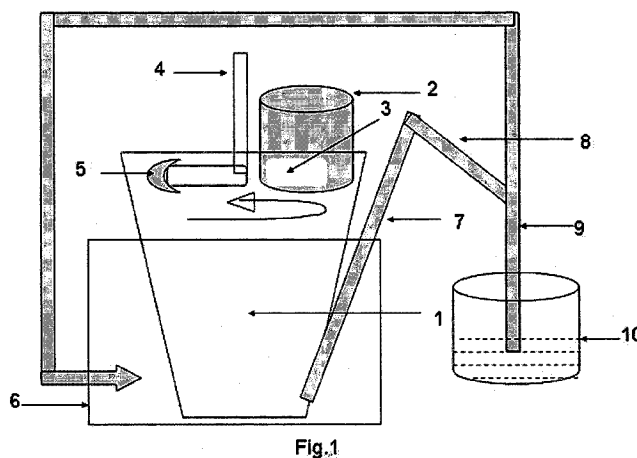




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[Continued on next page]

(54) Title: PREPARATION OF PHOSPHORUS FROM PHOSPHORIC ACID AND CARBON



(57) Abstract: A process and system for manufacturing phosphorus from phosphoric acid and carbon is disclosed. The reaction $4\text{H}_3\text{PO}_4 + 16\text{C} \rightarrow 6\text{H}_2 + 16\text{CO} + \text{P}_4$ takes place at around 850 °C. The process is cost-effective and less energy consuming compared to conventional methods.



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PREPARATION OF PHOSPHORUS FROM PHOSPHORIC ACID AND CARBON

FIELD OF INVENTION

This invention relates to a process for manufacturing elemental phosphorus. More particularly, this invention relates to a process for manufacturing elemental phosphorus from phosphoric acid and carbon by heating a mixture of phosphoric acid and charcoal, wherein the composition of reaction mixture, distribution of raw materials within reactor and the manner of heating thereof is crucial.

BACKGROUND AND PRIOR ART

Conventional method of manufacturing elemental phosphorus involves heating a mixture of rock phosphate, coke and silica in an electric arc furnace to about 1650°C. The reactants undergo resistive heating whereby tricalcium phosphate contained in the rock phosphate undergoes reduction to produce phosphorus along with carbon monoxide and calcium silicate slag. High energy consumption and slag formation are major disadvantages of this method.

Use of phosphoric acid for beneficiation and pelletization of phosphatic raw material for manufacturing elemental phosphorus is known in the art and well documented in USSR Patents 649651, 823277, 742376, Japan Kokai, 77155197, US Patents 2040081, 4372929, 4373893, 4383847, 4421521. By addition of phosphoric acid to phosphatic raw material, tricalcium phosphate gets partially converted into mono- or di-calcium phosphate which consumes lesser energy compared to tricalcium phosphate.

US patent 6207024 discloses a method for producing phosphorus from phosphoric acid and carbon wherein the source of energy is microwaves. Though this method consumes lower energy compared to conventional process, there is scope for further reduction in energy consumption and simplifying the process. Moreover, this method is not suitable especially for production of phosphorus on a large scale as microwaves quickly lose energy as they pass through the reaction mass.

Production of phosphorus from phosphoric acid and carbon is not practiced on commercial scale so far because there are inherent problems associated with the process. When phosphoric acid is heated, it gets converted into pyrophosphoric acid and then metaphosphoric acid. Meta phosphoric acid sublimes at high temperatures. Thus when a mixture of phosphoric acid and carbon are heated with a view to obtain phosphorus, metaphosphoric acid formed undergoes sublimation without reacting with carbon. Moreover, polyphosphoric acid forms during the process causing lump formation and hardening of the reaction mass which makes it difficult to flow.

Thus there is a need for a process for manufacturing elemental phosphorus from phosphoric acid on a large scale, wherein the energy consumption is low and which overcomes abovementioned disadvantages and problems.

OBJECTS OF INVENTION:

The main object of invention is to provide a simple and cost-effective process for manufacturing elemental phosphorus from phosphoric acid and carbon.

Another object of the invention is to provide a process for manufacturing elemental phosphorus wherein energy consumption is low.

Another object of invention is to provide a process for manufacturing elemental phosphorus which is environmentally friendly and which avoids formation of calcium silicate slag.

SUMMARY OF INVENTION:

This invention relates to a method of manufacturing elemental phosphorus from phosphoric acid and carbon which involves the steps of heating a charge comprising of phosphoric acid and carbon under reducing environment and collecting the resultant phosphorus. The composition of reaction mixture, distribution of raw materials within reactor and the manner of heating thereof are crucial to get optimum results.

