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METHOD FOR CHLORINATING TITANIUM
OXIDE MATERIAL

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This invention relates to a method for chlorinating titanium oxide. More specifically it relates to a method for chlorinating finely divided titanium oxide material.

Titanium oxide materials are chlorinated by many known processes. In most of these prior processes the titanium oxide material is subjected to chlorination in briquetted, nodulized or in granular form, the granules being of substantially coarse size material. Finely divided materials normally have been avoided in most chlorination processes, because of the difficulties in handling extremely fine solid particles, so as to produce efficient particle contact with chlorine gas. Chlorination of such fine TiO_2 particles by a method in which the solid particles are suspended in an upward flowing gas stream, known in the art as a "fluo-solids" type process has been heretofore considered impossible due to dusting, channeling and plugging effects encountered.

An object of the present invention, therefore, is to present a method for chlorinating finely divided titanium oxide material. Another object is to provide a method in which the titanium oxide is chlorinated directly in an efficient and economical manner which eliminates the necessity for consolidation of the fine particles before processing. A further object is to present a chlorination process in which dusting, channeling and plugging effects are avoided. These and other objects will become apparent from the following more complete description of the invention.

In its broadest aspects this invention contemplates chlorinating finely divided oxide by a process of the general type known in the art as "fluo-solids," which comprises passing the titanium oxide and chlorine through a restraining bed, the restraining bed comprising a dynamic suspension of coarse material of lesser reactivity than the finely divided titanium oxide. The invention further contemplates a process for chlorinating titanium oxide having particles of a size less than 325 mesh, which comprises passing said titanium oxide and chlorine through a restraining bed of lesser reactivity than said finely divided titanium oxide, said bed comprising a dynamic suspension of coarse material having particles substantially all of a size within the range from 20 to 120 mesh.

Titanium oxide in this finely divided form, that is less than 325 mesh material, may be obtained in large quantities as the resultant product from many titaniferous iron ore beneficiation processes, or may be obtained from processes requiring extremely fine grinding. Titanium oxide in this

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form as previously stated is not easy to process, particularly through a chlorination step, because of the above mentioned difficulties encountered during such processing. By employment of the present invention, however, the finely divided titanium oxide is chlorinated in the presence of a restraining bed without encountering such difficulties.

The restraining bed which comprises a dynamic suspension of coarse material, i. e. material consisting of particles substantially all of a size within the range from 20 to 120 mesh, and through which the finely divided titanium oxide material passes, acts as a velocity decelerator and a detainer for the passage of the fine particles. The restraining bed diminishes the speed of the fine particles passing through the reaction zone and promotes effective and complete chlorination reaction with the titanium oxide material.

In a preferred embodiment of the invention the coarse particles may be held in a dynamic suspension by passing gases in an upward flow through the coarse material to form and maintain the restraining bed. It has been found that satisfactory suspension has been obtained when the space velocity of the upward flowing gases preferably is maintained from 0.35 foot per second to 1.0 foot per second.

The type of coarse material used in the restraining bed is unimportant except that it must be of lesser reactivity than the finely divided titanium oxide which is being chlorinated. The restraining bed may consist of, for example refractory silicates, corundum or calcined bauxite, calcined clay, or sand. The bed also may consist of coarse particles of titanium oxide material, such as rutile ore, or coarse titanium concentrates and residues. When the restraining bed is composed of coarser TiO_2 material, thus, due to its increased particle size, will actually be of lesser reactivity than the finely divided TiO_2 which it is intended to chlorinate. Thus a preferential chlorination may be obtained in which the fine TiO_2 is converted to $TiCl_4$ and the coarse particles constituting the restraining bed are substantially unaffected. Such a preferential chlorination is achieved when chlorine in amount to react only with the fine TiO_2 is employed. Excess of chlorine over this amount may result in some chlorination of the coarse TiO_2 material in the restraining bed.

The chlorine used in this process is preferably added in a quantity equal to the theoretical amount required to react with all of the finely divided titanium values to form titanium tetrachloride. Chlorine added in excess of the theo-

retical amount normally should be avoided, except when titanium oxide materials are employed in the restraining bed, since for economical reasons it is usually necessary to subsequently recover the unused chlorine values.

