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CUPROUS OXIDE

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The present invention relates to the production of cuprous oxide and particularly relates to a pyrometallurgical method for producing cuprous oxide.

Electrolytic methods for producing cuprous oxide are known which produce a cuprous oxide which is substantially free from metallic copper. Pyrometallurgical methods for producing cuprous oxides are also known. One of these methods involves the controlled oxidation of metallic copper to form cuprous oxide. It is possible by this method to produce a product which, by the old method of analysis according to Navy Specification 52C-4b analyzed substantially 100% cuprous oxide. This old method of analysis, however, reported both cuprous oxide and metallic copper as cuprous oxide.

There has recently been developed a new method of analysis which analyzes cuprous oxide and metallic copper separately, and as a result, specifications on the metallic copper content of cuprous oxide have, in many cases, been made more rigid. Cuprous oxide made by the old oxidation method does not come up to these new specifications.

Another pyrometallurgical method which has been proposed is to heat cupric oxide with metallic copper. The reaction in this case, however, is extremely slow, and requires several days' heating with thorough agitation to bring about completion of the reaction.

As previously indicated, electrolytically produced cuprous oxide is substantially free from metallic copper, and it is a primary object of this invention to provide a pyrometallurgical method for producing cuprous oxide whereby a metallic copper-free oxide may be produced by an economical method. The pyrometallurgical method is cheaper from both the investment and processing cost angle.

It has been found that if particles containing shells of cupric oxide, cuprous oxide, and metallic copper in the proportion necessary to produce substantially pure cuprous oxide are heated in an inert atmosphere, substantially pure cuprous oxide may be produced with a great saving in time over the prior art method of heat treating mixtures of cupric oxide and metallic copper.

The preferred method of producing these articles is to reduce a cupric oxide powder under controlled conditions until the amount of reduction is preferably 96 to 100% of that required to produce a copper-oxygen content corresponding to that of cuprous oxide. When this point in the reduction is reached, the original particles

of cupric oxide will contain an inner core of cupric oxide, an intermediate shell of cuprous oxide, and an outer film containing metallic copper. Upon the completion of the reduction to this point, further reduction is stopped and the heat treatment is continued in an inert atmosphere for a time sufficient to enable the substantially complete reduction of the inner core of cupric oxide by the metallic copper.

When the cupric oxide has been reduced to 96 to 99% cuprous oxide, there is ordinarily present up to about 3% metallic copper, and this is well over the limits for metallic copper. By carefully controlling the reduction, the amount of metallic copper can be reduced, but it is impossible, by the single stage reduction of cupric oxide, to satisfy the requirements of some of the newer specifications.

In carrying out the second step of the process, the heating should of course be carried out in an inert atmosphere. This may be accomplished by sealing the apparatus in which the reduction has been carried out or by the introduction of an inert gas such as CO₂ or steam. It is also preferred to have present in the heat treating or soaking step a catalyst for the reduction, such as soluble salts, moisture, etc.

Instead of starting with cupric oxide, one may also employ a controlled oxidation of copper powder to the point corresponding approximately to that of pure cuprous oxide. In such a case, the original particles of copper will have a core of copper, an intermediate shell of cuprous oxide, and an outer shell containing cupric oxide.

It is thus seen that in either case the individual particles contain the proper copper-oxygen ratio to produce cuprous oxide, and by heat treating such particles, the over-all time necessary to produce substantially pure cuprous oxide is greatly reduced over the heat treatment of a mixture of cupric oxide and copper. At the same time, it is possible by the present invention to produce a substantially metallic copper-free cuprous oxide by a pyrometallurgical method.

It is preferred to use as starting material cupric oxide. In the first place, it is a cheaper material than copper powder, and secondly, in the reduced particles the outer shell contains the metallic copper and therefore presents a greater reaction surface than when the metallic copper forms the core of the particle. This tends to insure a more complete oxidation of the metallic copper which is important since the requirements on the metallic copper content are more rigid than on the cupric oxide content.

