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## FLOTATION PROCESS FOR THE PURIFICATION OF SILICON CARBIDE

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This invention relates to the purification of silicon carbide. More particularly, it relates to the separation of by-products such as siloxicon and graphite from silicon carbide of grain sizes up to 1.5 mm. by the use of cation-active flotation agents.

During the production of silicon carbide from coal and sand in electric resistance furnaces there is generally produced in the marginal zones of the furnaces products of little commercial value other than as raw material for use with coal and sand in subsequent charges, although they contain substantial amounts of satisfactory grade silicon carbide. Many attempts have been made in the past to separate this silicon carbide by such methods as grinding, flotation, sedimentation, etc. All of these prior attempts to purify crude silicon carbide, however, have either been unsuccessful or have been economically unfeasible.

The present invention discloses for the first time a practical economical method whereby the well-crystallized silicon carbide produced from coal and sand in the marginal zones of the electrical furnaces can be satisfactorily separated from the undesired by-products comprising principally amorphous substances such as siloxicon or graphite (cf. Gmelin, vol. 15, Part B, page 857, 8th Edition, 1959, paragraphs 1 and 2), by subjecting the silicon carbide in grain sizes up to 1.5 mm. to flotation with cation-active flotation agents.

The cation-active flotation agents which can be satisfactorily used in accordance with the present invention preferably include those cation-active flotation agents made from substances whose cations carry the  $C_nH_{2n+1}$  group which is a positively charged complex, while the negatively charged acid radical, the anion, which is composed of a halogen or an acid group, is of only secondary importance in its effect on the activity of the collector. Suitable cation-active flotation agents include the primary, secondary or tertiary alkylamine salts, the quaternary ammonium salts, and alkyl and pyridine salts. Use can also be made of derivatives of triphenylamine and quaternary bases in which the nitrogen is substituted by oxygen, phosphorus, sulfur, arsenic or antimony, and also of picoline or morphine salts.

The cation-active flotation agents of the present invention are used in the concentrations customarily used in flotation processes, namely 100 to 200 grams of agent per ton of material being treated, and are preferably mixed with a suspension of the material.

The flotation operation is carried out in the same general manner as other flotation procedures well known in the flotation art. It has, for example, been found satisfactory to use as the suspending agent ordinary tap water, although in many cases it has been found advantageous to use soft water or a mixture of soft water and tap water. It is usually desirable to maintain the pH of the suspension between 5 and 10 by the addition of, for example, alkali solution, when necessary.

The flotation can be carried out in any suitable apparatus, one suitable form being a rectangular iron tank equipped with suitable agitating equipment. The material to be subjected to flotation is employed in granular form having a maximum particle size of approximately 1.5 mm., the fractions usually ranging from 1.5 to 0.7,

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0.7 to 0.2, and 0.2 to finer sizes. The granular mixture to be subjected to flotation is suspended in water and then thoroughly agitated and air blown into the suspension. After thorough and uniform dispersion of the material in the water small amounts (100 to 200 g. per ton of solid material) of a cation-active flotation agent are added to the suspension. A stable foam is immediately formed and carries with it to the surface of the agitated suspension a portion of the solids being treated, the particular material and amount thereof depending upon the composition being treated. The foam carrying the said fraction is then separated, the foam destroyed, the recovered fraction washed with water and dried. If the residue is the desired product, it is then drawn off at the end of the flotation operation and worked up in the usual manner.

The flotation can be carried out either batchwise or as a continuous operation by connecting a plurality of such cells in series. The residues remaining in the cells are then mixed and washed in two or more cells and again subjected to flotation. Whether a batch or continuous operation should be used depends primarily upon the size of the fraction to be separated by flotation.

If the material to be subjected to flotation contains adhering carbon it is generally necessary to remove the latter by a preliminary flotation or other suitable treatment before subjecting the material to flotation for the purpose of recovering the crystalline silicon carbide. When the adhering carbon is to be separated from the mixture by a flotation operation use may be made of a flotation agent with foam producing properties which reduces the surface tension of the water and facilitates the formation of air bubbles on the upper surface of the liquid. Suitable flotation agents for this purpose include terpene derivatives, pine oil, alcohols of the terpene series commercially known as "Flotol," terpineol and phenols, cresols and wood tar oil (Ullmann's Enzyklopadie der technischen Chemie, 1951, vol. 1, page 673). After removal of the adhering carbon the residue is subjected to flotation using the cation-active flotation agents described above for recovery of the crystalline silicon carbide.

