United States Patent Office

2,753,243

Patented July 3, 1956

2,753,243

PRODUCTION OF TITANIUM TETRACHLORIDE

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No Drawing. Application January 25, 1954, Serial No. 406,097

4 Claims. (Cl. 23—87)

This invention relates to the production of titanium tetrachloride by chlorination of briquettes containing a titanium oxide bearing material and a carbonaceous reducing agent.

It has been previously known to chlorinate briquettes containing titanium oxide and carbon at an elevated temperature. The briquettes may be formed of rutile, ilmenite or other titanium bearing material admixed with coke or coal and a binder such as tar or molasses. Generally the mixture is spread out and burned to drive off volatile components and to provide a coked, porous mass which is broken up to form so called briquettes. To produce $TiCl_4$, a bed of appreciable thickness of such briquettes is treated in a furnace at temperatures of the order of 450°–1000° C. by passing chlorine gas upwardly through the bed. The reaction produces $TiCl_4$ which is taken out of the top of the furnace as a gas and is subsequently condensed.

Serious difficulties have arisen in the operation of such a process, however, due mainly to the character and effect of the briquettes employed. When these are formed with a binder, such as tar, having sufficient cohesive action to produce a coherent mixture, the mixture also adheres strongly to the surfaces of containers and mixing devices in which it is formed and also to the pans or surfaces on which it is fired. In addition, briquettes heretofore proposed or used have deteriorated badly in the chlorination furnace, lacking physical strength and also being prone to disintegrate as the reaction with chlorine has progressed. Breaking and powdering of the briquettes creates poor furnace operating conditions either raising the back pressure against which the chlorine must be introduced to high levels, or packing in some section and allowing channels to form in others thus allowing chlorine to flow through the bed without contact with the briquettes resulting in poor efficiency.

It is therefore the object of this invention to provide an improved process for the manufacture of titanium tetrachloride. It is further object of this invention to provide an improved process for the manufacture of titanium oxide containing briquettes suitable for chlorination to produce $TiCl_4$. Another object of this invention is to provide an improved stronger, and more uniform titanium oxide-containing briquette adapted for chlorination to produce purer $TiCl_4$. These and other objects of this invention will be apparent from the following detailed description thereof.

This invention in its broadest aspects contemplates the manufacture of titanium tetrachloride by chlorinating at elevated temperature briquettes comprising a titanium oxide bearing material, a carbonaceous reducing agent and a binder comprising acid treated mineral tar or pitch. In order to form the briquettes of this invention, tar or pitch, preferably coal tar, is treated with a strong mineral acid such as sulphuric acid. The tar or pitch binder is admixed with comminuted titanium oxide bearing material such as rutile or ilmenite and a carbonaceous reducing

agent such as coke or coal. The mixture may be formed into suitable size and shape briquettes by pressing in a conventional briquetting machine for example of the type operating with pocketed rolls, referred to as Belgian rolls, and the formed briquettes are then fired. Or, alternatively, the mixture may be spread out in a relatively thin layer in pans or on a convenient surface, fired, and the fired mass broken up to make fragments of briquette size and characteristics.

The tar or pitch employed in the practice of this invention may be of any type having suitable binder properties selected from those of mineral origin which will include generally the group consisting if coal and petroleum tars and pitches. It will be appreciated that pitch is most generally obtained by further distillation of tar, which is itself a distillation residuum, and that these compositions differ mostly in their viscosity characteristics and in the amount and character of the remaining oils and other volatile constituents. It is preferred however, to employ coal tar which is readily available, and a relatively thin and fluid grade should be selected to provide easy handling and good binding properties. The tar or pitch is treated with strong sulphuric acid by thoroughly admixing with from 2% to 25% of its weight of acid. The temperature of the mixing operation should be such that the tar is generally liquid. In the case of tars which are liquid and relatively thin at normal temperatures of 15–30° C. the sulphuric acid readily forms a homogeneous product with the tar. The exact nature of the reaction is not clearly understood but it is postulated that a chemical and/or physical combination is obtained since the surface tension and cohesive qualities of the tar are noticeably changed. If the tar or pitch is solid or very viscous at room temperature or if normally liquid tar is to be treated under low ambient temperature conditions sufficient heat should be applied to liquify the material and to obtain the proper homogeneous acid treated tar product.

