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PREPARATION OF FEEDSTOCKS FOR CHLORINATION

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This invention relates in general to the production of feedstocks of improved reactivity incorporating an oxidized metal or metalloid-containing compound which may thereafter be chlorinated to yield the metal or metalloid chloride. More particularly, this invention relates to an improved feedstock containing boron in the form of boron oxide, a borate or the like or columbium or tantalum or both in the form of columbite or tantalite or the like, or vanadium in the form of vanadium oxide or the like, which is in the form of an agglomerate. The oxidized metals or metalloid-containing compounds of beryllium, hafnium, molybdenum, rhenium, tungsten, vanadium and zirconium may also be subjected to the process of this invention. As with the others, these metals may be used in the form of their ores or concentrates of their oxides or ores. However, for the sake of simplicity the present invention will be described hereinafter only with respect to the preferred metal species, boron, columbium, and tantalum, although it is to be understood that any of the other seven listed may be substituted. The resulting agglomerate has improved porosity whereby when it is desired to treat the agglomerate with gaseous chlorine, gaseous HCl, gaseous CCl_4, $COCl_2$, C_2Cl_6 or any of the other known chlorinating agents so as to yield the metal or metalloid chloride, a lessened resistance is displayed to the diffusion of the chlorinating gas therethrough.

It has been proposed to react a chlorinating gas at elevated temperatures with a coked and/or sintered feedstock which contains the metal or metalloid and oxygen together with a carbonaceous reducing agent and a coking binder to hold the feedstock in an agglomerated condition. However, these agglomerates may be resistant to the diffusion of the gas therethrough, thus reducing the reactive rate of the boron or columbium and/or tantalum or vanadium containing agglomerate to chlorination.

It is therefore an object of this invention to provide a method for the preparation of oxidized boron or columbium and/or tantalum or vanadium containing feedstocks which have improved porosity thereby making possible greater reactivity with a chlorinating gas.

The further object of this invention is to provide a feedstock having improved porosity and lessened resistance to the diffusion of a gas therethrough, thereby effectively raising the percentage of metal available for reaction with the chlorine in the said feedstock.

Further objects and advantages of this invention, if not specifically set out will become apparent during the course of the discussion which follows.

Generally, it has been found that agglomerated feedstocks having improved reactivity on treatment with gaseous chlorinating agents at high temperatures may be prepared by forming a mixture of a carbonaceous reducing agent and an oxidized metal or metalloid compound together with a coking binder; adding thereto a liquid hydrocarbon and then agglomerating the mixture so formed under the influence of high pressures. Following this step, the briquettes, pellets or tablets so formed are heated to a relatively high temperature, preferably within the range 100–700° C. whereby to volatilize the liquid hydrocarbon and any water which may be present and to produce a coking bond in the briquettes, pellets or tablets. The devolatilization removes the hydrocarbon from the feedstock particles thereby leaving voids and also

leaving the metal or metalloid containing constituent and the carbonaceous material in a firm coke structure which is primarily formed from the coking binder. Further, a portion of the hydrocarbon volatiles may thermally crack near the surface of the feedstock particles forming a coke structure there. The porous nature of the particles so formed allows for increased diffusion of chlorinating gas during the subsequent chlorination thus increasing the effective rate of the chlorination reaction.