DESCRIPTION OF DRAWINGS

Fig.1 is a schematic diagram of the system for production of phosphorus from phosphoric acid and carbon. Each component of the system is numbered and described in the preferred embodiment of the invention as given herein.

DETAILED DESCRIPTION OF INVENTION:

The present invention involves a process of manufacturing elemental phosphorus from phosphoric acid and carbon as given in the following

reaction: $4\text{H}_3\text{PO}_4 + 16\text{C} \rightarrow 6\text{H}_2 + 16\text{CO} + \text{P}_4$. The reaction takes place at around 850°C.

A typical example of source of carbon is charcoal powder. Since carbon content varies from source to source, its amount to be taken may be determined by estimating carbon content in the source thereof. If there is a component of ash or other impurities in the source of carbon, provision should be made to periodically remove the same when it accumulates in the reactor.

Phosphoric acid contains water which also reacts with carbon at high temperatures and hence excess carbon is necessary to compensate loss due to reaction with water.

When a mixture of phosphoric acid and carbon is heated by arc process or by heating with flame, phosphoric acid gets converted into metaphosphoric acid, significant part of which sublimes without reacting with carbon. Experiments were carried out by both, arc process and thermal heating.

In arc process the reaction mass gets heated up to desired temperature only within limited radius near the arc due to non-conducting nature of raw material. Remaining reaction mass gets heated up to comparatively lower temperature causing mere sublimation of meta phosphoric acid without reacting with carbon.

In the process involving thermal heating, the desired temperature can be obtained first at the periphery of the reactor but reaction mass around center of the reactor gets heated up gradually and initially temperature

in this part is not high enough for reaction to take place. Consequently, phosphoric acid in this part of reactor gets converted into metaphosphoric acid which sublimes without reacting with carbon.

To overcome abovementioned problems, the inventors of present invention have developed a process wherein the distribution of raw materials within reactor and manner of heating is specific, as described hereunder in the preferred embodiments.

As per an embodiment of the present invention, the mixture of phosphoric acid and charcoal powder is taken in the reactor. On the top of the mixture, plain charcoal powder is added. The reactor is closed with a lid through which provision is made for outlet of phosphorus and collection thereof under water. The reactor may be heated with oxy-acetylene flame in such a way that the upper part of reactor (wherein only charcoal powder is filled) is heated first and then the lower portion of the reactor (containing mixture of phosphoric acid and charcoal powder) is heated. Thus a hot carbon zone is created above reaction mixture to ensure complete reduction of phosphoric as well as sublimed metaphosphoric acids into the desired product i.e., elemental phosphorus.

As per another preferred embodiment of present invention, a system is designed as shown in Fig.1 for efficient production of phosphorus based on abovementioned mechanism. According to said embodiment, a reactor(1) partially filled with plain charcoal powder, is provided with a container(2) for reaction mixture (H_3PO_4 + Charcoal powder) fitted in the upper part of the reactor as shown in the Fig.1. Said container is provided with a window(3) through which blades(5) of stirrer(4) can

rotate, causing gradual addition of reaction mixture in the reactor. The blades of the stirrer may optionally be plough-type. Rate of addition of reaction mixture can be controlled by adjusting RPM of the stirrer. The reactor is provided with an outlet(7) emerging from the lower part of the reactor. The outlet pipe is arranged to extend in the upward direction so as to prevent solids from coming out of the reactor against gravity. The upper part of the outlet pipe is bent (8) downwards and connected to a vertical pipe(9). A cooling means such as spraying/sprinkling of water may be provided in the vertical pipe(9), preferably in the upper part of said vertical pipe, to liquefy phosphorus vapors. The lower end of the vertical pipe extends into a container(10) partially filled with water under which phosphorus can be collected. This arrangement of bent pipes prevents liquid phosphorus from entering back against gravity into the reactor. The upper end of the vertical pipe can be let open for CO and H₂ to flare off or optionally it can be extended into the furnace(6) so as to utilize byproducts CO and H₂ for heating purpose. The reactor is heated first so as to increase the temperature of plain charcoal powder contained therein to above 850°C. The stirrer is then started to gradually add mixture of H₃PO₄ and charcoal powder in the reactor containing hot charcoal powder. This system ensures that H₃PO₄ in whatsoever form passes through hot carbon zone and reduces to phosphorus before coming out through the outlet. The reactor, container containing reaction mixture and stirrer are sealed to prevent phosphorus coming into contact with oxygen from air.

The scope of this patent is not limited by the shape of any components of the system, as long as it operates on the mechanism disclosed herein.

