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(71) Applicant *(for all designated States except US)*: **STRAITMARK HOLDING AG** [—/CH]; Bundesplatz 1, CH-6300 Zug (CH).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **SCHIPPER, Willem, J.** [NL/NL]; Oude Vlissingseweg 4, NL-4336 AD Middelburg (NL).

(74) Agent: **RIPPEL, Hans Christoph**; Eastsite One, Seckenheimer Landstr. 4, 68163 Mannheim (DE).

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(54) Title: PROCESS FOR THE MANUFACTURE OF P_4O_6 WITH HIGH YIELD

(57) Abstract: A process for the production of a reaction product consisting essentially of P_4O_6 is carried out by reacting oxygen with phosphorus in an exothermic reaction in a reaction unit. Heat created by the exothermic reaction is removed by feeding P_4O_6 and/or by-products of the process into the reaction unit. The generated reaction product is then quenched to a lower temperature where no essential decomposition of the reaction product occurs, and at least part of P_4O_6 is separated from the reaction product obtained after quenching. The resulting yield of P_4O_6 based on the phosphorus used is improved and the heat of the exothermic reaction can be controlled in an economic way.

PROCESS FOR THE MANUFACTURE OF P4O6 WITH HIGH YIELD

The invention relates to a process for the manufacture of phosphorus(III)oxide with the empirical formula P_4O_6, made by the reaction of phosphorus and oxygen wherein the reaction product is obtained with high yield and in essentially pure form. It forms, therefore, an excellent “basic material” (which term when used herein shall always include its use as a starting material, raw material and intermediate) in the manufacture of organic phosphorus(III)compounds, an industrially important class of chemicals. The term “P_4O_6” as used herein is intended to encompass all formulas conventionally used for phosphorus(III)oxides like P_2O_3 (phosphorus trioxide).

P_4O_6 has not previously been prepared on a commercial scale, and although already proposed it has not been commercially used, for example as a basic material for the manufacture of organic phosphorus(III)compounds. Instead of using P_4O_6 as a raw material, such chemicals are usually made starting from phosphorus trichloride (PCl_3). However, the application of PCl_3 has several disadvantages. It requires the use of a large amount of chlorine to react with white phosphorus. PCl_3 contains only 22.7 weight percent of phosphorus, and, moreover, intermediates and end products to be made from PCl_3, usually do not contain chloride. Consequently chlorine is released in the form of considerable amounts of undesired by-products, including often hydrochloric acid, to be separated in complex and expensive process steps. Local circumstances may allow sale as low-value by-product, but disposal is necessary in many cases.

Alternatively to PCl_3, phosphorous acid, H_3PO_3, can be used as the basic material in a number of production processes, thus avoiding part of the adverse effects associated with PCl_3. However, H_3PO_3 is also made commercially from PCl_3, by hydrolysis, which implies that the disadvantages associated with the presence of chlorine will still appear, only at a different stage in the production chain. Moreover, H_3PO_3 has the drawback to show a markedly different reactivity compared to PCl_3.

The use of its corresponding anhydride, P_4O_6, would not show said disadvantages which would allow using it as such basic material in a broader range of chemistry. Further, its phosphorus content is markedly higher than that of PCl_3 or H_3PO_3, making it the most concentrated source of trivalent phosphorus, and thus it would be the more valuable and suitable basic material in chemical synthesis.

The disclosed processes to manufacture P_4O_6 are commonly carried out by direct reaction of white phosphorus and oxygen in stoichiometric quantities. The reaction mixture is generated in a flame which without cooling can reach temperatures up to 6000 K. It is known that P_4O_6 is unstable and decomposes at temperatures above 700 K, forming unwanted oxides of phosphorus (particularly mixed P(III/V)oxides and phosphorus suboxides) and elemental phosphorus. Therefore, many proposals were made how to quench and cool the obtained reaction mixture immediately and effectively, to avoid decomposition and to obtain a product of high yield and purity becoming suitable as the basic material in the manufacture of commercially important phosphorus(III)compounds.

