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METAL POWDERS

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The present invention relates to metal powders and more particularly to a process for preparing finely divided metal powders from metal compounds.

Metal powders for use in powder metallurgy have long been prepared by processes involving mechanical subdivision of the metal such as grinding or milling. Such processes are still used to a great extent and are generally satisfactory for producing metal powders for conventional applications. This technique, however, is subject to the disadvantage in that a wide range of particle sizes is obtained and hence where uniformity of size is required for a particular application considerable screening and classification is necessary. These operations add expense to the process itself and also increase the cost of the finished product. Another disadvantage is that extremely fine metal powders cannot be conveniently prepared by mere mechanical subdivision. Because of these disadvantages, chemical means have been sought for preparing finely divided metal powders. One such process which is used extensively consists of the pyrolysis of metal compounds such as carbonyls and halides. While such processes generally produce good quality powders, the high temperatures required have some adverse effects on the products. High temperatures, for example, tend to cause some degree of agglomeration of the particles so that the resulting powder is not as fine as would be the case if lower temperatures could be employed. It is also believed that in preparing iron powder for permanent magnets, a high temperature will tend to adversely affect the magnetic properties of the final product.

It is, therefore, an object of this invention to overcome the disadvantages of the prior art and provide a novel and improved method for preparing metal powders. A further object of this invention is to provide an improved low temperature process for preparing metal powders from the respective metal compounds. Another object is to provide a process for producing finely divided iron powder by a low temperature process so as to render the product well suited for use in the fabrication of permanent magnets. A still further object of this invention is to provide a process for conveniently preparing powdered metal alloys. These and other objects of the present invention will become apparent as the description proceeds and the features of novelty which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this specification.

The above and other objects of my invention are accomplished by reducing a metal compound with the product obtained when contacting an alkali metal with an ether, particularly the ethers of polyhydric alcohols. In a preferred embodiment, the metal compound is reduced with the product obtained when an alkali metal is contacted with an ether of a polyhydric alcohol having a hydroxyl content of between about 0.005 to 2% by weight. Best results are obtained when the hydroxyl content is between about 0.05 to 1% by weight. It has long been known that the alkali metals and particularly sodium can be employed as reducing agents to win metals

from their respective ores and compounds. These processes, however, generally employ high temperatures and the resulting metal product is not in the form of finely divided particles, that is of the order of 10 microns or less. I have discovered, however, that extremely fine, and in most cases pyrophoric, metal powders can be prepared by reducing metal compounds with the product obtained when contacting an alkali metal of particle size from about 1 to 50 microns with an ether having a hydroxyl content less than about 2% by weight. My process is particularly advantageous in that low temperatures, that is temperatures below the melting point of the metal and preferably room temperature and temperatures as low as about a −10° C., are employed. Because of these low operating temperatures, the process is thus particularly well suited to the preparation of iron powder to be used in the manufacture of permanent magnets. Employing such low temperatures results in a metal powder which is of smaller particle size than that obtained by other processes employing alkali metals as the reducing agent. Certain metal compounds as, for example, ferric chloride are soluble in the ether and this characteristic also contributes to the attainment of the finer particle size of the product. Substantially quantitative yields of powder are obtained by my process and the product is characterized by the uniformity and high degree of fineness of the particles. In most cases, the particles are so fine as to be highly pyrophoric, thus indicating particle sizes of the order of 1 micron and less.

It has been discovered that the activity of the alkali metals is enhanced by contacting the metals with the ethers, especially the ethers of polyhydric alcohols having a free hydroxyl content. It is not known precisely what takes place; however, the physical appearance of the metal changes, that is, it assumes a flocculent appearance. It has been suggested that the alkali metal may be held in loose combination with the ether. However, experimental evidence has also shown that no splitting of the ether takes plate. The product obtained when contacting an alkali metal with an ether displays a high degree of reactivity and can be employed in many chemical reactions which could not be carried out successfully using alkali metal in its free state. This reactivity is further indicated by the fact that the flocculent material is unstable and decomposes upon exposure to air or moisture. In accordance with this invention, these advantageous properties are utilized to prepare metal powders.

The flocculent material is conveniently prepared by merely comingling an ether with alkali metal in a subdivided state. In general, any ether can be employed such as dimethyl ether, methylal, and the like, although I especially prefer the ethers of polyhydric alcohols particularly those which have a minor impurity which can be measured as the free hydroxyl content. It is preferred that the ether have a free hydroxyl content of at least 0.005 to about 2% by weight. Of the ethers of the polyhydric alcohols, the glycol ethers are preferred since they form the flocculent material most readily. Among such ethers are tetraethylene glycol dimethyl ether, triethylene glycol methylethyl ether, ethylene glycol methylethyl ether, ethylene glycol diethyl ether, dibutylene glycol dimethyl ether, and the like. One of the ethers of a polyhydric alcohol that I have found to be especially suitable is ethylene glycol dimethyl ether, having a free hydroxyl content of between about 0.05 to 1% by weight.

