcohol solution and substantially devoid of water, is then treated in the same manner as described in Example II. A similar product is obtained.

Example IV

About 97 grams of nickelous nitrate hexahydrate [$Ni(NO_3)_2.6H_2O$] are dissolved in about 500 cc. of water. Dilute ammonium hydroxide is gradually added until no further precipitation occurs. After the precipitated nickelous hydroxide has settled, the supernatant liquor is siphoned off, and methyl alcohol is added to make up to approximately the original volume. The precipitate is mixed throughout the liquid body by agitation and is again allowed to settle, the supernatant liquor again being drawn off. Repeated additions of methyl alcohol and decantations are made until the amount of water present is reduced to about 1%. Upon drawing off the major part of the final portion of methyl alcohol as supernatant liquor, the body is again made up to approximately the original volume by the addition of ethyl ether. The precipitated nickelous hydroxide is mixed in the ether, and, by repeated settling, decanting, and adding fresh ether, the methyl alcohol content of the solution is reduced to about 1%. About 40 grams of hydroquinone are added to the suspension, which is introduced into the autoclave and heated therein in an atmosphere of nitrogen, as described in Example I, to a temperature of about 245° C. The procedure followed thereafter is similar to that set forth in Example I. About 5.5 grams of jet black nickel with an apparent density of about 0.18 gram per cubic centimeter, as compared with a density of 8.90 grams per cubic centimeter for solid nickel, are obtained. While the nickel thus produced does not hold together quite so well as the copper, so that it cannot as practicably be cut into blocks, it has been found that the nickel tends to crumble rather than to powder. The jet black nickel formed has been found to be practically pure nickel.

Example V

Nickelous chloride hexahydrate is dissolved in methyl alcohol and there precipitated with dilute ammonium hydroxide. By repeated settling, siphoning off the supernatant liquor, and adding fresh portions of benzene, the methyl alcohol and water present can be reduced to about 1%. Thereafter, by continuing the settling and siphoning operations and adding fresh portions of n-hexane, the benzene content can also be reduced to about 1%. The n-hexane solution containing nickelous hydroxide suspended therein is then introduced into the autoclave, and all air is evacuated and swept therefrom. The pressure within the autoclave is then raised to about 300 pounds per square inch with hydrogen, and the autoclave is slowly heated to a temperature of about 350° C., the pressure rising during this heating. The vapors are bled from the autoclave, and the system is evacuated. It is permitted to stand for some hours until cool, when it is opened. Jet black nickel in a form similar to that described in the preceding example is thereby produced.

Where sodium hydroxide or other alkali or an alkaline salt is employed as the precipitating medium, in place of ammonium hydroxide, it may be found necessary to carry out the precipitation in an aqueous medium and then to leach out the soluble inorganic salts with additional portions of water before replacing the water with an organic solvent. In this way, the metal catalysts can be produced free of inorganic salts.

Example VI

Cupric hydroxide and nickelous hydroxide are precipitated together by adding sodium hydroxide in excess to a solution of about 15 grams of cupric nitrate trihydrate and about 18 grams of nickelous nitrate hexahydrate in about 300 cc. of water. After the precipitate has settled, the supernatant liquor containing sodium nitrate and part of the excess sodium hydroxide is decanted. Additional portions of water are added, the precipitate mixed therein by agitation, and the supernatant liquor decanted, these operations being repeated until substantially all of the soluble sodium nitrate and sodium hydroxide are removed.

After the last decantation, acetone is added to bring the liquid body up to approximately the original volume; the precipitate is then mixed throughout the volume and is permitted to settle, and the supernatant liquor is again withdrawn. This procedure is repeated with additional portions of acetone until the amount of water present is of the order of about 1%. A further portion of acetone is saturated with anhydrous gaseous ammonia, and this portion is then added to the precipitate. After the precipitate has again been mixed throughout the entire volume and has settled in a volume of about 150 cc., the supernatant liquor is against withdrawn, and the precipitate, suspended in the acetone containing dissolved ammonia, is put in an autoclave, as described in Example I.

The autoclave is evacuated, and the pressure inside is built up to about 300 pounds per square inch with anhydrous gaseous ammonia. After being sealed, the autoclave is slowly raised to a temperature of about 325° C. During this heating, the pressure rises and the ammonia is decomposed in situ to generate nascent hydrogen within the smallest pores and cavities and to act therein as a reducing agent. The vapors are bled from the autoclave into dilute acid, and the system is evacuated. The autoclave is allowed to stand for some hours until cool, when it is opened. A solid spongy product, reddish black in color and having an apparent density of about 0.26 gram per cubic centimeter, is obtained.

Example VII

Stannic hydroxide is precipitated by dissolving fuming anhydrous stannic chloride in methyl alcohol and adding ammoniacal methyl alcohol in excess thereto, followed by a small amount of water. A gel begins to form in a few minutes time, and this is permitted to settle for a few

hours. The supernatant liquor is removed, and portions of n-hexane are added, mixing the stannic hydroxide throughout the liquid body, allowing to settle, and removing the supernatant liquor after each addition. The n-hexane containing stannic hydroxide suspended therein is put in an autoclave under a pressure of about 250 to about 350 pounds per square inch of hydrogen, and the procedure set forth in the preceding examples is followed. The autoclave is heated to about 400° C., the temperature being slowly raised over a period of about two hours. Upon evacuation, cooling, and opening of the autoclave, the product is found to be a spongy mass of elemental tin of low apparent density.