The particle size of the material treated should preferably be such that it contains substantially no material greater than 15 microns in diameter. Where material of larger particle size is used, final conversion of metallic copper to cuprous oxide is slowed down considerably, and one approaches the condition present in a mere mixture of cupric oxide and metallic copper. Also, as indicated, it is preferred to have a catalyst present, and it has been found that an electrolytic copper oxide powder is very satisfactory as a raw material. The oxide powder, of course, need not be 100% cupric oxide, as it may also contain cuprous oxide. Thus it is not necessary that an oxide used as a starting material be 100% cupric oxide which would be a requirement in any single step reducing process for producing pure cuprous oxide.

Example I

16,000 pounds of a mixture of electrolytically produced cupric and cuprous oxide was charged into a reducing furnace and the charge was heated to 600° to 800° F. Water gas was introduced into the furnace and the heating continued for 36 hours with suitable agitation. Periodically the course of the reduction was observed by taking a sample by means of a thief sampler containing an inert gas. At the end of 36 hours, the reduction had proceeded to a point between 96 to 99% of that required to produce pure cuprous oxide by the old method of testing according to Navy Specification 52C-4b. At the end of 36 hours, the reducing gas was cut off and the heating and agitation continued for 24 hours in an inert atmosphere at which time tests of the material according to A. S. T. M. Specification D 283-39 showed that the material was substantially free of metallic copper.

It is thus seen that in the charge employed, 60 hours were required for the production of the cuprous oxide. By the old method of mixing, the same charge in the same equipment would have required a considerably longer time for the completion of the reaction.

While it has been indicated that it is possible, by the present method, to produce a substantially metallic copper-free cuprous oxide, it is to be understood that many of the advantages of the present invention may be obtained without conducting the heat treating step to the point where complete oxidation of metallic copper is effected. The economies and savings indicated are as applicable in proportion to the production of cuprous oxide containing some metallic copper as when a substantially metallic copper-free product is produced.

We claim:

1. The process of producing cuprous oxide powder which comprises heating a cupric oxide powder in a reducing atmosphere for a time sufficient to provide a copper-oxygen ratio substantially the same as that found in cuprous oxide, stopping the reduction at this point, and continuing the heating at a temperature of about 600° F. to 800° F. in an atmosphere inert at the temperature employed until substantially all of the metallic copper and cupric oxide has been converted to cuprous oxide, whereby the particles are composed substantially uniformly throughout of cuprous oxide.

2. The process of preparing cuprous oxide powder which comprises heating cupric oxide powder in a reducing atmosphere until the amount of reduction is 96 to 100% of that required to give a copper-oxide content corresponding to that of cuprous oxide, and thereafter heating the powder at a temperature of about 600° F. to 800° F. in an atmosphere inert at the temperature employed until substantially complete conversion of the metallic copper and cupric oxide to cuprous oxide takes place, whereby the particles are composed substantially uniformly throughout of cuprous oxide.

3. The process of preparing cuprous oxide powder which comprises heating a copper powder in an oxidizing atmosphere until the total copper and total oxygen content corresponds substantially to that of cuprous oxide, and thereafter heating the powder at a temperature of about 600° F. to 800° F. in an inert atmosphere until substantially complete conversion of metallic copper and cupric oxide to cuprous oxide takes place, whereby the particles are composed substantially uniformly throughout of cuprous oxide.

4. The method of producing cuprous oxide powder which comprises heating a powder selected from the class consisting of copper powder and cupric oxide powder under such conditions and in an atmosphere selected from the class consisting of oxidizing and reducing atmosphere so chosen as to effect oxidation and reduction respectively of said copper powder and cupric oxide powder to form cuprous oxide until the ratio of copper to oxygen is substantially that present in pure cuprous oxide, and thereafter continuing the heating at a temperature of about 600° F. to 800° F. in an atmosphere which is inert at the temperature employed for a time sufficient to effect substantially completely the simultaneous conversion of metallic copper and cupric oxide to cuprous oxide, whereby the particles are composed substantially uniformly throughout of cuprous oxide.

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