(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 September 2004 (10.09.2004)

(10) International Publication Number
WO 2004/076348 A1

(51) International Patent Classification: C01B 25/32

(21) International Application Number:
PCT/IN2003/000039

(22) International Filing Date: 27 February 2003 (27.02.2003)

(25) Filing Language: English

(26) Publication Language: English

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Published: with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A PROCESS FOR THE MANUFACTURE OF FEED GRADE DICALCIUM PHOSPHATE

(57) Abstract: This invention relates to the preparation of feed grade dicalcium phosphate from a source containing monocalcium phosphate such as super phosphate, concentrated super phosphate and the like. The first step consists of leaching water soluble mono calcium phosphate therefrom with water or recycle wash water from one of the subsequent steps. The supernatant liquid treated with a frist quantity of hydrated lime to precipitate impurities such as Fe, Al and F. The filtrate obtained after removing the precipitate is further treated with hydrated lime to raise the pH till mono calcium phosphate present therein gets converted into dicalcium phosphate which crystallizes out wash water from the second and the third stages are recycled to the system. By-product obtained is gypsum, which is used in cement industry or as a fertilizer filter.
“A PROCESS FOR THE MANUFACTURE OF FEED GRADE DICALCIUM PHOSPHATE”

Dicalcium phosphate known, as DCP is a commonly used animal feed supplement and it is desirable to obtain dicalcium phosphate free of contaminants, particularly fluoride containing compounds. Feed grade dicalcium phosphate has a chemical formula CaH PO₄ 2H₂O wherein phosphorus expressed as P is 18% and calcium expressed as Ca is at least 23%. Maximum fluorine content is 0.16%.

Rock phosphates and bone ash are natural sources of calcium phosphate in the form of tricalcium phosphate of the chemical formula Ca₃ (PO₄)₂. Acidification of tricalcium phosphate with mineral acids yields phosphates and phosphoric acids. Acidification of rock salt with hydrochloric acid also produces mono calcium phosphate which remain in solution which is treated to remove fluorides as precipitates. The supernatent liquid containing monocalcium phosphate is treated with lime to obtain dicalcium phosphate and calcium chloride which is discarded as a by-product. Phosphoric acids which are obtained on acidification of natural phosphates are purified and then neutralized to produce dicalcium phosphate.

In the US patent no.6183712 a process wherein calcium phosphate is reacted with a mineral acid and the product thus obtained is hydrolyzed to form a corresponding calcium salt has been reported. This patent also discloses a process wherein naturally occurring phosphate is reacted with phosphoric acid and the product is treated with acetic or oxalic acid.
DISCLOSURE OF THE INVENTION:

Dicalcium phosphate substantially free of fluorides is prepared by a novel process which particularly avoids production of unwanted calcium chloride as a by-product. This simple process produces high grade dicalcium phosphate and is energy efficient. The reaction steps are carried out at ambient temperature and no heat input is required except for the drying step.

The first step in this process is in the production of single super phosphate generally known as SSP, triple super phosphate (TSP) a well known fertilizer and a super phosphate of a grade between SSP and TSP. Tricalcium phosphate present in rock phosphate or any other natural sources of phosphates on treatment with sulphuric acid or phosphoric acid gets converted into mono calcium phosphate according to the following reaction.

\[ \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{CaSO}_4 + \text{H}_2\text{O} \]
\[ \text{Ca}_3(\text{PO}_4)_2 + \text{H}_3\text{PO}_4 \rightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2 \]