In contacting these ethers with the alkali metal, it is preferred that the alkali metal be in a subdivided state. For this reason it is convenient to use dispersions or suspensions of finely divided alkali metal in inert liquid mediums. Such dispersions are well known in the art and are generally prepared by fusing an alkali metal in the presence of an inert liquid and subjecting the entire

mixture to vigorous agitation while maintaining the temperature above the melting point of the alkali metal. A number of inert mediums are useful in preparing these dispersions, typical examples of which are hydrocarbons such as benzene, xylene, toluene, kerosene, gasoline, mineral oil, heavy alkylate and the like. For some purposes, the ether can be the sole suspending medium when the ether employed is substantially chemically inert to the alkali metal. The partcile size of the alkali metal present in the dispersion is preferably of the order of 1 to 50 microns depending to some extent upon the degree of agitation. The metallic concentration of these dispersions is subject to broad variation and can be anywhere from trace amounts up to about 60 per cent by weight of the total. In preparing the flocculent material, dispersions having metal concentrations of the order of 20 to 50 per cent and particles averaging less than 20 microns are preferred.

As indicated above, the flocculent material is formed by merely comingling the ether and a dispersion of alkali metal. The mixing is done conveniently at room temperature and is accompanied by slight evolution of heat. A flocculent, grayish-white material is formed which is insoluble in the dispersion medium. The exact molar ratio of ether to alkali metal is not known with certainty and it can vary. In preparing the flocculent material, it is preferred to employ an ether to metal ratio of the order of 4:1 to 10:1.

In accordance with my invention, metal powders are produced from metal compounds by reducing the compound with the product obtained when contacting an alkali metal with an ether. Although the invention can be successfully applied to any metal compound capable of being reduced by an alkali metal, the halogen salts of the various metals are preferred. Thus, the corresponding metal powders can be prepared from metal halides such as, for example, ferric chloride, ferrous chloride, ferric fluoride, zinc chloride, cobaltous chloride, cobaltous bromide, cadmium bromide, stannic chloride, stannous chloride, stannic bromide, stannic iodide, manganese dichloride, nickel chloride, nickel iodide, silver chloride, silver bromide, and other metal halides. I especially prefer those metal halides which are readily reduced at temperatures between about 10 and 30° C. or below the boiling point of the ether. Although the halides are the preferred starting materials in my process, other inorganic as well as organic metal compounds can be employed such as, for example, the sulfates, nitrates, carbonates, acetates, formates, and the like of the above and other metals. Specific examples of such other compounds include nickel sulfate, nickel acetate, nickel formate, chromic nitrate, chromic sulfate, cobaltous acetate, ferric sulfate, and the like. In general, however, the oxides are somewhat difficult to reduce and for this reason they are not preferred since they require elevated temperatures.

One method of carrying out the reaction to produce metal powders consists of initially forming the alkali metal-ether product and thereafter comingling this product with the metal compound. The yield obtained is substantially quantitative and stoichiometric amounts of the reactants can therefore be employed. It is preferred, however, to have the alkali metal present in excess so as to insure complete reduction of the metal compound at a rapid rate. The reactants are comingled in any suitable vessel which is provided with a stirring arrangement. The metal powder is precipitated from the reaction medium and is then separated by conventional means such as filtration, centrifugation and the like.

Another method for carrying out the reaction consists of contacting the alkali metal with the ether in situ. In operating according to this embodiment of my invention, the metal compound and the ether are comingled in a vessel provided with a stirring device and also provided with means for adding alkali metal dispersion. The alkali metal dispersion is then added to the reaction mixture and

it is preferable to provide means for controlling the rate of the addition so as to afford some degree of control over the reaction. The reaction itself is exothermic and begins at room temperature or lower. In order to maintain a relatively low temperature in the reaction, means can be provided for chilling the reaction vessel.

As previously indicated, one of the outstanding and advantageous features of this process is that it is carried out at low temperatures which are substantially below the melting point of the metal being produced. The reaction has been carried out successfully at temperatures as low as about —10° C., and a temperature below the boiling point of the ether is preferred although somewhat elevated temperatures can be employed as, for example, above the boiling of the ether when pressure is applied. Temperatures between about 10° C. and 30° C. are recommended when preparing iron powder which is to be subsequently used in making permanent magnets. In addition to the use of a cooling bath, the temperature of the reaction can also be controlled by providing the reaction vessel with a reflux condenser. In such a case if the heat evolved in the reaction is sufficient to vaporize the ether, it will then be refluxed back into the mixture.

