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PROCESS FOR MANUFACTURING THE CHLORIDES OF THE ALKALINE-EARTH METALS FROM THE SULPHATES OF THE ALKALINE-EARTH METALS

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It has been suggested already to manufacture chlorides of the alkaline earths—such as barium or strontium—by melting together their sulphates in the presence of coal or similar agents with chlorides of the alkaline earths, for instance, calcium chloride. In this known process the sulphates are not treated with chemical agents in the melted mass, but the melted mass is only cooled down suddenly. A blast roasting of the raw material has also been performed until agglomeration takes place. In the agglomeration process however the single particles do not melt, but stick together without a melting of the whole mass.

The essential feature of the present invention consists in dissolving the sulphates of the alkaline earths—such as barium sulphate—in their corresponding chlorides of the alkaline earths, such as barium chloride, and first converting said sulphates in the ordinary manner by means of coal, its coking products, reducing gases or hydrocarbons into the sulphides or oxides of the alkaline earths, whereupon the latter are changed into the chlorides of the alkaline earths by injecting hydrochloric acid, or chlorine gas and, if necessary, steam into the fluid bath. The addition of steam is effected for the purpose to obtain sulphide of hydrogen (H_2S) instead of chloride of sulphur (Cl_2S_2).

The alkaline-earth chloride introduced at the beginning of the process remains unchanged during the whole process in contrary to the known process mentioned above in which the introduced calcium chloride is consumed by converting the barium sulphide—the reduction product of the barium sulphate—into barium chloride. In the new process we have from the beginning a fluid bath, so that it is not difficult to bring chlorine gases and hydrochloric acid gases by injecting them into the bath, into close contact with all parts of the bath.

It must be pointed out here that the decomposition of the sulphides of the alkaline earths by means of chlorine gas or hydrochloric acid is a known fact; this reaction however was not executed as yet in the melted bath. In performing the reaction in the bath the course of the reaction is not the same because in treating the sulphides of the alkaline earths, for instance, with chlorine gas, the formation of polysulphides of the alkaline earths cannot be observed.

The sulphates of the metals of the alkaline earths are easily dissolved in their corresponding melted chlorides of the alkaline earths under a diminution of the melting point forming a fluid bath into which any gas can be easily injected. Inasmuch as the evaporation velocity of the chlorides of the alkaline earths is essentially smaller than that of the chlorides of the alkali metals, the melted masses of the chlorides and sulphates of the alkaline earths advantageously differ from the melted masses of the chlorides of the alkali metals and the sulphates of the alkaline earths.

The reduction of the sulphates of the alkaline earths can be performed by means of any carbon-containing substance being in the solid, liquid or gaseous state. It is convenient, however, to use coke for this purpose because the reduction with coke will be performed in the quickest way and is a quantitative one. During or after the reduction a current of hydrochloric acid or chlorine gas alone or together with steam is blown through the bath, and in this way it is at your own will to recover in addition to the newly formed chlorides of the alkaline earths sulphuretted hydrogen or sulphur chloride as a by-product.

After having converted the whole alkaline-earth sulphate by means of coke and the injection of the gases mentioned above into alkaline-earth chloride, we have again a melted mass of alkaline-earth chloride impurified only by the coke in excess. The bath can either be used anew in the process or after the settling down of the coke the melted mass which may be made colourless by the injection of air can be tapped. With the aid of rotating pans there can be made immediately from the melted mass a pure and grainy alkaline-earth chloride being absolutely free from water.

The process can be performed, for instance, as follows:

In a furnace with tar-oil and producer gas heating arrangement about 230 kg. of crystallized barium chloride are first melted down with the aid of the tar-oil burner which requires about 1½ hours. Then 50 kg. of heavy spar are introduced into the bath; after the dissolution of the heavy spar which requires about 10 minutes, the tar-oil burner is turned off, and heating is continued with producer gas. A sample of the melted mass shows the following composition:

76,25% barium chloride
0,29% barium sulphide
22,05% insoluble in water (containing 21,1% $BaSO_4$).

Whilst stirring 11 kg. of coke powder are now introduced into the bath and simultaneously chlorine gas injected through two fire-clay tubes is passed through the bath. After about half an hour the reaction is for the most part finished, and after ten minutes more the current of chlorine gas is cut off. The chlorine consumption amounts to about 15 kg. In order to discolour the bath which is still of a drak colour, air is now injected through two fire-clay tubes into the bath, and then the melted mass is tapped. An analysis shows the following figures:

92,01% barium chloride
4,51% barium oxide
2,10% water-insoluble (containing 0,83% $BaSO_4$).

The formation of barium oxide can be avoided, if hydrochloric acid gas is injected into the bath. In this case a barium chloride containing 98% can be easily obtained the percentage of which may be raised still more by clarifying the bath.

In this manner no wet concentration whatever is necessary so that not only the mechanical equipment is made simpler and cheaper, but also the costs of production are substantially reduced.

We claim:—

1. Process for manufacturing the chlorides of the alkaline earths from the sulphates of the alkaline earths consisting in dissolving the sulphates of the alkaline earths in their corresponding melted alkaline-earth chlorides, converting said sulphates by means of reducing substances into the alkaline earth sulphides, and changing said alkaline earth sulphides into alkaline earth chlorides by injecting chlorine gas into the fluid bath.

2. Process for manufacturing the chlorides of the alkaline earths from the sulphates of the alkaline earths consisting in dissolving the sulphates of the alkaline earths in their corresponding melted alkaline-earth chlorides, converting said sulphates by means of reducing substances into the alkaline earth sulphides, and changing said alkaline earth sulphides into alkaline earth chlorides by injecting hydrochloric acid into the fluid bath.

3. Process for manufacturing the chlorides of the alkaline earths from the sulphates of the alkaline earths consisting in dissolving the sulphates of the alkaline earths in their corresponding melted alkaline earth chlorides, converting said sulphates by means of solid carbon into alkaline earth sulphides and changing said alkaline earth sulphides into the alkaline earth chlorides by injecting chlorine into the fluid bath.

4. Process for manufacturing the chlorides of the alkaline earths from the sulphates of the alkaline earths consisting in dissolving the sulphates of the alkaline earths in their corresponding melted alkaline earth chlorides, converting said sulphates by means of liquid carbon into alkaline earth sulphides and changing said alkaline earth sulphides into the alkaline earth chlorides by injecting chlorine into the fluid bath.

5. Process for manufacturing the chlorides of the alkaline earths from the sulphates of the alkaline earths consisting in dissolving the sulphates of the alkaline earths in their corresponding melted alkaline earth chlorides, converting said sulphates into the sulphides of the alkaline earths by means of reducing substances and changing said alkaline earth sulphides into the chlorides of the alkaline earths by injecting chlorine containing substances and steam into the fluid bath.

6. Process for manufacturing the chlorides of the alkaline earths from the sulphates of the alkaline earths consisting in dissolving the sulphates of the alkaline earths in their corresponding melted alkaline earth chlorides, converting said sulphates by means of gaseous carbon into alkaline earth sulphides and changing said alkaline earth sulphides into the alkaline earth chlorides by injecting chlorine into the fluid bath.

In testimony whereof we have affixed our signatures.

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