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GASEOUS REDUCTION OF OXYGEN-CONTAINING COPPER

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This invention relates generally to the pyrometallurgical refining of molten copper by the consecutive steps of oxidation and reduction. More particularly it relates to the reduction step wherein unwanted oxygen contained in oxygen-containing copper is removed from the copper by the use of a gaseous reductant. Still more specifically the invention relates to the successful and economical use of gaseous reductant in lieu of heretofore used tree trunks, commonly referred to as "poles."

The use of poles or logs, commonly referred to in the copper refining art as "poling," is well known. Poling is practiced to remove unwanted oxygen from the molten copper which contains this oxygen. In the poling of copper the pole of green timber is forced below the surface of the molten copper bath so as not only to erupt the liquid metal into a fountain in the reducing atmosphere of the draft-dampened furnace but also to stir vigorously the whole bath by the rapid evaporation of moisture and volatile matter from the green wood. The duration of poling a large batch of copper is several hours for the reduction of the oxygen to the end-point which is usually less than 0.1 to 0.2% as desired. This procedure is, comparatively speaking, very expensive and is subject to many drawbacks. Nevertheless, the poling practice has continued for considerably more than half a century and is still conventional practice despite many prior suggestions, in issued patents and in the literature, of methods for accomplishing the same ends as the poling operation, which purport to eliminate the use of poles and it has many times been suggested that other reducing agents, such as coal, charcoal, petroleum, natural gas or manufactured reducing gases of various kinds, be used in lieu of timber poles.

Notwithstanding these many prior art suggestions, none of them, so far as we are aware, has ever achieved only metallurgical success or both metallurgical and economical success. None of the prior suggestions, so far as we are aware, has been practiced industrially. For one reason or another they have not been satisfactory and have not gone into use. So the use of poles still continues in the art despite the ever increasing scarcity and cost of suitable timber poles and despite the many drawbacks attributable to their use.

In accordance with our invention the use of timber poles or logs, with its attendant hazards and drawbacks, is eliminated and we are able to remove unwanted oxygen from molten oxygen-containing copper by the use of a gaseous reductant which has proved itself in actual large scale commercial operations not only to be successful and effective for the metallurgical purpose but also more economical and less hazardous to use than timber poles.

In accordance with our invention we use as the reductant a gaseous reducing agent which is obtained by a partial oxidation of low molecular weight hydrocarbons of the straight chain paraffin series (C_nH_{2n+2}) and preferably natural gas in which methane (CH_4) is the predominant constituent, it being understood of course that there is normally present in natural gas, smaller amounts of hydrocarbon compounds of molecular weight higher than methane, such as ethane (C_2H_6), propane (C_3H_8) and often there is present compounds of still higher

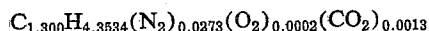
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molecular weight, such as butane (normal C_4H_{10} and iso C_4H_{10}), pentane (C_5H_{12}) and not infrequently small amounts of nitrogen (N_2), carbon dioxide (CO_2) and even oxygen (O_2) and perhaps other gases or elements in very small amounts. And while we prefer to produce our gaseous reducing agent from a natural gas in which methane is the predominating hydrocarbon compound, our invention contemplates as a starting material for producing a suitable gaseous reducing agent the use of hydrocarbon mixtures in which other hydrocarbon compounds than methane predominate, such as hydrocarbon gases in which ethane, butane, propane, pentane or mixtures of these hydrocarbons predominate.

In practicing our preferred method, which we have now carried out in day-to-day operations on a large commercial scale with excellent results at a large copper smelting and refining plant we have used natural gas supplied by a natural gas public utility company and produced from New Mexico and Texas fields. While the natural gas supplied may vary somewhat from time to time, the following is a typical analysis of the natural gas.

Component	Volumetric Content, percent
Methane— CH_4	83.40
Ethane— C_2H_6	9.40
Propane— C_3H_8	2.29
Butane Normal— C_4H_{10}	0.13
Butane iso— C_4H_{10}	0.16
Pentane— C_5H_{12}	0.21
Nitrogen— N_2	4.07
Carbondioxide— CO_2	0.31
Oxygen— O_2	0.03

The calculated molecular weight of that gas is 18.79. The calculated formula is



And it is significant to observe that the gas is free from sulfur which we consider to be extremely important in the successful operation of our process.

In accordance with our preferred method, natural gas is partially oxidized (as distinguished from complete oxidation or complete burning) with an oxygen-containing gas, air being preferred as the oxygen-containing gas because of its ready availability and cheapness as well as its effectiveness for the purpose. In brief, the natural gas is subjected to a partial combustion with air in the presence of a suitable known catalyst, for example, nickelized alumina or other suitable catalyst, under conditions which convert the major part of the combined carbon (C) present in the mixture of natural gas and air to carbon monoxide gas (CO) and the major part of the combined hydrogen (H) present in the natural gas to hydrogen (H_2). Minor amounts of CO_2 and H_2O will be formed and possibly some carbon (C) and there may be a minor amount of hydrocarbon, such as CH_4 , present which remains unreacted, and of course the nitrogen (including argon and other rare gases) in the air or in the natural gas itself, is inert and is present in the resultant gaseous mixture. This resultant gaseous mixture of this partial oxidation of natural gas is referred to herein as "reformed-gas."

As an example of this resultant gaseous mixture or reformed-gas, there is shown below the analysis of this reformed gas as produced by us in a gas reformer and used in the practice of our process for removal of unwanted oxygen from molten copper, the copper having been subjected to the oxidizing step of fire-refining, in-