The finely divided metal powder is recovered from the reaction mixture by conventional means such as filtration or centrifugation although the latter is preferred because of the extremely small particle size of the product. Prior to separating the product, however, it is desirable to "kill" any excess sodium that may be present in the reaction mixture by the addition of an alcohol such an isopropyl alcohol so as to form alcoholate. Following the alcohol treatment, the reaction mixture is then digested with water from which dissolved oxygen has been dispelled so as to dissolve the alcoholate and any other impurities that may be present such as alkali metal salts. Following this treatment, the powder is separated from the mixture by centrifugation and washed with alcohol, acetone and ether so as to remove any traces of water. The product is then dried under vacuum.

Since the metal powders produced by this invention are in most cases pyrophoric, it is sometimes desirable to carry out the reaction and separation steps under a blanket of inert gas such as dry nitrogen. It should be pointed out, however, that this procedure need not necessarily be followed and when the reaction is carried out by contacting the alkali metal with the ether in situ, it has been found that an inert atmosphere need not be employed. In order to further describe my invention, the following examples illustrate the process wherein the alkali metal is contacted with the ether initially and then reacted with the metal compound, In these examples the proportions and percentages given are on a weight basis.

Example I

Thirty-four parts of ethylene glycol dimethyl ether having a hydroxyl content of 0.44% by weight and 19.2 parts of a 50 percent sodium dispersion in heavy alkylate were placed in a reaction vessel equipped with a stirring mechanism. The vessel was then placed under an inert atmosphere and 8.4 parts of ferric chloride were added. Upon the addition of ferric chloride, reaction began immediately at room temperature and was accompanied by evolution of heat. In this run no attempt was made to control the reaction temperature although it did not exceed about 85° C. Finely divided iron powder was formed and tended to settle out as a precipitate. After completion of addition of the chloride, a period of about 30 minutes, the reaction had subsided indicating that substantially all of the chloride had reacted and that reaction was essentially instantaneous. Isopropyl alcohol was then added to the mixture for the purpose of killing the excess sodium. The contents of the reaction vessel were then digested with degassed distilled water after which the iron powder was separated by means of a centrifuge. The powder was washed with anhydrous ethyl

alcohol and diethyl ether. The residual ether was removed from the metal particles by drying under a vacuum. The yield obtained by this method was 2.6 parts of iron powder, thus representing a recovery of about 90 per cent of theoretical. The powder was highly pyrophoric and upon exposure to air, rapidly oxidized with the evolution of sparks and smoke.

Example II

The procedure followed in this example was substantially the same as that described in Example I with the exception that 73.1 parts of the ether having a hydroxyl content of 0.44% by weight, 8.9 parts of a 50 per cent sodium dispersion in heavy alkylate, and 4.6 parts of ferric chloride were utilized. A sample of the product was placed upon a piece of filter paper and exposed to air. The powder was highly pyrophoric and actually burned or scorched the paper.

Example III

Seventy parts of ethylene glycol dimethyl ether having a hydroxyl content of 0.44% by weight and 10.6 parts of a 50 per cent sodium dispersion in heavy alkylate were placed in a flask and mildly agitated. Thereafter, 5.4 parts of ferric chloride were added and allowed to react for a period of 20 minutes during which time the temperature did not exceed 85° C. At the end of this time, the reaction had subsided and iron powder was precipitated. The washing procedure outlined in the above example was followed and the product was recovered in like manner. Again, upon exposure to air, the product proved to be highly pyrophoric.

In the above examples, it was noted that upon addition of the ether to the dispersion, the physical appearance of the metal had changed. That is, it assumed a grayish-white flocculent appearance.

The following example will serve to illustrate that embodiment of my invention wherein the metal compound is first added to the ether and the dispersion added to this mixture.

Example IV

Sixty parts of ferric chloride were dissolved in 320 parts of ethylene glycol dimethyl ether having a hydroxyl content of 0.44% by weight. These reactants were contained in a vessel provided with a stirrer, reflux condenser and a cooling bath. To this solution 64.2 parts of a 28 per cent sodium dispersion in heavy alkylate was slowly added. When the dispersion came in contact with the solution, the grayish-white flocculent material was noted to be formed prior to being consumed in the reaction with the ferric chloride. The entire amount of dispersion was added over a period of 45 minutes during which time the reaction mixture was maintained at a temperature between 10 and 30° C. It was noted that the reaction initiated at a —6° C. and was complete upon completion of the addition of the dispersion. Seventy-eight parts of isopropyl alcohol were added to kill the excess sodium, and thereafter 500 parts of degassed distilled water were added slowly. The iron powder which had been precipitated was then recovered, washed and dried as described in the foregoing examples. Upon exposure to air, the powder was pyrophoric.