During this reaction a fraction of the fluorides present in the starting material escapes as reaction vapours. However, the monocalcium phosphate produced is still contaminated with fluorides. This product obtained is known as green super in the industry and has a very high unreacted free acid content. Green super on keeping gets cured and the unreacted free acid as well as the excess of phosphoric acid formed during the reaction and the unreacted calcium phosphate present therein slowly react with each other to yield more of mono calcium phosphate. Soluble fluoride content of this product depends on the available free acid when cured fully, single super phosphate contains approximately 1.2 to 2.2% of free acid content.
This fully cured product is treated with water or recycle liquor from a subsequent process step to dissolve mono calcium phosphate present therein. Solid impurities are separated and the filtrate containing free acid is treated with a solution of hydrated lime to increase its pH and to precipitate out impurities such as iron, aluminum and fluorine containing compounds. Monocalcium phosphate solution free from such contaminants is further treated with a solution of hydrated lime to neutralize and to produce dicalcium phosphate free of fluoride ions. If required a mixture of mono and dicalcium phosphate may also be produced by adjusting the quantity of hydrated lime. This product is found to have at least 18% or more P than normal dicalcium phosphate and exhibits higher digestibility when used as a feed additive.

This invention relates to a process for the preparation of feed grade dicalcium phosphate substantially free of fluorides from a source containing monocalcium phosphate such as simple super phosphate, concentrated super phosphate or fertilizer grade phosphate which comprises the steps of (a) leaching out soluble monocalcium phosphate therefrom with water or recycle wash water from at least one subsequent steps, (b) adding a first quantity of a solution of hydrated lime thereto to precipitate and separate contaminants like iron, aluminum and fluorine containing compounds therefrom (c) adding a further quantity of hydrated lime to the filtrate containing monocalcium phosphate to produce dicalcium phosphate as precipitate which is separated washed and dried, wash water from steps (b) and (c) being recycled to step (a) to leach out further monocalcium phosphate.

Single super phosphate may be prepared by treating tricalcium phosphate with an acid such as sulphuric acid or phosphoric acid.
BRIEF DESCRIPTION OF DRAWING:

Fig. I attached herewith shows different stages of the process schematically. This figure also shows utilization of wash water in a continuous process of producing dicalcium phosphate according to this invention.

BEST METHOD OF CARRYING OUT THE INVENTION:

The following non-limitive examples illustrate this invention.

Example 1:

Fully cured single super phosphate is agitated thoroughly with water or wash water recycle for about an hour to dissolve all water soluble components. pH of this solution is found to be between 2.2 to 2.6. This solution contains monocalcium phosphate and is marked as filtrate 2 in the flow diagram. pH of the filtrate is raised by adding a small quantity of hydrated lime solution. Impurities like iron, aluminum and fluorides are precipitated. This precipitate is separated, washed with water to recover phosphate therefrom. This mainly consists of gypsum and is used in cement industry or fertilizer industry. The solution obtained after separation of the precipitate contains monocalcium phosphate under pH3.2, the filtrate has 5.2% of P and 0.0153% of F.

A further quantity of hydrated lime is added to the filtrate obtained after the separation of solids to raise the pH to 6.5 to 6.7. Dicalcium phosphate crystallises out from the solution. This is separated by filtration and the filtrate is recycled particularly to wash the filter cake obtained after the first addition of hydrated lime.
The precipitated dicalcium phosphate is washed and dried. On analysis this product conformed to the following analysis.

<table>
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<tr>
<th>Element</th>
<th>Percentage</th>
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<tr>
<td>P</td>
<td>18.17%</td>
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<tr>
<td>Ca</td>
<td>24.45%</td>
</tr>
<tr>
<td>F</td>
<td>0.12%</td>
</tr>
</tbody>
</table>

Example 2:

Single super phosphate containing 16.5% of water soluble P₂O₅ and 1.3% of free acid expressed as P₂O₅ is used for this experiment. 250gm of this cake is taken and agitated with 1000g of water for half an hour and then filtered. The filter cake is washed with water in two lots of 250g each.

| Total water soluble P₂O₅ | 41.25g |
| Water added              | 1000g  |
| Filtrate obtained        | 982g   |

