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CHLORINATION PROCESS

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This invention relates to the chlorination of ores. It is well established that many metal bearing materials, particularly metal oxide bearing materials, may be chlorinated at elevated temperatures. A wide variety of literature has been developed in this field and the processes have been commercially used. For example, titanium bearing materials, such as ilmenite, rutile, essentially pure titanium dioxide, titanomagnetite, and like ores or other materials containing 10 to 50 percent or more of titanium, have been chlorinated successfully. Typical processes for effecting such chlorination are described in U. S. Patents Nos. 2,184,884, 2,184,885, 2,184,887, 2,253,470, and 2,253,471.

Typical chromium ores or chromium bearing materials which preferably contain in excess of about 10 percent chromium may be chlorinated. Such processes are described in U. S. Patents Nos. 2,185,218, 2,240,345, and 2,368,323. These processes and other processes for chlorination of chromium oxide bearing ores, as well as metallic ferrochromium and the like, are well known in the art.

Tin ores which contain in excess of 5 to 10 percent of tin also have been subjected to chlorination as described in U. S. Patent No. 2,345,210. In all of the above mentioned patents, the chlorination of ores containing other metallic components, including iron, aluminum, and the like, are also disclosed.

Various other metallic bearing materials, notably oxide bearing materials which contain aluminum, zirconium, arsenic, beryllium, bismuth, germanium, gold, tellurium, columbium, and the like, may be subjected to chlorination for production of the corresponding metal chlorides. In many cases it is desired to avoid formation of mixtures of chlorides and consequently it is not uncommon to chlorinate relatively pure metal compounds such as titanium carbide, titanium oxide, or the corresponding oxides, carbides, nitrides, and the like, of other metals.

In the practice of the above described chlorination processes, briquettes of the metal ore or metal oxide or like metal bearing material with carbon are prepared. The amount of carbon normally used is that stoichiometrically required to reduce a major portion (usually at least one-half) or even all of a metal oxide or like compound to the metallic state.

In these processes, the briquettes are placed in a shaft furnace and are subjected to contact with gaseous chlorine at an elevated temperature, normally ranging above about 500° C., and usually ranging from about 800 to 1200° C., and the chlorination occurs with the chlorides being vaporized and condensed in suitable condensation equipment.

Considerable difficulty is observed due to the fact that the briquettes tend to disintegrate during chlorination. As a consequence, substantial quantities of unchlorinated material tend to be swept away from the reaction furnace by the chlorinating gases and the evolved

vapors of chlorination. This materially reduces the efficiency of the process and increases its cost. Furthermore, it complicates the problem of condensing the vapors and recovering them in a pure or substantially pure form.

According to the present invention, a novel method has been provided whereby briquettes which tend to disintegrate less readily are produced. In accordance with this method, the metal oxide bearing material, such as titanium dioxide, ilmenite ore, chromite ore, or the like, is mixed with a bituminous coal, preferably a soft coking coal, and the mixed product is heated while tumbling at a temperature at which components of the coal (tar, high boiling hydrocarbons, and the like) are fused at least to a degree that they are sticky or adhesive. As a consequence of tumbling of this character, the product forms into balls or like agglomerates. These agglomerates are then calcined at an elevated temperature, preferably high enough to effect removal of substantially all of the volatile hydrocarbons from the product. The resulting product is found to be well bonded and shows little or no tendency to disintegrate during chlorination.

According to a further embodiment of the invention, it is found advantageous to prepare these briquettes by incorporating, in addition to the coal and ore or like titanium or other metal bearing material, a substantial quantity of a previously carbonized bituminous coal, preferably a carbonized mixture of the metal oxide bearing material and bituminous coal. Such previously carbonized material should have a particle size substantially less than that desired in the briquettes, and usually about one-eighth inch in diameter or below. Such material may be obtained by breaking up or grinding previously formed carbonized briquettes. By incorporating such a previously carbonized material in the coal-metal oxide bearing material to be briquetted, it is found that the previously carbonized material tends to serve as nuclei upon which the balls may build up to the size desired.

The practice of the above described invention will be discussed in detail as applied to the chlorination of titanium oxide bearing materials such as ilmenite, titanium oxide or rutile. It will be understood, of course, that the embodiments discussed with reference to titanium bearing materials may also be applied to the preparation of briquettes for chlorination of other metal bearing materials such as those mentioned above.

Titanium bearing materials to be chlorinated normally contain the titanium in the form of oxide and may contain more or less iron which also is present as an oxide. The titanium content of the material normally is in excess of about 10 percent titanium. Rutile may contain very little iron, for example, 1 to 2 percent iron. Also, the material to be treated may have been processed previously in order to remove a portion of the iron. On the other hand, ilmenite ore contains a substantial amount of iron, usually ranging well above 10 percent iron. A typical ilmenite ore is one which contains about 26 percent iron and 35 percent titanium, both metals being present in the oxide form. Various other ores containing 10 to 35 percent iron and 20 to 50 percent or more of titanium may be subjected to treatment.