The process for manufacturing P_4O_6 as described in DD 216516 A1 comprises steps of combining the reactants, evaporated phosphorus and an oxygen-inert gas mixture, in a mixing nozzle. The reaction occurs in a reactor generating a mixture of phosphorus oxides at a temperature between 2000 and 6000 K depending on the quantity of inert gas used. The reaction mixture passes the reactor after a very short residence time not exceeding 0.005 seconds. Since P_4O_6 is instable in the temperature range between 1500 and 700 K, the reaction mixture is kept in the reactor at a temperature of 1600 to 1200 K only for a very short time and then rapidly cooled below 700 K, and finally to 300 K, which means in three steps avoiding decomposition of the reaction mixture. In a first cooling step the reaction product is rapidly cooled in the reactor leaving the reactor with a temperature between 1600-1200 K by adding a suitable amount of inert gas into the reactor and further by cooling the wall of the reactor, for example with water. That first cooling step is carried out in a reactor at a rate of $0.1*10^6$ to $10*10^6$ Ks^{-1}. After leaving the reactor the reaction mixture is further rapidly cooled in a second cooling step immediately following the first cooling step. Hereby the same high cooling rate as used in the first cooling step is employed, preferably by adding large quantities of inert gas to the reaction mixture, cooling down to a temperature of about 700 K. Finally in a third cooling step the reaction mixture is cooled indirectly and condensed to below 300 K. Optionally during the last cooling step liquid P_4O_6 or liquid reaction mixture is added to form a liquid film on the inside wall of the cooling means to avoid condensation of by-products and resulting in scaling and obstruction on the inner surface of the cooling means. The reaction mixture is then purified, for example by distillation. As it is stated in examples 2 and 3 of this publication, according to which liquid P_4O_6 or liquid reaction mixture is added to the reaction mixture in the third cooling step, the yield is only 80.8 %, and 75.9 % respectively, of P_4O_6 based on the weight of phosphorus used. So this process is generally not suitable to manufacture P_4O_6 in yields of commercial interest.

The process for manufacturing P_4O_6 as proposed by DD 292213 A5 uses the same principle as mentioned in DD 216516 A1, reacting gaseous phosphorus and oxygen in a reactor, but uses modified cooling steps. First, indirect cooling decreases the temperature of the gaseous reaction mixture to 1000-750 K. In the following cooling step the reaction product is condensed by external cooling with water and further by adding liquid P_4O_6 or liquid reaction mixture as coolant and to form a liquid film on the inner surface of the cooling means thus avoiding condensation of by-products, scaling and obstruction on that inner surface of the cooling means. The yield of P_4O_6 based on the phosphorus used is about 85 % which means it is not essentially improved compared with the process of DD 216516 A1.

Also DD 292637 A5 discloses a process for manufacturing P_4O_6 by reacting phosphorus and oxygen in a mixture with nitrogen in a tubular reaction chamber with the object that the reaction product obtained by this process will have a lower content of unwanted oxides of phosphorus. For this purpose a specifically designed tubular segment is used aimed at mixing the gas stream. This segment is placed between the tubular reaction chamber and a quenching unit. The inner cross section of the tubular segment is smaller than the inner cross section of the tubular reaction chamber. The reaction chamber is externally cooled with water, and the reaction product leaving the reaction chamber with a temperature between 2200 and 1600 K is fed into the tubular segment which is externally cooled with air. Due to that specific design of the tubular segment the temperature of the reaction product distributed over the cross section of the tubular segment shall become more homogeneous before it enters the quenching unit. After the reaction mixture is cooled down to a temperature of 1000 to 750 K, in the following cooling step the reaction mixture is further cooled externally with water, and also internally by adding liquid P_4O_6 and/or liquid reaction mixture, preferably on the inner surface of the cooling means, hereby cooling the reaction mixture down to a temperature of preferably less than 600 K. Then further cooling is applied in the following quenching step. That quenching step uses again liquid P_4O_6 or liquid reaction mixture reducing scale forming of by-products on the inside wall of the cooling and quenching means, but again obviously does not lead to an improved yield of P_4O_6 based on the phosphorus used. It is about 85 % which means not essentially higher than those achieved with the process described in DD 216516 A1 and DD 292213 A5.