More particularly, it has been found that an improved feedstock suitable for reaction with gaseous chlorinating agents at elevated temperatures may be formed from those materials which are customarily employed in the preparation of such feedstocks together with a certain amount of liquid oil, preferably a hydrocarbon, in the lubricating oil range. On being subjected to heat, the latter volatilizes whereby to provide voids in the agglomerate, thus allowing for increased diffusion of chlorinating gas therethrough during treatment with chlorine to yield the metal or metalloid chloride. Examples of suitable boron-containing oxidized materials are boron oxide, boric acid, decahydrate or anhydrous borax or naturally occurring borax materials such as colemanite, kernite or rasorite. These may be used individually or in combinations of two or more. An example of a suitable columbium containing material is columbite, while tantalite is a suitable tantalum raw material. These may be used individually or in combinations of two or more. Examples of suitable vanadium containing materials are vanadium pentoxide and trioxide. Preferred carbonaceous reducing agents used in this process are the commercially available reactive forms of carbon such as charcoal, petroleum coke and bituminous coal and coke. These also may be used individually or in combination. Coking binders which are employed are preferably coal tar or coal tar pitch. Certain other binders such as asphalt, starch, molasses or sugar, either independently or in combination, may be used. The important feature of this invention resides in incorporating with one or more of the aforementioned materials from each of the various categories between about 2% and 20% by weight based upon the weight of the dry mixture and preferably between about 5% and 15% by weight of a liquid, viscous hydrocarbon oil, preferably petroleum oil. The oil is thoroughly mixed with the feedstock mixture as by mechanically agitating the mixture or by spraying the liquid through a nozzle into the tumbling feedstock mixture, or by any other suitable means. The effect of the addition of this liquid hydrocarbon to the feedstock mixture prior to the application of heat and pressure is that the final feed particles have a lesser density than would be realized without the addition of said hydrocarbon. After the completion of the volatilizing operation, the void space within the pellets increases so as to facilitate diffusion of chlorinating gas through said particles. This is accomplished without any great loss of strength in the particles. Thus, by providing additional voids and passages in the pellets this invention allows for the more rapid and thorough penetration of the chlorinating gas through the feed particles thereby allowing for a more rapid and complete reaction with the oxidized metal. This invention provides additional surfaces upon which the chlorination reaction may take place by opening up the interior of the agglomerates.

The carbonaceous material and the metal containing material are preferably pulverized and ground to between minus 60 mesh and plus 200 mesh—although any size convenient to the agglomeration step to be detailed below may be used. The mixture so formed is then intimately mixed with 5 to 50%, and preferably between 10 and 25% of the powdered or liquid coking binder. Following this, between 2 and 20% by weight based upon the weight of the dry mixture, and preferably between 5 and 15% of a

liquid oil, preferably petroleum oil, is blended in. It is preferred to use a viscous hydrocarbon oil because of its low cost and effectiveness. By "viscous oil" is meant an oil which is free flowing at room temperature yet which has substantial body, such as petroleum lubricating oils in the range of 39–200 Saybolt Universal seconds viscosity at 210° F. and an A.S.T.M. pour point not higher than 10° F. The foregoing range includes motor oils falling within the S.A.E. viscosity range 5–80 as well as various gear oils and other oils. Oils which fall within the above specified range will pour and mix with adequate facility to be used in the invention herein described. The homogeneous mixture so formed is preferably agglomerated to a size such that a granular feed material suitable for a conventional moving bed or other reaction is obtained. This is accomplished by the application of high pressure to the raw feedstocks such as is achieved in commercial briquetting machines, pelleting presses, or tableting machines. The particles obtained are next dehydrated, devolatilized and coked and, may be simultaneously therewith or immediately subsequent thereto, sintered. The dehydration and devolatilization is accomplished at temperatures of 100 to 700° C. and the sintering at temperatures of 500 to 1000° C. The hardened material obtained after the devolatilization and/or sintering may be used directly or, if necessary, may be then broken up into granules of the desired size—from 1/16 inch to 4 inches, or preferably from 1/4 inch to 1 inch. (The briquettes, pellets or tablets may be of approximately this size on emergence from the machines.) Substantially all water and volatile material are removed from the feed and the proper coking bond is produced in the briquettes, pellets or tablets when the initial heating step of 100 to 700° C. is carried out for a period of about 2 to 10 hours. In the case of boron, if a sintering operation is desired wherein the boron-containing material is allowed to wet the carbonaceous material to increase the reactivity of the feed material an additional 2 to 6 hours at 500 to 1000° C. is necessary. Preferably, the devolatilization, etc., is accomplished in about 8 hours and the sintering in about 4 hours. The briquettes, pellets or tablets are then charged continuously or in slugs into the top of the vertical shaft moving bed reactor. The generally used apparatus and suitable operating techniques are set forth in copending application Serial No. 628,304, filed December 16, 1956, for "Process of Making Boron Trichloride," now abandoned, and in a continuation-in-part application thereof, Serial No. 78,187, filed December 23, 1960.

The feed particles normally pass into the chlorination zone of the reactor at a temperature somewhat less than the temperature prevailing in the reaction zone and are there heated to the temperature prevailing in the reaction zone by the reaction of a chlorinating agent with the feed particles, if, as is most generally the case, the particular composition of the feed particles produces an exothermic reaction with the chlorinating agent, and/or the transfer of heat from the hot product gases passing through and around the fresh feed particles to the fresh feed particles, the heat for the reaction having been supplied by external means, such as electrical heaters, in the event the particular composition of the feed particles produces an endothermic reaction with the chlorinating agent or if heat losses in the system are of such magnitude so as to require additional heat input.