Example VIII

About 2.6 grams of bismuth oxychloride (bismuthyl chloride) are dissolved in methyl alcohol by bubbling a small amount of gaseous hydrogen chloride into the alcohol, and a solution of ammonia in methyl alcohol is then quickly added to precipitate bismuth hydroxide. The white flocculent precipitate thus formed is allowed to settle to a volume of about 70 cc. and is then washed with fresh portions of methyl alcohol. The precipitate suspended in the alcohol is introduced into an autoclave and treated as described in Example II supra. A fluffy product having an apparent density of about 0.12 grams per cubic centimeter and analyzing as metallic bismuth with a small amount of bismuth oxide admixed therewith is obtained.

Example IX

The procedure of Example VIII is similarly applied to a precipitate of silver oxide prepared by adding ammonium hydroxide to a solution of silver nitrate to form the soluble silver-ammonia complex ion and then adding more silver nitrate until the precipitate reappears. The porous metallic silver removed from the autoclave has a very low apparent density.

The invention constitutes a rapid and simple method of preparing activated metals in a state of very low apparent density and very large surface area. When employed as activated catalysts, the metal products thus formed need no support for allowing free passage of vapors through them, although such support or filler may be used to provide even greater bulk. These metal products can be wetted and dried without loss of form or original properties, and they can be easily reactivated after use as catalysts, as by treatment with a suitable organic solvent and/or heating to about 300° C. in the presence of hydrogen, methanol or other reducing atmosphere and/or other means. The novel metal products produced in accordance with the new method herein described can be employed for any reactions in which metals are advantageously used as activated catalysts, as well as in any processes where a large surface area and/or finely comminuted form of the metal is desirable. Suitable uses are as catalysts for hydrogenation, dehydrogenation, condensation reactions, etc., as couples, and as acceptors, as of oxygen and halogens. Nickel produced essentially as herein specified has been used to great advantage in catalytically hydrogenating unsaturated fatty acids, and the novel copper catalyst described has given results as a dehydrogenation catalyst which are considerably superior to those obtained with copper catalysts provided in any other form. Metals in intimate mixture with each other can also be prepared in any required proportion, and such mixtures are frequently desirable for use as catalysts and as couples.

The reference to the present novel metal products as "rigid" and as "of relatively high mechanical strength" is intended to define them as of such strength as to be able to support themselves when used as catalysts or otherwise in connection with chemical reactions and to be able to withstand ordinary shocks met in such use. Gases can pass through even a long contact tube packed with the novel metal products described.

The term "bulky" as applied to precipitates is intended to include those which are amorphous, flocculent or gelatinous.

By "apparent density" of the products of the process is meant the weight of an amount of the material which occupies a unit volume including the volume of interstitial spaces, pores and cavities.

Although the present invention has been described in connection with illustrative examples thereof, it will be understood by those skilled in the art that other variations and modifications of the invention can be made and various equivalents can be substituted therefor without departing from the principles disclosed herein.

I claim:

1. A process for producing bulky metallic preparations containing a substantial proportion of elemental metal which comprises heating a liquid phase medium containing a suspension of solid material comprising a bulky precipitate of a reducible metal compound, in the presence of a reducing influence and under sufficient pressure to maintain a liquid phase, up to substantially the critical temperature of said liquid medium whereby the medium is vaporized without substantial agitation due to boiling and without substantially affecting the bulkiness of the solid material.

2. A process for producing bulky metallic preparations containing a substantial proportion of elemental metal which comprises heating a liquid phase medium containing a bulky precipitate of a reducible metal compound in the presence of a reducing influence and of a non-oxidizing atmosphere to a temperature of at least about the critical temperature of the medium, and maintaining during heating up to about the critical temperature a pressure sufficient to prevent ebullition of the medium.

3. A process for producing metals of low apparent density which comprises slowly heating a liquid phase medium containing a bulky precipitate of a reducible metal compound in the presence of a reducing agent and of a non-oxidizing atmosphere to a temperature above the critical temperature of the medium, subjecting said medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium whereby said medium is vaporized at about the critical temperature, and removing the vaporized medium while maintaining the temperature above the critical temperature.

4. A process for producing metals of low apparent density which comprises slowly heating a liquid phase medium containing a bulky precipitate of a reducible metal compound in the presence of a reducing agent and of a non-oxidizing atmosphere to a temperature above the critical temperature of the medium, subjecting said medium during heating to a pressure at

least sufficient to maintain a liquid phase up to the critical temperature of the medium whereby said medium is vaporized at about the critical temperature, slowly removing the vaporized medium while maintaining the temperature above the critical temperature, and slowly cooling the residue in a non-oxidizing atmosphere.