Yields of about 85 % or less means that the reaction product contains a high amount of unwanted by-products of different oxides of phosphorus and a significant amount of elemental phosphorus which pose a separation and disposal challenge. It is possible to separate the by-products from the product stream by commonly known techniques, but the commercial value of these solids is limited. Applying them in derivatives chemistry, such as submitting the material to hydrolysis or alcoholysis, will lead to a mixture of P(III)- and P(V)-based derivatives which has severe commercial disadvantages compared to the analogous derivatives made from either pure P(III)oxide or P(V)oxide.
Also, the fraction made up by phosphorus suboxides is seen to be unreactive under normal reaction conditions for such derivatives chemistry. For instance in hydrolysis and alcoholysis, only the mixed P(III/V) oxides are seen to react. The suboxides are inert under the conditions applied, and remain as a suspension in the end product. This poses a separation challenge, a disposal problem and a decrease in yield (based on phosphorus). The occurrence of a significant amount of these unwanted by-products is therefore seen to have a negative influence on the economics of the known P_4O_6 processes, as up to 20 % of the phosphorus is lost to a stream of little or no commercial value.

Further the processes for manufacturing P_4O_6 of the prior art do not lead to a product suitable as a basic material for commercially manufacturing organic phosphorus(III)compounds, because P_4O_6 is not obtained in sufficient quality, in view of its high content of elemental phosphorus (P_4) dissolved in P_4O_6. P_4O_6 is a liquid at temperatures slightly above room temperature, and when made according to the known processes it contains elemental phosphorus up to its maximum solubility in P_4O_6. Such content of elemental phosphorus may be up to 10 percent as mentioned in DD 116457 A1 and DD 216465 A1. DE 1172 241 B discloses a process for manufacturing P_4O_6 with a phosphorus content between 1 and 10 %, but the yield of P_4O_6 is very low. Especially phosphorus is an impurity difficult to remove by distillation because its boiling point and vapour pressure are relatively close to those of P_4O_6. Whereas the processes for manufacturing P_4O_6 of the prior art propose various methods to obtain phosphorus oxide of the desired +3 oxidation state with limited formation of oxides with different oxidation states, a method to reduce the content of elemental phosphorus in the reaction product has not been disclosed.

Accordingly elemental phosphorus necessarily remains in the P_4O_6 when it is used as a basic material in derivative chemistry. This is of great disadvantage especially when reactions in watery or otherwise polar media are carried out. This leads to the formation of a phosphorus emulsion or suspension, because P_4 has poor solubility in polar media. The appearance of such an emulsion or suspension poses an important separation challenge, as P_4 is toxic and pyrophoric and thus requires extensive investments to ensure its safe and reliable removal and disposal. The presence of elemental phosphorus seriously reduces the potential of economical applications of P_4O_6.

It is therefore an object of the invention to find a process for the manufacture of P_4O_6 avoiding these disadvantages of the processes described in the prior art which means allowing the synthesis of P_4O_6 in higher yields, and reducing or eliminating the amount of by-products as occurring in the known processes.

It is a further object of the invention to provide P_4O_6 obtained by reaction of phosphorus and oxygen, in high purity and being essentially free of by-products such as mixed P(III/V) oxides, phosphorus suboxides and elemental phosphorus, thus showing excellent properties when used as a basic material in further chemical reactions, especially when used for the manufacture of organic phosphorus(III)compounds, and to create a production process for the manufacture of P_4O_6 of that high quality.