The amount of acid may vary from about 2% to about 25% by weight of the tar or pitch. Less than 2% will be found to produce little of the desired effect and more than about 25% does not produce any appreciable additional benefit. The rutile, carbon and acid treated tar are mixed together so as to produce a final composition after firing which contains rutile and carbon in the ratio of about 3–1 to 5–1. The rutile-carbon ratio may vary considerably but ratios less than 3–1 are not generally advantageous. Both the rutile and the coke or coal or other reducing agent are comminuted. The degree of fineness is not of great importance and in general superior results are obtained when these materials are not ground too fine. For the rutile or ilmenite a particle size generally less than 60 mesh has proved beneficial and the coal or coke of a comparable size range will be satisfactory, although these finenesses may vary considerably according to specific conditions.

The amounts of carbon employed in the mixture in relation to the rutile will be somewhat greater than the anticipated proportions in the final fired briquette. Losses of both carbon and volatile materials occur during firing. Therefore, it will be found that about 3 to 6 parts of rutile or ilmenite to 1 part of coke or coal to ½ to 2½ parts of tar will produce fired briquettes of the suitable composition.

The proportions of the materials are thoroughly mixed together preferably by means of a mechanical mixing device such as a pug mill. The mixture is then fired by spreading out in a relatively thin layer in metal pans and heated to a temperature high enough to ignite the volatile constituents. After combustion is substantially complete it is preferred to subsequently heat in the absence of air at a temperature around 400° to 700° C. to

further reduce the volatile content. After the final heating the fired mass may be cooled and then broken into fragments to form briquettes. The fired material will be found to be a coherent, porous mass with substantial mechanical strength readily adapted for chlorination. Alternatively the mixture after blending in the pug mill may be formed into suitable size and shape briquettes by pressing on a conventional briquette machine. These briquettes may be fired in the same manner as the previously described un-pressed material.

As an example of the properties obtained in briquettes produced according to this invention compared to properties obtained in briquettes produced employing conventional binding agents, two batches of briquettes were made from the same original batch of rutile and coke. A mixture was prepared containing 68 parts of rutile, 16 parts coke and 17 parts of tar and a second batch was prepared containing the same amount of rutile and coke but substituting the same weight of acid treated tar according to this invention. The two mixes were heated in a gas fired furnace to a temperature at which ignition of the volatile constituents occurred. After all the volatiles had been burned heating was continued for about an hour at a temperature between 550 to 650° C. with the furnace closed to make sure that substantially all the volatile materials had been driven off from the mixture. The pans containing the fired mixture were than taken from the furnace, allowed to cool and the layers of the mix broken into fragments, roughly 1 inch square. These final fired briquettes were characterized, in the case of those produced using acid treated tar, by superior mechanical strength and resistance to disintegration during chlorination.

To test for mechanical strength, the fired briquettes were compressed between two plane surfaces until fracture and disintegration occurred, and the pressure measured as pounds per square inch required was taken as an indication of the briquette strength. To determine resistance to disintegration during chlorination the briquettes were treated with chlorine in a small laboratory reactor producing titanium tetrachloride. At the end of the chlorination reaction the briquettes were screened to separate a fines portion less than 8 mesh. The percentage of the original charge which had disintegrated to form fines was taken as an indication of the resistance to disintegration.

The results obtained in testing the two batches made as above are shown in Table 1 below:

TABLE I

	Straight Tar	Acid Treated Tar
Strength.....p. s. i..	93	117
Resistance to disintegration.....percent..	50	34

It has been found additionally, that chlorination of briquettes produced according to this invention results in production of a purer grade of titanium tetrachloride. Raw materials for instance, rutile or ilmenite most generally contain a proportion of vanadium which is a harmful impurity in the $TiCl_4$ product. Purification of titanium tetrachloride is often necessary to eliminate vanadium compounds. In the case of $TiCl_4$ produced from briquettes containing acid treated tar, however, the crude $TiCl_4$ produced has been found to contain substantially less vanadium than $TiCl_4$ produced by conventional and heretofore known methods. It is postulated that the sulphur content of the briquettes when made with acid treated tar may react in some manner with vanadium to form non-volatile or insoluble compounds. It has been found that the acceptability of $TiCl_4$, particularly for the manufacture of pigments and for the production of titanium metal is to a large degree dependent on its freedom from vanadium. Tests made in which briquettes according to this invention were chlorinated, produced $TiCl_4$ having a vanadium content of between .01 and .2% compared to between .3 and .5% obtained when conventional briquettes of the same general composition without containing acid treated tar were employed.

The following example will illustrate a selected embodiment of this invention.