In the case of boron, the temperature of the entering feed particles for the most economical feed compositions, for example anhydrous borax, is normally below the melting point of the boron-containing constituent and the reaction temperatures are normally above the melting point of the boron-containing constituent and in general above the melting point of a by-product of the reaction, sodium chloride, in the event that the boron-containing constituent also contains a sodium salt or a mixed sodium salt. The greatest economy of raw materials for the boron trichloride reaction is found when the ratio of the boron-containing constituent to the carbonaceous constituent most closely approaches the theoretical ratio as defined by the equation of the reaction, as for example, the use of anhydrous borax as the boron-containing constituent:

(1) $Na_2B_4O_7+7C+7Cl_2 \rightarrow 4BCl_3+7CO+2NaCl$ or

(2) $2Na_2B_4O_7+7C+14Cl_2 \rightarrow 8BCl_3+7CO_2+4NaCl$

Both overall reactions take place with Reaction 1 being preferential at the normal temperatures of operation. It has also been found that when the ratio of boron-containing constituent to carbonaceous constituent in the feed particles is higher than some general value, as, for example, for the case of anhydrous borax, this ratio has been found to be generally in the region of 18% of the theoretical ratio as expressed in Equation 1, the boron-containing constituent upon passing through its melting point temperature in the reactor liquifies and the excess boron-containing constituent over the quantity as expressed above, which remains in the feed particle, flows out of the feed particle and may collect on its surface or form liquid particles or drops which contain no carbonaceous material. Therefore, this excess boron-containing constituent becomes inactive to further chlorination but may yet be active in removing previously formed boron trichloride product to form a by-product of the reaction, a loose structure of boron oxide and boron trichloride.

Through the practice of this invention the additional voids and passages and increased contact surface available in the feed patricles affords a more rapid reaction to the extent that the boron-containing constituent in excess of the amount as described above is essentially completely reacted before it has reached the outside surface of the feed particles and, therefore, a higher ratio of boron-containing constituent to carbonaceous constituent can be effectively used than would otherwise be practical without the practice of this invention. The practice of this invention has allowed feedstocks to be prepared in which the ratio of the boron-containing constituent to the carbonaceous constituent has exceeded several fold the practical limit of this ratio as previously described without the practice of this invention. As an example, using anhydrous borax as the boron-containing constituent, the above described ratio has been higher than 60% of the theoretical ratio with better than 90% efficient reaction of the borax in the feed particles.

What has been said above as pertaining to boron feedstocks may also be said for columbium and/or tantalum and vanadium feedstocks except wherein sintering or liquification of the metal or metalloid feedstock is concerned—the columbium and/or tantalum feedstocks sinter or liquify at too high a temperature for this to be practical and the vanadium feedstocks react at too low a temperature to need to be sintered.

The following are non-limiting examples of the practice of this invention.

Example 1.—Fourteen pounds of powdered anhydrous borax were mixed with ten pounds of powdered coal tar pitch and twenty-six pounds of powdered charcoal. This mixture was split into two halves. To the "A" half of this mixture, three and one-quarter pounds of S.A.E. 30 petroleum oil were added and the mixture blended; to the other, or "B" half, nothing was added.

Each half was pelleted through a pelleting press using a 3/8" hole diameter straight run die, resulting in pellets 3/8" thick and from 1/4" to 1" long.

From the middle third of each half from the pelletizer, a one pound representative batch was taken. Both batches were dehydrated, devolatilized, and coked by continuously raising their temperature from ambient to 700° C. over a six-hour period in a muffle. During this process, essentially all of the oil from the "A" batch was removed.

Sufficient pellets were taken from each bath in the size range 1/2" to 5/8" long to make samples approximately 15 grams in weight which in both cases filled a one inch diameter quartz reactor tube to a height of three inches.

The temperature of the reactor tube was brought to and held at 700° C. by external electrical heaters and a heavy excess of chlorine, held constant during each chlorination at a rate of approximately four grams per minute, preheated to 700° C., was passed upwards through the tube and pellets. This heavy excess of chlorine, many times that which was used up in chlorinating the boron-containing feed, was used to flood the pellets with chlorine so as to obtain a maximum rate of reaction unencumbered by any dearth of the gaseous reactant. In this way the rate of reaction as found should be a measure of the efficiency of the solid reactants or pellets.