These objects are surprisingly achieved by a process for the production of a reaction product consisting essentially of P_4O_6 by reacting oxygen, or a mixture of oxygen and an inert gas, with gaseous or liquid phosphorus in an exothermic reaction in a reaction unit maintaining an average temperature in said reaction unit suitable to generate the reaction product, by removing heat created by the exothermic reaction by feeding P_4O_6 and/or by-products obtained from earlier reactions or from the running process into the reaction unit, then quenching the generated reaction product in one or more quenching unit(s) to a lower temperature where no essential decomposition of the reaction product occurs, and separating at least part of P_4O_6 from the reaction product obtained after quenching.

Carrying out the process for the production of a reaction product consisting essentially of P_4O_6 is performed as follows. First, oxygen, or a mixture of oxygen with an inert gas, such as nitrogen, is reacted with gaseous or liquid phosphorus in essentially stoichiometric amounts to form P_4O_6 in a reaction unit generating the reaction product in that reaction unit. Heat created by the exothermic reaction of phosphorus and oxygen in the reaction unit is removed to keep the reaction in that reaction unit at an average temperature below 2200 K and above 1500 K which is generally suitable to generate the reaction product. Removing the heat is achieved by adding P_4O_6 or by-products, such as obtained from earlier reactions producing the reaction product or as a recycle from the current process, and/or adding a mixture of P_4O_6 and said by-products, into the reaction unit. The appropriate amounts of P_4O_6 and for by-products that must be fed into the reaction unit to control the cooling of the reaction product in the reaction unit can be easily determined by someone skilled in the art and depend e. g. on the process parameters and the reaction unit. The said by-products generally consist of mixed oxides of P^{3+} and P^{5+}, as well as of lower oxidation states of phosphorus than +3. Adding these products can preferably be made by recycling these materials obtained by the running process, and/or in a process carried out earlier, after quenching, for example adding P_4O_6 separated from the by-products and/or the resulting residue consisting of by-products after separation of P_4O_6.
This is followed by quenching the reaction product in one or more quenching unit(s) to a lower temperature where no essential decomposition of the reaction product occurs.

The quantities of the reactants phosphorus and oxygen are adjusted to be close to or correspond essentially to the theoretical stoichiometric amounts of P_4O_6, which means the molar ratio of phosphorus (P_4) to oxygen (O_2) should generally be in the range of 1:2.7 and 1:3.3. P_4O_6 and by-products consisting mainly of mixed higher P(III/V) oxides and phosphorus suboxides, or a mixture of P_4O_6 and said by-products, to be added as coolant to the reaction unit, are typically obtained from previous executions of the process and/or from the running process, thus recycling unwanted by-products, and are seen to have a similar molar P_4 to O_2 ratio.

Preferably the reaction unit is cooled to maintain an average temperature of the reaction product within the reaction unit between 1600 and 2000 K, particularly between 1650 and 1850 K.

The reaction product is then passed from the reaction unit to one or more quench units where it is rapidly cooled down, preferably in one step, to temperatures where no essential decomposition of P_4O_6 occurs. Generally such temperature is below 700 K. Such quenching can be carried out by leading the reaction product via cooling means, thus creating internal and/or external cooling. Preferably it is carried out by adding reaction product, preferably in liquid form already quenched, preferably produced by the same process, and/or adding more or less purified liquid P_4O_6 end product as a coolant to the reaction product. Optionally, the product is cooled in said quenching step, or in a separate cooling step following quenching, to temperatures that enable easy handling and/or processing the condensed reaction product, which means below the boiling point of P_4O_6, preferably below 350 K.