In the practice of the invention, the titanium dioxide or titanium ore is mixed with bituminous coal. The bituminous coal preferably should be one which is a soft coking coal. Coals having a low ash content normally are preferred in order to avoid contamination of the product. Pittsburgh seam bituminous coal and like coals capable of producing coal briquettes are quite suitable.

The amount of coal should be sufficient to supply the stoichiometric amount of carbon required to reduce the

titanium present as oxide to metallic state. Where iron or other metal is present, proper allowance must be made to provide the amount required to reduce these metals. This is particularly true of a metal such as iron which tends to chlorinate before titanium. The amount of coal used for this purpose will depend to a considerable degree on the amount of fixed carbon in the coal. In general, however, the amount is in the sufficient proportion to establish about 10 to 100 percent by weight of carbon in the ultimate briquette, based upon the weight of the titanium oxide undergoing chlorination. Larger amounts of carbon may be used but are usually unnecessary. In addition, a quantity of a previously carbonized mixture of titanium oxide bearing material and coal is added. The particle size of this material preponderantly is about one-fourth inch in diameter or below. The mixed materials are then fed into a rotating drum which is heated to a temperature at which the coal becomes sticky due to fusion of organic components therein. The exact temperature required depends upon the nature of the coal. Temperatures ranging from about 250 to 600° C. are normally adequate. A good average temperature is about 400 to 450° C. As a consequence of the tumbling, the mixture of the coal and the ore tends to collect upon the nuclei of the previously carbonized material and to form agglomerate which, as they are tumbled, tend to shape themselves into balls or rounded briquettes. This process is continued until the balls have built up to a desirable size. This size is largely a matter of choice but normally ranges from ½ to 2 inches in diameter.

Following formation, the balls or briquettes are placed in a calcining furnace and are calcined in order to remove hydrocarbon components. This calcination may be conducted suitably in a rotary furnace. The temperature of calcination is subject to some variation depending upon the time of calcination and also upon the nature of the volatile components, but normally ranges from 750 to 1200° C.

Of course, the calcination is effected under conditions such as to avoid burning of the briquettes. That is, air is excluded and the atmosphere in which the product is calcined is effectively a reducing atmosphere.

Following the production of the briquettes, they are subjected to chlorination with or without cooling. The chlorination may be effected most readily by introducing the briquettes into a shaft furnace whereby to form a bed of briquettes, introducing chlorine into the bottom of the bed, and allowing the chlorine to permeate the bed and effect the chlorination. The reaction proceeds at a temperature well about 500° C., usually in the range of 800 to 1200° C. At this temperature, titanium tetrachloride is formed with or without other chlorides, such as iron chloride, depending upon the presence of these metals in the ore undergoing chlorination. The resulting vapors are carried from the shaft furnace and are condensed in suitable condensing equipment.

The following is a typical example of the invention herein contemplated:

Example I

The ore used is ilmenite ore having the following analysis:

	Percent by weight
Titanium	31.3
Iron	23.3
SiO_2	4.3
Al_2O_3	2.5
Magnesium and calcium	0.9

Two thousand pounds of this ilmenite ore is mixed with 1430 pounds of a low ash, soft-coking, Pittsburgh seam bituminous coal, and 860 pounds of a previously carbonized mixture of coal and ilmenite ore. The ore used was ground to a degree where 98 percent passed through 200 mesh. The coal had a particle size of less than one-fourth inch. The previously carbonized material had a particle size of less than one-eighth inch.

The resulting mixture was fed into a rotating drum 8 feet in diameter and 16 feet long and was heated to a temperature of 500° C. The drum was rotated at approximately 5 R. P. M. and the mixture was tumbled in this drum for a period of about 35 minutes. Thereafter, the heat was turned off and the tumbling continued for about 10 minutes to harden the resulting balls which were produced, and the resulting product was discharged from the drum and was lightly crushed and screened to give a product having the size of approximately ½ x 4 inches. The fines which were screened from this product were recycled as a carbonized mixture of coal and ore for production of a further batch of briquettes.

The resulting briquettes were chlorinated in a shaft furnace having an internal diameter of 16 inches by feeding the briquettes to a reaction bed in the furnace in which chlorination was effected at approximately 900 to 1000° C. Over a period of 58 hours, 6,164 pounds of the briquettes were fed at the rate of 62½ pounds each ½ hour to the bed until the entire amount of 6,164 pounds had been fed. During the period of 58 hours, 12,656 pounds of chlorine was fed into the reactor at a substantially uniform rate. Approximately 4,621 pounds of crude titanium tetrachloride was produced. During the operation, essentially no blowover of material, due to disintegration of the briquettes, took place.

It will be understood that the process disclosed in the above identified example may be applied to other materials, including pure titanium dioxide, titanomagnetite, and various titanium dioxide concentrates. Moreover, it is possible to effect a selective chlorination of the iron from titanium in ilmenite by limiting the amount of carbon, as is described in U. S. Patent No. 2,184,884. Thus, the briquettes in such a case may be prepared using a substantially lower concentration of carbon.