Example V

Fifty-eight parts of ferric chloride were dissolved in 250 parts ethylene glycol dimethyl ether having a hydroxyl content of 0.44% by weight. As in Example IV, the reaction vessel was provided with a stirrer, reflux condenser and cooling bath. Firty-four parts of a 50 per cent sodium dispersion in heavy alkylate were placed in a separatory vessel and slowly added to the chloride solution. All of the dispersion was added over a period of 30 minutes during which time the reaction temperature was maintained between 20 and 40° C. The reaction was substantially complete at the end of this period since the last few parts of dispersion added to the vessel give no apparent reaction. Iron powder had been precipitated from the mixture which was then treated with alcohol and degassed distilled water as in the previous examples. The iron powder was recovered and processed as described in the preceding examples and upon exposure to air was found to be highly pyrophoric.

Example VI

Finely divided silver powder was prepared by introducing 1 part of silver bromide and 25 parts of the ethylene glycol dimethyl ether to the reactor and adding 3 parts of a 50% dispersion of sodium in heavy alkylate to the mixture. Again the grayish-white flocculent material was observed to be formed. The reduction was initiated at room temperature with a slight evolution of of heat and was essentially complete within three minutes.

Example VII

Finely divided tin powder was prepared by a procedure as described in Example VI using stannic iodide as the starting material.

Example VIII

Lead powder was prepared by reducing lead chloride by a procedure similar to that described in Examples I, II, and III above using the material obtained when contacting sodium with ethylene glycol dimethyl ether as the reducing agent.

Example IX

Zinc powder was obtained by reducing zinc chloride with material obtained when contacting sodium with ethylene glycol dimethyl ether by a process substantially similar to that described in Examples I, II, and III above.

When other metal compounds which are reducible by an alkali metal are substituted for the metal halides of the above examples equally good results are obtained. For example, powder nickel can be prepared from nickel chloride, tin from stannic chloride, cobalt from cobaltous acetate, iron from ferric sulfate and the like. Similarly, other alkali metals can be employed. For example, potassium or lithium contacted with ethylene glycol dimethyl ether can be employed as the reducing agent in my process with equally good results. Also other ethers can be substituted for the ethylene glycol dimethyl ether of the above example. For example, any of the alkali metals such as sodium, potassium, lithium and the like can be contacted with tetraethylene glycol dimethyl ether, triethylene glycol dimethyl ether, methylal, or other ethers of polyhydric alcohols so as to form the products which can be employed as reducing agents in my process to prepare metal powders from the corresponding metal compounds.

My process is also useful in the preparation of alloy powders. In preparing alloy powders the procedure outlined in the above examples is followed except that compounds of two or more different metals are reacted simultaneously with the product obtained when contacting an alkali metal with an ether. For example, an iron-zinc alloy powder can be prepared by simultaneously reducing a mixture of ferric chloride and zinc chloride by substituting this mixture for the metal halides in the above examples. Powder alloys of iron-silver, iron-nickel, as well as other mixtures of different metal powders are prepared in like manner.

The powders prepared in accordance with my invention can be used in conventional powder metallurgy practices wherein fabricated articles are made by pressure molding techniques. Iron powder prepared by my process is particularly useful in the manufacture of permanent magnets.

This application is a continuation-in-part of my previously filed application, S. N. 279,468, March 29, 1952, now abandoned.

It is to be understood that the above examples are given only by way of illustration, and I intend by the

appended claims to cover all modifications which fall within the spirit and scope of my invention.

I claim:

1. A process for the preparation of metal powders comprising reducing at least one metal compound other than an alkali metal compound with the product obtained when contacting an alkali metal with an ether.

2. The process of claim 1 wherein said ether has a hydroxyl content of between about 0.005 to 2% by weight.

3. A process for the preparation of metal powders comprising reducing at least one metal compound other than an alkali metal compound with the product obtained when contacting an alkali metal with an ether, said alkali metal being of particle size of between about 1 to 50 microns dispersed in an inert liquid hydrocarbon and said ether having a hydroxyl content less than about 2% by weight.

4. A process for the preparation of metal powders comprising reducing at least one metal compound other than an alkali metal compound with the product obtained when contacting an alkali metal with an ether of a polyhydric alcohol.

5. A process for preparing iron powder comprising reducing ferric chloride with the product obtained when contacting sodium metal in the form of finely divided particles suspended in an inert organic liquid with ethylene glycol dimethyl ether having a free hydroxyl content of between about 0.05 to 1% by weight.

6. The process of claim 5 wherein said ferric chloride is first dissolved in said ethylene glycol dimethyl ether and subsequently said sodium is added thereto.

7. A process for preparing alloy powders comprising reducing simultaneously a mixture of two or more different metal compounds other than an alkali metal compound with the product obtained when contacting an alkali metal with an ether.

References Cited in the file of this patent

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