In one particular embodiment there is provided a process for the production of a reaction product consisting essentially of P_4O_6 by reacting oxygen, or a mixture of oxygen and an inert gas, with gaseous or liquid phosphorus in molar ratio of phosphorus (P_4) to oxygen (O_2) in the range of from 1:2.7 to 1:3.3 in an exothermic reaction in a reaction unit maintaining an average temperature in the range of 1500 to 2200K in said reaction unit suitable to generate the reaction product, by removing heat created by the exothermic reaction by feeding P_4O_6 and/or by-products obtained from earlier reactions or from the running process into the reaction unit, where the residence time of the reaction product in the reaction unit is at least 0.5 seconds, then quenching the generated reaction product in one or more quenching unit(s) to a temperature below 700K where no essential decomposition of the reaction product occurs, and separating at least part of P_4O_6 from the reaction product obtained after quenching.

For further use of the reaction product as a basic material to produce organic phosphorus(III) chemicals, and to allow the re-use of by-products in the reaction unit, it is advisable to purify the cooled and condensed reaction product, for example by distillation, separating P_4O_6 from solid and higher boiling by-products. The purified, preferably distilled product contains at least 96, preferably at least 97, especially 99 or more weight per cent of P_4O_6.

After quenching, at least part of P_4O_6 is separated from the reaction product obtained after quenching by any method known in the art to separate liquids from a mixture with solid products, preferably by distillation. The remaining residue of by-products, which are partly solid at room temperature, therefore said residue is also called "solids", and consist mainly of solid P(III/V) oxides and suboxides of phosphorus obtained by said separation step, or a fraction thereof containing that solid by-products and a more or less significant fraction of P_4O_6 as well, is fed into the reaction unit where they are evaporated and decomposed under the influence of heat generated in the reaction unit by the reaction of freshly dosed reactants, and take part in the reaction again, thus improving the yield of the process.

As a further advantageous effect, the by-products fed back to the reaction zone remove at least part of the heat created by the exothermic reaction of phosphorus and oxygen. The evaporation or sublimation, and decomposition of the by-products due to the heat generated by the reaction unit provide a considerable cooling effect on the contents of the reactor unit. Due to the exothermic nature of the process originating from the reaction of freshly dosed oxygen and phosphorus, the cooling requirements of the process to keep it at the desired operating temperature are considerable. The dosage of the stream of by-products may be adjusted and is generally sufficient to alleviate the need for any further external and/or internal cooling, making the apparatus less complicated and costly.

That stream of solids fed into the reaction unit consists either entirely of unwanted solid by-products obtained further downstream in the process, or of a mixture, for instance in form of a slurry, of the unwanted solids and a certain quantity of P_4O_6. Forming said slurry, P_4O_6 is generally not completely separated from the solids contained in the reaction mixture after quenching, and the residue is fed back into the reactor as a mixture/slurry of the solid by-products distributed in the liquid product P_4O_6. This preferred embodiment also eliminates the need to completely separate the solids as a dry side stream from the quenched product. Instead a thickening is sufficient, which may be achieved by methods known to those skilled in the art.

Using an amount of P_4O_6 together with the solid by-products in a mixture has the further advantage that the constituents of the solids of the by-products are made easier available again to the reaction, allowing for an easier dosage of the solids into the reactor compared to the dosage of only solids, but the more important object is to perform a cooling action on the contents in the reaction unit, preferably in amounts maintaining these in the reaction unit at the desired operating temperature preferably without any further external and/or internal cooling. However, additional cooling or heating may be performed by other means if necessary.

In order to meet the cooling requirements of the reaction unit more or less completely and to reach and maintain the operating temperature there, preferably without any additional external and/or internal cooling, in a preferred alternative embodiment of the process, the mass of the stream of the residue of by-products recycled to the reaction unit, for example in form of said slurry, is further adjusted, preferably by addition of a controlled amount of pure or impure P_4O_6 (containing, for example, higher boiling impurities of the process) to said mixture. Alternatively, or additionally, a separate stream, for instance of additional pure or impure P_4O_6, may be fed into the reaction unit to create an additional cooling effect.