5. A process for producing metals of low apparent density which comprises establishing a bulky precipitate of a reducible metal compound in a first liquid medium; successively adding portions of a second liquid medium at least partly miscible with the first liquid medium and having a lower critical temperature than the first liquid medium, mixing, settling, and removing supernatant liquor until the content of the first liquid medium is reduced to about 1% to about 3%; heating the second liquid medium containing the bulky precipitate in the presence of a reducing agent and of a non-oxidizing atmosphere to a temperature of at least about the critical temperature of the medium; and subjecting said second liquid medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium.

6. A process for producing metals of low apparent density which comprises precipitating a metal hydroxide in an aqueous medium; successively adding portions of a non-aqueous liquid medium at least partly miscible with water and having a critical temperature below that of water, mixing, settling, and removing supernatant liquor until the water content is reduced to about 1%; slowly heating said liquid medium containing the metal hydroxide in the presence of a reducing agent and of a non-oxidizing atmosphere to a temperature of at least about the critical temperature; and subjecting said liquid medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium.

7. A process for producing metals of low apparent density which comprises establishing a bulky precipitate of a reducible metal compound in a liquid phase medium having reducing properties at high temperature, heating said medium containing the bulky precipitate in the presence of a non-oxidizing atmosphere to a temperature at which the medium exhibits reducing properties and at least about the critical temperature of the medium, subjecting the medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium whereby said medium is vaporized at about its critical temperature, and removing the vaporized medium while maintaining the temperature above the critical temperature of said medium.

8. A process for producing copper of low apparent density which comprises heating a liquid phase medium containing a bulky precipitate of a copper compound in the presence of a reducing agent and under sufficient pressure to maintain a liquid phase up to substantially the critical temperature of said liquid medium whereby the medium is vaporized without substantial agitation due to boiling and without substantially affecting the bulkiness of the solid material.

9. A process for producing nickel of low apparent density which comprises heating a liquid phase medium containing a bulky precipitate of a nickel compound in the presence of a reducing agent and under sufficient pressure to maintain a liquid phase up to substantially the critical temperature of said liquid medium whereby the medium is vaporized without substantial agitation due to boiling and without substantially affecting the bulkiness of the solid material.

10. A process for producing copper of low apparent density which comprises slowly heating a liquid phase medium containing a bulky precipitate of a copper compound in the presence of a reducing agent and of a non-oxidizing atmosphere to a temperature of at least about the critical temperature of the medium, subjecting said liquid medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium whereby the liquid medium is vaporized at about its critical temperature, and removing said vaporized medium while maintaining the temperature above the critical temperature of the medium.

11. A process for producing nickel of low apparent density which comprises slowly heating a liquid phase medium containing a bulky precipitate of a nickel compound in the presence of a reducing agent and of a non-oxidizing atmosphere to a temperature of at least about the critical temperature of the medium, subjecting said liquid medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium whereby the liquid medium is vaporized at about its critical temperature, and removing said vaporized medium while maintaining the temperature above the critical temperature of the medium.

12. A process for producing copper of low apparent density which comprises establishing a precipitate of cupric hydroxide in an aqueous medium; successively adding portions of a non-aqueous liquid phase medium having a critical temperature below that of water, mixing, settling, and removing supernatant liquor until the water content is reduced to about 1%; slowly heating said liquid medium containing cupric hydroxide in the presence of a reducing agent and of a non-oxidizing atmosphere to a temperature above the critical temperature of the liquid medium; subjecting said liquid medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium whereby the liquid medium is vaporized at about its critical temperature; removing the vaporized medium while maintaining the temperature above the critical temperature of said medium; and slowly cooling the residue in a non-oxidizing atmosphere.

13. A process for producing nickel of low apparent density which comprises establishing a precipitate of nickelous hydroxide in an aqueous medium; successively adding portions of a non-aqueous liquid phase medium having a critical temperature below that of water, mixing, settling, and removing supernatant liquor until the water content is reduced to about 1%; slowly heating said liquid medium containing nickelous hydroxide in the presence of a reducing agent and of a non-oxidizing atmosphere to a temperature above the critical temperature of the liquid medium; subjecting said liquid medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium whereby the liquid medium is vaporized at about its critical temperature; removing the vaporized medium while maintaining the temperature above the critical temperature of said medium; and slowly cooling the residue in a non-oxidizing atmosphere.

14. A process for producing copper of low apparent density which comprises adding am-

monium hydroxide to an aqueous solution of a copper salt to produce cupric hydroxide; adding a further amount of ammonium hydroxide to dissolve the cupric hydroxide and to form the copper-ammonia complex ion; adding a further amount of an aqueous solution of a copper salt to reprecipitate cupric hydroxide; successively adding portions of a non-aqueous liquid phase medium having a critical temperature below that of water, mixing, settling, and removing supernatant liquor until the water content is reduced to about 1%; slowly heating said liquid medium containing cupric hydroxide to a temperature above the critical temperature of the liquid medium; subjecting said liquid medium during heating to a pressure at least sufficient to maintain a liquid phase up to the critical temperature of the medium whereby the liquid medium is vaporized at about its critical temperature; removing the vaporized medium while maintaining the temperature above the critical temperature of said medium; and slowly cooling the residue in a non-oxidizing atmosphere.

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