The recovery of the crystalline silicon carbide is carried out in the following manner: The outer surface of a silicon carbide block which has been melted in the usual manner and consisting of silicon carbide incrustations and zones which in addition to silicon carbide contain substantially amorphous zones of high content of impurities, thus rendering the product of little commercial value. The silicon carbide block containing such impurities is comminuted by any known means and the resulting crystals sorted according to their crystalline structure. The product which has been reduced to particle sizes not in excess of 1.5 mm. and in which the silicon carbide is mixed with impurities is then separated by screening into several fractions of different particle size, as for example:

Fraction I	1:5 to 0:7 mm.
Fraction II	0:70 to 0:20 mm.
Fraction III	0:20 mm. and finer.

The sizes included in these ranges depend, however, on the requirements of the process.

If the above described comminuted material contains adhering carbon the latter is first removed by treating the material in a preliminary flotation process with a foaming agent of the type described above and consisting of such agents as terpene derivative, pine oil, alcohols of the terpene series, terpineol, cresols, phenols, wood tar oil, and the like. After removal of any adhering carbon, if present, or if no adhering carbon is present, the material is then subjected to the following treatment for the recovery of the crystalline silicon carbide.

The comminuted material described above, substantially free from adhering carbon is subjected to flotation using

a cation-active flotation agent of the type previously described. The crystalline silicon carbide is thereby floated to the surface and removed with the foam, the foam destroyed and the crystalline silicon carbide washed and dried. The amorphous impurities, consisting essentially of "Siloxicon" and noncrystalline reaction products, collect in the residues in the flotation cells.

It is thus possible by the process of the present invention to separate crystalline silicon carbide from amorphous silicon carbide. The fact of separating chemical compounds of the same composition but differing in crystalline structure is unexpected and serves to distinguish the present invention from prior flotation processes by which it was only possible to separate substances of different composition.

The following specific examples are given to illustrate the process of the present invention. It is understood, however, that various modifications of the described operations can be employed without departing from the scope of the present invention and that such modifications which come within the knowledge of one skilled in the art are intended to be included within the scope of the appended claims.

#### Example I

A granular mixture of 500 kg. of silicon carbide, "Siloxicon" and adhering carbon, ranging in particle size from 0.70 to 0.20 mm. was suspended in water in a conventional flotation cell provided with independent air intake. After the gradual addition of 100 g. of Flotol A (registered trademark of the Farbwerke Hoechst for terpene alcohols) a noticeable formation of foam resulted, which in about 30 minutes time caused the adhering carbon to separate and adhere to the foam and was then removed with the foam.

The residue in the flotation cell was then subjected to a further flotation operation in the cell by the addition of 100 g. of Flotanol F (registered trademark of Farbwerke Hoechst for ether alcohols). After air agitation for 20 minutes the crystalline silicon carbide was removed with the resulting foam from the flotation cell, while the impurities were retained in the residue in the cell. After removal from the cell the foam was destroyed, and the crystalline silicon carbide washed with water and dried.

#### Example II

In this experiment 500 kg. of amorphous silicon carbide containing only traces of adhering carbon were treated as described in Example I using as the flotation agent 100 g. of a fatty acid amine cation-active flotation agent. After air agitation for 20 minutes, the resulting foam was removed with the adhering crystalline silicon carbide, the

foam destroyed, the silicon carbide washed with water and then dried. The product thus obtained was substantially pure crystalline silicon carbide.

What is claimed is:

1. In a process for the separation of crystalline silicon carbide from substantially carbon-free crude silicon carbide produced from coal and sand, the step which consists of subjecting said substantially carbon-free silicon carbide in particle size not substantially in excess of 1.5 mm. to flotation in an aqueous medium in the presence of a cation-active flotation agent selected from the group consisting of primary, secondary and tertiary alkyl amine salts and quaternary ammonium salts, and recovering the resultant foam with the adhering crystalline silicon carbide.
2. In a process for the separation of crystalline silicon carbide from crude silicon carbide produced from coal and sand, the steps which comprise subjecting said crude silicon carbide in particle size not substantially exceeding 1.5 mm. to flotation in an aqueous medium in the presence of a flotation agent selected from the group consisting of terpene derivatives, pine oil, alcohols of the terpene series, terpineol, phenols, cresols, and wood tar oil, removing the foam and attached impurities, and subjecting the residue consisting of substantially carbon free crude silicon carbide to flotation in the presence of a cation-active flotation agent selected from the group consisting of primary, secondary and tertiary amine salts and quaternary ammonium salts, and recovering the resultant foam with the adhering crystalline silicon carbide.
3. The process of claim 1 wherein the cation-active flotation agent is an amine salt.
4. The process of claim 2 wherein the cation-active flotation agent is an amine salt.
5. The process of claim 1 wherein the pH of the flotation medium is maintained at 5-10.
6. The process of claim 1 wherein the flotation medium is tap water.
7. The process of claim 1 wherein the cation-active flotation agent is a fatty acid amine acetate.

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