In said preferred alternatives of the process, the solid by-products, or the mixture containing solid by-products and P_4O_6 forming a slurry, are fed back into the reactor unit in a stream of liquid P_4O_6 product, where that stream provides the full cooling requirement of the reaction unit by controlling the amount, temperature and composition of that stream, thus completely eliminating the need for any further active external and/or internal cooling by other means. The mass of the stream, its feeding temperature and the content of P_4O_6 in the stream may be adjusted to meet the exact cooling requirements of the reactor unit. Adjusting the cooling effect by dosing additional P_4O_6 to said stream is preferred, which can be made either by dosing directly into the reactor unit, and/or by adding it to the slurry of solid by-products.

Whereas it is preferred that the residue of by-products (particularly in form of said slurry) and optionally together with additionally pure or impure P_4O_6 is added to the reaction unit together with the freshly dosed stream of the reactants phosphorus and oxygen, optionally with an inert gas, said residue may also be fed into the reaction unit through a separate inlet. Oxygen, or a mixture of oxygen and an inert gas, like nitrogen, gaseous or liquid phosphorus, and a stream containing said residue of by-products of the process and optionally additional P_4O_6, are passed into the reaction unit where they are combined and where phosphorus and oxygen immediately react with each other in a strongly exothermic reaction generating the reaction product.

The resulting P_4O_6 separated from the reaction product after quenching is obtained in high yield based on the amount of phosphorus used, and shows excellent purity which makes it valuable as the basic material in the formation of organic phosphorus(III)compounds.

Surprisingly, although the residue of by-product separated from the liquid components of the reaction product after quenching consists of a mixture of different compounds, the overall stoichiometry of that mixture is at, or close to, the required O:P ratio for the production of P_4O_6. So it was surprisingly found that the constituent compounds, mainly phosphorus suboxides and mixed P(III/V)oxides, when added to the reaction unit decompose there to a mixture that is essentially identical to the reaction mixture obtained when only using a feed of phosphorus and oxygen (or optionally a mixture of oxygen and nitrogen), in the required stoichiometric ratio to form P_4O_6.

It is still a further object of the invention to provide P_4O_6 obtained by reaction of phosphorus and oxygen in high purity being essentially free of elemental phosphorus and unwanted phosphorus oxides, thus showing excellent properties when used as a basic material in further chemical reactions, especially when used for the manufacture of organic phosphorus(III)compounds.

This further object is surprisingly achieved by a preferred embodiment of the process, wherein the reaction mixture is maintained for a certain residence time of at least 0.5 seconds within the reaction unit, and, preferably, when the temperature of the reaction unit is kept within the preferred range of 1600 and 2000 K. As a further effect, these preferred conditions ensure a complete evaporation, sublimation and dissociation of the solids-P_4O_6 mixture returned to the reactor unit. A residence time of about 1 second would already lead to the effect that a reduced content of elemental phosphorus within the final product of less than 1 weight percent is achieved. When a residence time of 1 second or more, for example between 1 and 8 seconds, is used, the content of elemental phosphorus in the reaction mixture becomes very low and the yield of P_4O_6 will reach an optimal value. The remaining elemental phosphorus is present the final product in a quantity between 1 and 0.5 weight percent or less. Further, that residence time shows the advantageous effect that all dosed recycled material fed into the reaction unit are transferred into gaseous or vaporous form and were completely decomposed. By choosing a residence time of more than 8 seconds, preferably up to 30 seconds a content of 0.5 or less, preferably less than 0.25 weight percent of elemental phosphorus will be present in the final product, and the yield of P_4O_6 is also very high. A residence time of more than about 40, especially more than 60 seconds does not lead to any essential further improvement with regard to the composition of the reactor contents, which is of influence on the yield and the content of the elemental phosphorus in the final product. In the process a residence time as disclosed herein in combination with the specific average temperature of 1600 to 2000 K is employed at the same time.

The residence time expresses how fast the reaction product moves through the volume of the reactor unit and expresses the average time the reaction product spends in the reactor unit. As is generally known the residence time is defined to be the quotient of the reactor volume divided by the volumetric flow rate. This means that the residence time could be adjusted by tuning the volumetric flow rate of the reaction product in relation to the used volume of the reaction unit. The volumetric flow rate is defined as the volume of the reaction product which passes through the reactor unit per unit of time.