During three time periods of the clorination, from two to three minutes, from five to six minutes, and from ten to eleven minutes after chlorination had begun, the entire gas stream exiting the reactor was passed through a scrubber to collect the boron values and the amount of boron trichloride produced analyzed.

The boron trichloride production rate as determined by the above analysis was essentially constant during the three time periods of each run and averaged for the non-oil or "B" batch 0.158 gram of BCl_3 per minute and for the oil or "A" batch 0.481 gram of BCl_3 per minute.

Example 2.—Twenty-eight pounds of anhydrous borax powder were mixed with seventeen pounds powdered coal tar pitch and fifty-five pounds powdered charcoal. Five pounds of S.A.E. 10 petroleum oil were blended into this mixture and the homogeneous material was pelleted as in Example 1. The pellets were devolatilized, dehydrated and coked by effectively raising their temperature to 700° C. over an eight hour period and charged by frequent intermittent screw feeding to essentially maintain a constant bed level at the rate of 0.51 cubic foot per hour to a vertical moving bed reactor which was maintained at its surface at 750° C. This reactor was a combination of carbon and graphite tubes six inches inside diameter with a five foot long heated reaction zone. Chlorine vapor was fed continuously at a rate of 26½ pounds per hour to the bottom of the reactor.

Analysis of the pellets fed to the reactor showed 32.4% borax and analysis of the spent charge showed 93.2% of this borax reacted out.

In another test, approximately fifty pounds of anhydrous borax powder were mixed with fifty pounds of powdered coal tar pitch and one hundred pounds powdered charcoal. No oil was used. The homogeneous mixture was preheated to 200° F. and briquetted by means of a Belgian roll briquette press to pillow shaped briquettes approximately ¾" long and ½" thick. The briquettes were handled in the same manner as in the last reported test and charged in the same fashion at the rate of 0.60 cubic foot per hour to the moving bed reactor which was maintained at its surface at 750° C. Chlorine vapor was fed continuously at the rate of 21 pounds per hour to the bottom of the reactor.

Analysis of the briquettes fed to the reactor showed 31.2% borax and analysis of the spent charge showed 26.9% of this borax reacted out. The borax to charcoal ratio of the raw feedstock was 21% of the theoretical maximum based on Equation 1.

Example 3.—Eighty-five pounds of anhydrous borax powder were mixed with twenty-nine pounds of powdered coal tar pitch and fifty-six pounds powdered charcoal. Nineteen and one-half pounds of S.A.E. 50 petroleum oil were blended into this mixture and the homogeneous material was pelleted as in Example 1 and devolatilized, dehydrated and coked as in Example 2 and charged in the same fashion as in Example 2 at the rate of 0.62 cubic foot per hour to a vertical moving bed reactor as described in Example 2 which was maintained at its surface at 750° C. Chlorine vapor was fed continuously at a rate of fifty-four pounds per hour to the bottom of the reactor.

Analysis of the pellets fed to the reactor showed 58.0% borax and analysis of the spent charge showed 93.6% of this borax reacted out. The borax to charcoal ratio of the raw feedstock was 63% of the theoretical maximum based on Equation 1.

Example 4.—Eight and one-tenth pounds of —100 mesh columbite ore were mixed with five pounds of powdered coal tar pitch and sixteen and one-quarter pounds of powdered charcoal. This mixture was split into two halves. To the "A" half of this mixture one and one-half pounds of S.A.E. 30 petroleum oil were added and the mixture blended; to the other, or "B" half, nothing was added.

Each half was pelleted through a pelletizing press using a ½" hole diameter die resulting in pellets ½" thick and from ½" to 1" long.

A representative batch sample was taken from the central pelleted portion of both "A" and "B." Both batches were dehydrated, devolatilized and coked by continuously raising their temperature from ambient to 700° C. over a six hour period in a muffle. During this process essentially all of the oil from the "A" batch was removed. Sufficient pellets were taken from each batch in the size range ⅝" to ⅞" long to make samples approximately 15 grams in weight which in both cases filled a one inch diameter quartz reactor tube to a height of between three and four inches. The temperature of the reactor tube was brought to and held at 600° C. by external heaters and an excess of chlorine, held constant during each chlorination at a rate of approximately 2.2 grams per minute, preheated to 600° C., was passed upwards through the tube and pellets for a duration of 11½ minutes in each case. The gas exit line from this reactor was maintained at 600° C. until it reached a detachable filter-weighing tube which was maintained cold so as to condense out any gases condensable at ambient temperatures; columbium, tantalum iron, silicon, etc., chlorides being condensable at ambient temperature, chlorine, phosgene, carbon monoxide and the like not being condensable at ambient temperature.