EXAMPLE-1 (comparative example)

A mixture of 25 g. powdered charcoal and 50 g. H_3PO_4 (85%) was taken in a graphite crucible. The crucible was covered with a lid which was sealed with cement to make it air-tight. The lid was provided with an inlet for purging N_2 and an outlet for the purpose of collecting phosphorus. A graphite electrode was inserted through a hole in the lid. Nitrogen was purged into the abovementioned system to remove air (oxygen). The graphite crucible was made -ve electrode and the graphite rod inserted through the lid was +vely charged with the help of a welding machine. When the machine was switched on, an arc was generated at the point of contact of electrodes. Phosphorus liberated from the reaction mass was taken out through the outlet and it was collected under water. Though phosphorus was formed in this method, the quantity was not significant with respect to theoretical yield. Sublimation, agglomeration and hardening of reaction mass due to formation of polyphosphoric acid were disadvantages of this method.

EXAMPLE-2 (comparative example)

The above experiment as described in Example-1 was repeated except that the graphite crucible was heated with oxy-acetylene flame. It was difficult to quickly attain desired temperature of the entire reaction mass uniformly. Sublimation of metaphosphoric acid could not be avoided. Thus significant proportion of phosphoric acid escaped without reacting with carbon. Agglomeration of reaction mass was observed.

Thus in above methods described in EXAMPLE 1 & 2, there are two disadvantages viz. sublimation of metaphosphoric acid without reaction with carbon and agglomeration and hardening of reaction mass due to

formation of polyphosphoric acids. Experiments were also conducted with excess carbon wherein agglomeration was avoided but large excess of carbon is not desirable.

EXAMPLE-3

68 g. 85% phosphoric acid was mixed with 100 g. powdered charcoal. This mixture was first added to a cylindrical graphite reactor. 19 g. powdered charcoal was added to the reactor on the top of the mixture of charcoal and phosphoric acid. The reactor was heated first from the top and gradually downwards to ensure that the charcoal powder added on the top of the mixture of phosphoric acid and charcoal attains reaction temperature prior to the mixture, so as to avoid escape of phosphoric acid without reacting with carbon. Reaction started at around 850°C. Total 8.7 g. phosphorus was recovered.

EXAMPLE-4

19 g. powdered charcoal was added to the reactor(1) shown in Fig.1. 68 g. 85% phosphoric acid was mixed with 100 g. powdered charcoal and the mixture was taken into the container(2). The reactor containing charcoal powder was heated so as to increase the temperature of charcoal powder to above 850°C. The motor of the stirrer was then started to gradually add mixture of phosphoric acid and charcoal powder into reactor containing hot charcoal powder. Phosphorus was collected continuously under water in the container(10) while continuously refilling the mixture of phosphoric acid and charcoal powder in the container(1).

CLAIMS

1. A process for preparation of phosphorus by heating phosphoric acid and carbon, wherein the reaction mass comprising phosphoric acid and carbon is heated and the product is passed through a pre-heated carbon zone before passing through the outlet.
2. A process as claimed in claim 1 wherein phosphoric acid and carbon are taken in the molar ratio of at least 1:5.
3. A system for manufacturing phosphorus by process as claimed in claim 1 or 2, comprising components including:
 - (a) a reactor partially filled with source of carbon;
 - (b) a container for reaction mixture (H_3PO_4 +source of carbon) fitted in the upper part of the reactor, said container is provided with a window through which blades of a stirrer can rotate causing gradual addition of reaction mixture into the reactor;
 - (c) an outlet emerging from the lower part of the reactor.
4. A system for manufacturing phosphorus as claimed in claim 3 wherein said outlet is arranged to extend in the upward direction, upper part of the outlet pipe bent downwards and connected to a vertical pipe, lower end of said vertical pipe extending into a container partially filled with water under which phosphorus can be collected.
5. A system as claimed in any of the claims 3 or 4 wherein the upper end of said vertical pipe is either let open for CO and H_2 to flare off or optionally extended into the furnace so as to utilize byproducts CO and H_2 for heating purpose.

6. A process for manufacturing phosphorus by using system as claimed in any of the claims 3-5 comprising steps including:

- (a) partially filling said reactor with carbon and filling mixture of H_3PO_4 & carbon into said container;
- (b) heating reactor partially filled with carbon so as to increase the temperature of carbon contained therein to at least 850°C ;
- (c) starting stirrer to gradually add mixture of H_3PO_4 & carbon into the reactor containing hot carbon;
- (d) collecting phosphorus under water through the outlet.

7. A process for preparation of phosphorus as claimed in any of the claims 1 or 2, wherein the reaction mass comprising phosphoric acid and carbon is gradually added to a source of carbon pre-heated to reaction temperature.