When using an average temperature within the range of 1650 to 1850 K in combination with a residence time as mentioned above and the separation and recycling of unwanted phosphorus containing by-products back to the reactor, the resulting reaction product is obtained in especially high yield and purity.

After that purification step the reaction product contains preferably more than 97, preferably more than 99, particularly at least 99.5 weight percent of P_4O_6 based on the total weight, and shows generally a maximum content of elemental phosphorus of less than 3.0, preferably less than 1.0, particularly 0.5 or less weight percent. Under optimum conditions of the process as described herein, the content of elemental phosphorus is even about 0.25

or less weight percent. The content of elemental phosphorus is measured by ^{31}P NMR. The final product shows excellent purity which makes it valuable as excellent basic material in the synthesis of organic phosphorus(III)compounds.

An arrangement suitable to carry out the process of the invention of manufacturing P_4O_6 by the reaction of phosphorus and oxygen comprises a reaction unit where the reactants and the recycle stream or streams are combined and reacted with each other in a reaction zone. It further comprises a quenching unit connected with one or more outlets of said reaction unit, means for separating at least part of P_4O_6 in pure form from the residue of solid by-products, and means for feeding the residue and/or P_4O_6 to the reaction unit. Downstream one or more further cooling unit(s) may be arranged to complete cooling of the reaction product. In a preferred embodiment of the invention the volume of the reaction unit is designed to secure the appropriate residence time in relation to the intended volumetric flow of the reaction product. Although generally not necessary, the reaction unit may further comprise means for cooling the reaction unit externally and/or internally for removing the energy generated by the reaction process and maintaining the required temperature. The reaction unit may have any appropriate shape such as a cylindrical chamber or vessel or any other suitable form. The reaction unit further comprises means for passing the reactants involved in the process and the recycle stream of by-products separately or jointly into the reaction zone within the reaction unit, these means may have the form of pipes or tubes allowing directed or undirected dosage of the reactants and/or the stream of by-products through respectively arranged outlets. When the reactants phosphorus and oxygen are combined or get into contact with each other in the reaction zone, they spontaneously react with each other. The reaction can be carried out, for example, by combining the passages of both reactants in the hole of a nozzle. The dosage of the recycle stream, and of an optional temperature control stream of purified or unpurified P_4O_6, can be performed jointly with the fresh reactants, or separately. The reaction unit further comprises at least one outlet through which the vaporous reaction product is transferred to the quenching unit. All elements and units are made of suitable material to accomplish the process.

The following Example demonstrates, without limiting the scope of the claimed invention, a preferred embodiment of the process.

Example

A stream of 3.99 mole of white phosphorus (P_4) per hour was continually fed into an evaporator and evaporated at 770 K at atmospheric pressure. The ensuing stream was fed into the chamber of a reactor of 7800 ml volume. A continuous stream of oxygen gas, 12.0 moles per hour (as O_2) was introduced in the same reactor. Through a separate opening in the top of the reactor, a stream of 1105 g/h of a slurry, which had been obtained in a previous experiment, was dosed into the reactor. The slurry consisted of 24 weight% of higher solid P oxides and suboxides, 1% P_4 and 75% P_4O_6. The slurry was kept at 303 K before dosing. These reaction parameters corresponded to a residence time of 11 seconds in the reactor. The reactor chamber was seen to reach a temperature of 1780 K without external cooling. The reaction product leaving the reactor chamber at its exit was then contacted with a stream of 50 l/h of earlier condensed, liquid reaction product, obtained from previous experiments performed under the same parameters, circulating at 317 K. The reaction product was condensed and cooled down to temperatures of the recirculating liquid which was kept at essentially constant temperature by external cooling.

The experiment was halted after 60 minutes.