The process also may be used in the chlorination of the other metal bearing materials, following the practice disclosed in the above identified example, with or without the modifications taught in any of the above identified patents.

Although the present invention has been described with reference to the specific details of certain embodiments, it is not intended that such details shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

What is claimed:

1. A method of preparing a metallic chloride which comprises mixing a material which comprises a finely divided oxide of a metal which forms a volatile chloride with an amount of pulverulent bituminous coal having a particle size below about ¼ inch at least equal to the amount stoichiometrically required for reduction of said metal oxide to metallic state, tumbling said mixture at a temperature of 250 to 600° C. whereby the coal becomes adhesive and agglomerates of coal and said finely divided material are built up, thereafter calcining the resulting agglomerates to remove hydrocarbon components, and chlorinating the agglomerates thus obtained.

2. The process of claim 1 wherein the agglomerates are calcined at a temperature of 750 to 1200° C. to remove hydrocarbons prior to chlorination.

3. The process of claim 1 wherein there is incorporated in the mixture or ore and coal, particles of a previously carbonized mixture of coke and said ore.

4. A method of preparing titanium tetrachloride which comprises mixing a finely divided ore which contains at least 10 percent titanium in the form of oxide with an amount of pulverulent bituminous coal having a particle size below about ¼ inch sufficient to provide in the mixture at least 10 percent by weight of carbon, heating the mixture to a temperature of 250 to 600° C. whereby the coal becomes adhesive, tumbling the mixture at said temperature and thereby forming agglomerates compris-

ing particles of ore and particles of coal bonded together, thereafter calcining the resulting agglomerates to remove hydrocarbon, and chlorinating the resulting agglomerates to form and vaporize titanium tetrachloride.

5. A method of preparing a metal chloride which comprises mixing a finely divided ore which contains a metal oxide capable of forming a metal chloride which is volatile at a temperature below 600° C. with an amount of bituminous coal at least sufficient to provide in the mixture at least 10 percent by weight of carbon, heating the mixture to a temperature at which the coal becomes adhesive, tumbling the mixture at said temperature and thereby forming agglomerates comprising particles of ore and particles of coal bonded together, thereafter calcining the resulting agglomerates to remove hydrocarbon, and chlorinating the resulting agglomerates at a temperature above 500° C.

6. The process of claim 5 wherein the temperature of heating during tumbling is 250 to 600° C.

7. A method of preparing a metal chloride which comprises mixing a finely divided ore which contains a metal oxide capable of forming a metal chloride which is volatile at 600° C. with an amount of bituminous coal sufficient to provide in the mixture at least 10 percent by weight of carbon, heating the mixture to a temperature of 250 to 600° C. whereby the coal becomes adhesive, tumbling the mixture at said temperature and thereby forming agglomerates comprising particles of ore and particles of coal bonded together, separating the agglomerates into a coarse fraction and a fine fraction, mixing the fine fraction with a further portion of said finely divided ore and an amount of bituminous coal sufficient to provide in the mixture at least 10 percent by weight of carbon thereby forming a second mixture, heating the second mixture to a temperature of 250 to 600° C. whereby the coal becomes adhesive, tumbling the second mixture at said temperature whereby the particles of said fine fraction serve as nuclei and agglomerates comprising particles of ore and coal bond thereto thus forming further agglomerates, and chlorinating further agglomerates thus formed.

8. A method of preparing titanium tetrachloride which comprises mixing a finely divided ore which contains at least 10 percent titanium in the form of oxide with an amount of pulverulent bituminous coal having a particle size below about ¼ inch sufficient to provide in the mixture at least 10 percent by weight of carbon, heating the mixture to a temperature of 250 to 600° C. whereby the coal becomes adhesive, tumbling the mixture at said temperature and thereby forming agglomerates comprising particles of ore and particles of coal bonded together, separating the agglomerates into a coarse fraction and a fine fraction mixing the fine fraction with a further portion of said finely divided ore and an amount of bituminous coal sufficient to provide in the mixture at least 10 percent by weight of carbon thereby forming a second mixture, heating the second mixture to a temperature of 250 to 600° C. whereby the coal becomes adhesive, tumbling the second mixture at said temperature whereby the particles of said fine fraction serve as nuclei and agglomerates comprising particles of ore and coal bond thereto thus forming further agglomerates, and chlorinating further agglomerates thus formed and thereby producing titanium tetrachloride.

9. The process of claim 7 wherein the coarse fraction is chlorinated at a temperature of at least 500° C. after separation from the fine fraction.

10. The process of claim 1 wherein the mixture is tumbled at a temperature of 400 to 450° C.

11. The process of claim 5 wherein the resulting agglomerates are calcined at 750 to 1200° C. to remove volatile hydrocarbons.

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