The filtrate contains pH 2.39

| P₂O₅          | 3.45% |
| F content     | 0.030%|
| P₂O₅ in gm    | 33.87gm|

Quantity of wash 456g

| P₂O₅ content | 1.1% |
| P₂O₅ content in gm | 5.06g |
| Total P₂O₅ recovered | 38.93g |
| % yield of P₂O₅ | 93.8% |

This clearly shows that substantial quantity of P₂O₅ has been recovered.
Example 3:

900gm filtrate containing 3.45% of P$_2$O$_5$ and a P/F ratio of 49.8 is treated with a solution of hydrated lime to raise the pH to 2.9. Contents are separated by filtration and the P$_2$O$_5$ and F value assessed. In 900gm of solution

- P$_2$O$_5$ content of the solution 3.45%
- Total P$_2$O$_5$ input 31.05g

Weight of the filtrate 891gm
P$_2$O$_5$ of the filtrate 3.41%
P/F ratio of the filtrate 148

This experiment shows that treatment of the filtrate with lime removes impurity and fluorine therefrom.

300gm of the filtrate is further heated with hydrated lime to raise the pH till 6.88 and the contents are then filtered to separate dicalcium phosphate therefrom. The solution and the products are analyzed and the results are given below.

- Dicalcium phosphate on a dry basis 63.8g
- P content of DCP 18.1%
- F content of DCP 0.076%

- Total P$_2$O$_5$ recovered 30.8g
- P$_2$O$_5$ content of the filtrate 0.12%
- Weight of the filtrate 760g
This confirms that dicalcium phosphate of high purity is obtained on further addition of hydrated lime to monocalcium phosphate containing filtrate.

The flow diagram clearly shows how wash water obtained in the second and third stage can be effectively recycled to leach out monocalcium phosphate and to wash the filter cake containing gypsum which is a by-product.

The appended claims do not exclude obvious equivalents and alteration known to persons skilled in the art from their scope.
CLAIMS:

1. A process for the preparation of feed grade dicalcium phosphate substantially free of fluoride from a source containing monocalcium phosphate such as superphosphate, concentrated super phosphate and fertilizer grade phosphate which comprises the steps of (a) leaching out monocalcium phosphate therefrom with water or recycle wash water from at least one subsequent steps, (b) adding a first quantity of a solution of hydrated lime thereto to precipitate and separate contaminants like iron, aluminum and fluorine containing compounds therefrom, (c) adding a further quantity of hydrated lime to the filtrate from step (b) which contains monocalcium phosphate to produce dicalcium phosphate as precipitate, which is separated, washed and dried, wash water from step (b) and (c) being recycled to step (a) to leach out further monocalcium phosphate.

2. The process as claimed in claim 1, wherein superphosphate is obtained by treating tricalcium phosphate with an acid such as sulphuric acid or phosphoric acid and then allowing the green super produced thereby to cure automatically.

3. The process as claimed in claim 1, wherein in step (b) said first quantity of hydrated lime is added to raise the pH from 2.2/2.6 to 2.9/3.2 and to precipitate impurities such as iron, aluminum and fluorides therefrom.

4. The process as claimed in claim 1, wherein said filtrate from step (b) containing monocalcium phosphate is treated with hydrated lime to raise the pH to 6.5 and above till dicalcium phosphate crystallizes out therefrom.

5. Dicalcium phosphate whenever prepared by a process as claimed in claims 1 to 4.
INTERNATIONAL SEARCH REPORT

CLASSIFICATION OF SUBJECT MATTER
IPC: C01B 25/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C01B 25/32

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 4312843 (MONTY et al.) 26 January 1982 (26.01.82) claims.</td>
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<td>A</td>
<td>GB 2112763 (STAUFFER CHEMICAL COMPANY) 27 July 1983 (27.07.83) claims.</td>
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search 5 August 2003 (05.08.2003)

Date of mailing of the international search report 12 September 2003 (12.09.2003)

Name and mailing adress of the ISA/AT
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Dresdner Straße 87, A-1200 Vienna
Facsimile No. 1/53424/535

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Telephone No. 1/53424/223

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