The reaction product was subjected to a simple distillation to separate it from high-boiling impurities. After condensation, 875 g of freshly formed reaction product was found, which meant that this amount did not include the material added as coolant in the reactor or the quenching. ^{31}P NMR demonstrated that the material was composed of 99.6 weight-% of P_4O_6, 0.1 weight-% of P_4 and 0.3 weight-% of the mixed higher oxides $P_4O_{7,8,9,}$ as well as P_4O_{10}. The P_4O_6 yield was 99.2% based on the amount of P_4 used which is an excellent value, and the content of elemental phosphorus was extremely low.

Claims

1. A process for the production of a reaction product consisting essentially of P_4O_6 by reacting oxygen, or a mixture of oxygen and an inert gas, with gaseous or liquid phosphorus in an exothermic reaction in a reaction unit maintaining an average temperature in said reaction unit suitable to generate the reaction product, by removing heat created by the exothermic reaction by feeding P_4O_6 and/or by-products obtained from earlier reactions or from the running process into the reaction unit, then quenching the generated reaction product in one or more quenching unit(s) to a lower temperature where no essential decomposition of the reaction product occurs, and separating at least part of P_4O_6 from the reaction product obtained after quenching.

2. The process according to claim 1, wherein a stream of by-products consisting of the remaining residue obtained by separating at least part of P_4O_6 from the reaction product after quenching, or a fraction thereof, is fed into the reaction unit hereby removing heat created by the exothermic reaction.

3. The process according to claim 2, wherein cooling of the reaction product in the reaction unit is effected by controlling the feeding of a stream of P_4O_6 into the stream of by-products, and feeding the resulting stream into the reaction unit.

4. The process according to any one of claims 1 to 3, wherein cooling of the reaction product in the reaction unit is solely or additionally effected by controlling the feeding of a stream of P_4O_6 into the reaction unit.

5. The process according to any one of claims 1 to 4, wherein the temperature of the reaction product in the reaction unit is maintained at an average temperature in the range of 1500 to 2200K.

6. The process according to claim 5, wherein the temperature of the reaction product in the reaction unit is maintained at an average temperature in the range of 1600 to 2000 K.

7. The process according to any one of claims 1 to 6, wherein the reaction product is maintained in the reaction unit for a residence time of at least 0.5 seconds.

8. The process according to claim 7, wherein the residence time is between 1 and 60 seconds.

9. The process according to any one of claims 1 to 8, wherein the molar ratio of phosphorus (P_4) to oxygen (O_2) is in the range of from 1:2.7 to 1:3.3.

10. The process according to any one of claims 1 to 9, wherein the reaction product is quenched to a temperature below 700 K.

11. The process according to any one of claims 1 to 10, wherein the reaction product is quenched, or cooled after quenching, to a temperature that enables easy handling and/or processing of the reaction product.

12. The process according to claim 11, wherein the temperature that enables easy handling and/or processing is below the boiling point of P_4O_6.

13. A process according to any one of claims 1 to 12, wherein liquid reaction product and/or liquid P_4O_6 is added as a coolant to the reaction product to be quenched.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/064988

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B25/12
ADD.

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)
C01B

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 practical, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DD 292 637 A5 (WITTENBERG STICKSTOFF AG [DE]) 8 August 1991 (1991-08-08) cited in the application claim 1 example 1	1-13
A	DE 33 19 606 A1 (PIESTERITZ AGROCHEMIE [DD]) 6 December 1984 (1984-12-06) the whole document	1-13
A	DE 11 72 241 B (AKAD WISSENSCHAFTEN DDR) 18 June 1964 (1964-06-18) the whole document	1-13

☐ 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
"E" earlier document but published on or after the international filing date
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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	Date of mailing of the international search report
14 April 2010	20/04/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Rigondaud, Bernard

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/064988

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DD 292637	A5	08-08-1991	NONE	
DE 3319606	A1	06-12-1984	NONE	
DE 1172241	B	18-06-1964	NONE	