The rate of chlorine addition may be varied considerably as desired, but if the chlorine rate is insufficient to suspend the restraining bed, dilutant gases, such as for example nitrogen, carbon dioxide, or helium, may be added along with the chlorine in quantity sufficient to suspend the coarse material. The temperature for chlorination of the finely divided titanium oxide material preferably should be carried out from 700° C. to 1000° C.

In order to more fully illustrate the preferred embodiments of this invention, the following examples are presented:

Example I

Finely divided titanium oxide residue used in this example was obtained as the resultant product from a titaniferous iron ore beneficiation process. The finely divided titanium oxide having particles of a size less than 325 mesh was added at the rate of 2.1 parts per minute along with 0.4 part per minute carbon to the lower portion of a reaction chamber in which a 2 foot restraining bed containing 600 parts of coarse titanium oxide material was held in dynamic suspension. The coarse titanium oxide material had a particle size range from 20 to 120 mesh. The bed also contained 120 parts carbon (20-60 mesh). The bed was maintained in suspension by passing 3.8 parts per minute of chlorine, which is equal to the theoretical amount to chlorinate the finely divided titanium values, and 4.7 parts per minute of carbon dioxide in an upward flow through the restraining bed. The temperature of the bed was held at 800° C. The exit gases from the reaction chamber contained 5.7 parts carbon dioxide, 0.2 part carbon monoxide, and 0.2 part chlorine. 88% of the finely divided titanium values were converted to titanium tetrachloride with 92.7% utilization of the chlorine obtained.

Example II

The procedure used in Example I was repeated except the coarse TiO_2 material was replaced with coarse calcined bauxite. The bauxite used in the restraining bed in this example had a particle size range from 30-120 mesh. The temperature of the bed was held at 900° C.

The finely divided TiO_2 material was chlorinated in the same manner as the previous example and substantially the same yields and efficiencies were obtained.

In order to compare the process of the present invention with a process in which no coarse bed is utilized, a control was run and is reported as follows:

The procedure described in the above example was used for this control run except no restraining bed of coarse material was employed in the reaction chamber. The finely divided titanium oxide, carbon, and the chlorine and carbon dioxide gases were introduced to the bottom of the empty reaction chamber, and the rates of addition were maintained in amounts equal to those shown in the above example. The control

run, which was carried out without the utilization of the restraining bed of coarse material in the reaction chamber, resulted in bad channeling and surging in the reaction chamber with high dust losses and very low chlorine efficiencies with respect to chlorination of the finely divided titanium oxide values. The control run clearly shows that the restraining bed is necessary when chlorinating less than 325 mesh titanium oxide material with gas velocity of 0.35-1.0 foot per second which is sufficient to suspend and maintain in suspension the 20-120 mesh coarse material.

It has been shown by the process of this invention that finely divided titanium oxide material may be chlorinated directly without the necessity of consolidation of the fine particles before processing. The process of this invention further eliminates the difficulties involved which are present in most processes i. e. with respect to bad channeling and surging of the bed and high dust losses. The present process is direct, simple and economical to employ.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto and other modifications and variations may be employed within the scope of the following claims.

We claim:

1. A method for chlorinating finely divided titanium dioxide material of a size less than 325 mesh which comprises introducing said titanium dioxide and chlorine gas into a reactor containing coarse particles forming a suspended bed at a temperature of 700° C. to 1000° C. in the presence of carbon to form gases of titanium tetrachloride and oxides of carbon, said chlorine gas being introduced at sufficient velocity to maintain the bed suspended in agitated condition but insufficient to carry the coarse particles of said bed out of said reactor, said particles being substantially all of size within the range of from 20 to 120 mesh, said particles being of lesser reactivity with chlorine gas than said finely divided material, and the amount of chlorine gas added substantially equal to that required to theoretically convert all of the finely divided titanium dioxide to titanium tetrachloride.

2. Method according to claim 1 in which the coarse particles are a refractory material.

3. Method according to claim 1 in which the coarse particles are titanium dioxide.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,020,431	Osborne	Nov. 12, 1935
2,184,887	Muskat	Dec. 26, 1939
2,443,673	Atwell	June 22, 1948
2,486,912	Belchetz	Nov. 1, 1949

OTHER REFERENCES

J. W. Mellor's: "Inorganic & Theoretical Chemistry"; pages 27, 28, vol. 7, 1927 ed., Longmans, Green & Co., N. Y., publishers.