Example I

A portion of petroleum tar having a viscosity of 19.9 Sp Engler was admixed with 21% of its weight of 96% sulphuric acid. The mixture was stirred until a homogeneous product was obtained.

The acid treated tar product was admixed with rutile (minus 60 mesh) and coke (minus 20 mesh) in the following proportions:

65 parts rutile
11 parts coke
26 parts acid treated tar

This mixture was spread out in a 7 x 10 inch pan in a layer about 2 inches thick. The pan and its contents were heated to ignite the volatile constituents which burned readily for about an hour. The mixture was then heated for an additional hour in a closed furnace in the presence of combustion gases only at a temperature of between 550 and 650° C. The firing operation had converted the mixture in the pan to a hard, coked porous layer which was readily removed from the pan without sticking to the sides or bottom thereof. The layer was broken into fragments of about 1 inch largest dimension to form briquettes. These briquettes were placed in a furnace maintained at 800°–900° C. and chlorine gas passed upwardly through the bed of briquettes. Titanium tetrachloride was taken off the top of the furnace and condensed to liquid in a separate condenser. At the end of an hour and a quarter chlorination period, the chlorine was shut off and the charge removed from the furnace. Testing of the spent briquettes showed that only 24% of the briquettes had disintegrated to form fines of smaller than 8 mesh.

The chlorination reaction was characterized by good efficiency for the chlorine employed and low back pressure during passage of gas through the bed.

The titanium tetrachloride produced contained a vanadium content of 0.2% compared to a normal content of from 0.3% to as high as 0.5% for $TiCl_4$ manufacture by conventional methods from the same raw materials.

The following is an example of the practice of this invention when employing pressed briquettes.

Example II

The acid treated tar product of Example I was admixed with coke and rutile in the following proportions:

31 parts rutile
10 parts coke
5 parts acid treated tar

The mixture was pressed into 1 inch ovoid briquettes on a briquetting machine equipped with Belgian rolls and the briquettes fired in the same manner as those in Example I. After firing the briquettes showed excellent mechanical strength.

The fired briquettes were chlorinated to produce $TiCl_4$ and after chlorination showed 21% of fines less than 8 mesh.

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 limits of the following claims.

I claim:

1. In a process for production of titanium tetrachloride by chlorination of briquettes containing a titanium oxide bearing material in admixture with a carbonaceous reduc-

ing agent, the steps which comprise; treating a binder selected from the group consisting of tar and pitch with strong sulphuric acid by forming an intimate mixture consisting of said binder and said acid, in amount from 2% to 25% by weight of said binder, admixing said acid treated binder with a titanium oxide bearing material and a carbonaceous reducing agent and forming said admixture into briquettes adapted for chlorination.

2. In a process for production of titanium tetrachloride by chlorination of briquettes containing a titanium oxide bearing material in admixture with a carbonaceous reducing agent, the steps which comprise; treating a binder selected from the group consisting of tar and pitch with strong sulphuric acid by forming an intimate mixture consisting of said binder and said acid, in amount from 2% to 25% by weight of said binder, admixing said acid treated binder with a titanium oxide bearing material and a carbonaceous reducing agent, spreading out said mixture in a layer, firing said layer by heating in air to ignite the volatile constituents thereof and breaking said fired layer to form briquettes adapted for chlorination.

3. In a process for production of titanium tetrachloride by chlorination of briquettes containing a titanium oxide bearing material in admixture with a carbonaceous reducing agent, the steps which comprise; treating a binder selected from the group consisting of tar and pitch with strong sulphuric acid by forming an intimate mixture consisting of said binder and said acid, in amount from 2% to 25% by weight of said binder, admixing said acid treated binder with a titanium oxide bearing material and

a carbonaceous reducing agent, pressing said mixture into briquettes and firing said briquettes by heating in air to ignite the volatile constituents thereof and to form briquettes adapted for chlorination.

4. In a process for production of titanium tetrachloride by chlorination of briquettes containing a titanium oxide bearing material in admixture with a carbonaceous reducing agent, the steps which comprise; treating a binder selected from the group consisting of tar and pitch with strong sulphuric acid by forming an intimate mixture consisting of said binder and said acid, in amount from 2% to 25% by weight of said binder, admixing said acid treated binder with a titanium oxide bearing material and a carbonaceous reducing agent, firing said mixture by heating in air to ignite the volatile constitutents thereof and subsequently heating said mixture in the absence of air at a temperature of between about 400° to 800° C. and forming said mixture into briquettes adapted for chlorination.

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