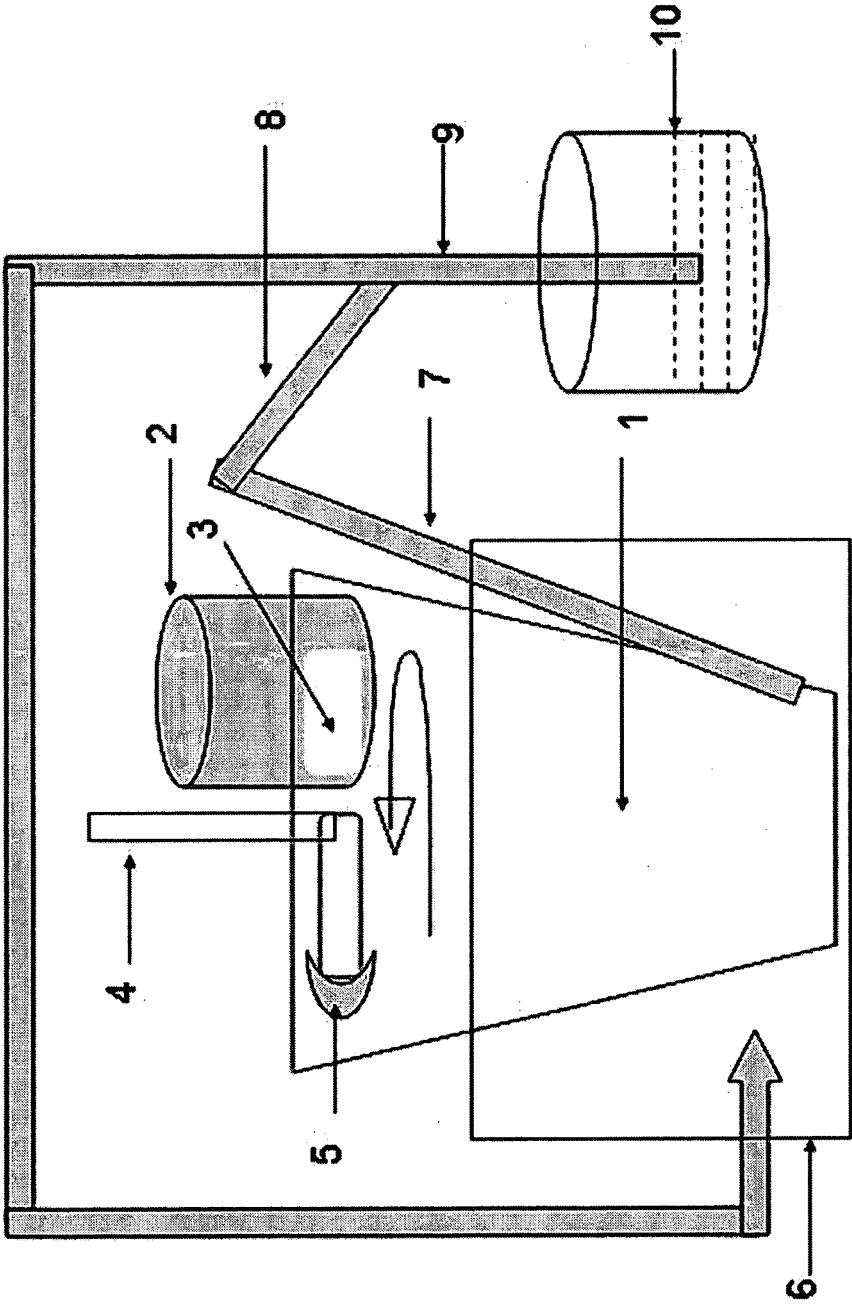


Fig.1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN 2009/000414

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁸: **C01B 25/02** (2006.01)

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)

IPC⁸: C01B

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

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

WPI, EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 207 024 B1 (SEVERENS) 27 March 2001 (27.03.2001) <i>Claims; figures</i>	1-7
A	JP 2000-247 616 A (NIPPON CHEM IND CO LTD) 12 September 2000 (12.09.2000) (abstract) World Patents Index [online]. London, U.K.: Derwent Publications, Ltd. [retrieved on 2010-02-23]. Retrieved from: Questel/Orbit, Paris, France. DW200065, Accession No. 2000-667382 <i>Abstract</i>	1-7

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
23 February 2010 (23.02.2010)Date of mailing of the international search report
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Austrian Patent Office
Dresdner Straße 87, A-1200 ViennaAuthorized officer
PAMMINGER W.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IN 2009/000414

Patent document cited in search report			Publication date		Patent family member(s)	Publication date
US	A	6207024			WO A1 0125147	2001-04-12
					AU A 7746900	2001-05-10
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