In the "B," or non-oil case, 1.427 grams of condensed product were obtained; in the "A," or oil case, 4.495 grams of condensed product were obtained.

In both cases columbium, expressed as the pentoxide, was approximately 15.5 weight percent of the charge and tantalum, expressed as the pentoxide, was approximately 9.7 weight percent. During chlorination in the "B" case 48.8% of the columbium and 40.2% of the tantalum was removed. In the "A" case 65.0% of the columbium and 55.0% of the tantalum was removed.

Iron is a major constituent of columbite. During the above chlorination, 0.436 gram of iron chloride were condensed in the "B" case and 0.882 gram in the "A" case.

Example 5.—Ten pounds of finely pulverized 85% vanadium pentoxide were admixed with 4 pounds of powdered coal tar pitch and 10½ pounds of powdered charcoal. This mixture was split into two halves. To the "A" half of the mixture, 1¾ pounds of S.A.E. 20 petroleum oil were added and the mixture blended; to the other, or "B" half, nothing was added. Each half was tableted in a pipe press using 5 tons' pressure on a ¾" pipe resulting in tablets approximately ¾" in diameter and ¾" to 1" in length.

A representative sample batch was taken from each "A" and "B." Both batches were dehydrated, devolatilized and coked by continuously raising their temperatures from ambient to 600° C. over an eight-hour period in a muffle. Pellets of approximately ¾" in length were taken from each batch in sufficient amount to fill a 40 mm. reactor tube for 18" in length. Material balance analysis showed essentially the same total amount of vanadium was introduced in each case. The temperature of the reactor tube and contents was brought to and held at 600° C. by external electrical heaters and chlorine gas was introduced and maintained at a rate of 5.7 grams per minute and sustained for a period of 10 minutes. The heated exit gas line, which normally ended in a water

scrubber had an adjustable by-pass so as to be able to flow exit gases through a water-cooled glass condenser before passing the non-condensed gases into the scrubber. In both "A" and "B" chlorinations, after three minutes of chlorination, the by-pass was opened to the condenser for 60 seconds and then closed.

The condensed product in each case, a mixture primarily of vanadium chloride and vanadium oxychloride, was analyzed for vanadium values. In the "B" case, 1.530 grams of vanadium expressed as the element were found and in the "A" or oil case, 1.877 grams were found.

Chemical analysis of the bed residues following chlorination showed that approximately 16% more vanadium had been removed in the "A" case than in the "B" case.

Obviously, many modifications and variations of the invention hereinabove set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

This is a continuation-in-part of application Serial No. 781,205, filed December 18, 1958, now abandoned.

We claim:

1. A process for preparing a solid feedstock of improved reactivity suitable for reaction with gaseous chlorinating agents comprising: forming a mixture of a carbonaceous reducing agent, an oxidized compound selected from the class consisting of boron, vanadium, tantalum, columbium, beryllium, rhenium, zirconium, hafnium, tungsten, molybdenum, a normally solid coking binder, and between 2% and 20%, based upon the combined weights of the said carbonaceous reducing agent, said oxidized compound and said coking binder, of a petroleum oil having a viscosity in the range of 38–200 Saybolt Universal seconds at 210° F. and an A.S.T.M. pour point not higher than 10° F.; subjecting said mixture to pressure whereby to agglomerate said mixture and dehydrating, devolatilizing and coking the agglomerates so formed by heating said agglomerates to an elevated temperature whereat said petroleum oil is volatilized whereby to produce a porous agglomerate having a lessened resistance to diffusion of chlorinating gas therethrough.

2. The process of claim 1 wherein the dehydration, devolatilization and coking is carried out at a temperature of between about 100° C. and 700° C.

3. The process of claim 1 wherein the dehydration, devolatilization and coking is carried out at a temperature of between about 100° C. and 700° C. and the product so formed is thereafter sintered at between about 500° C. and 1000° C.

4. The process of claim 1 wherein the oxidized compound is anhydrous borax.

5. The process of claim 1 wherein the oxidized compound is columbite.

6. The process of claim 1 wherein the oxidized compound is tantalite.

7. The process of claim 1 wherein the oxidized compound is vanadium pentoxide.

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