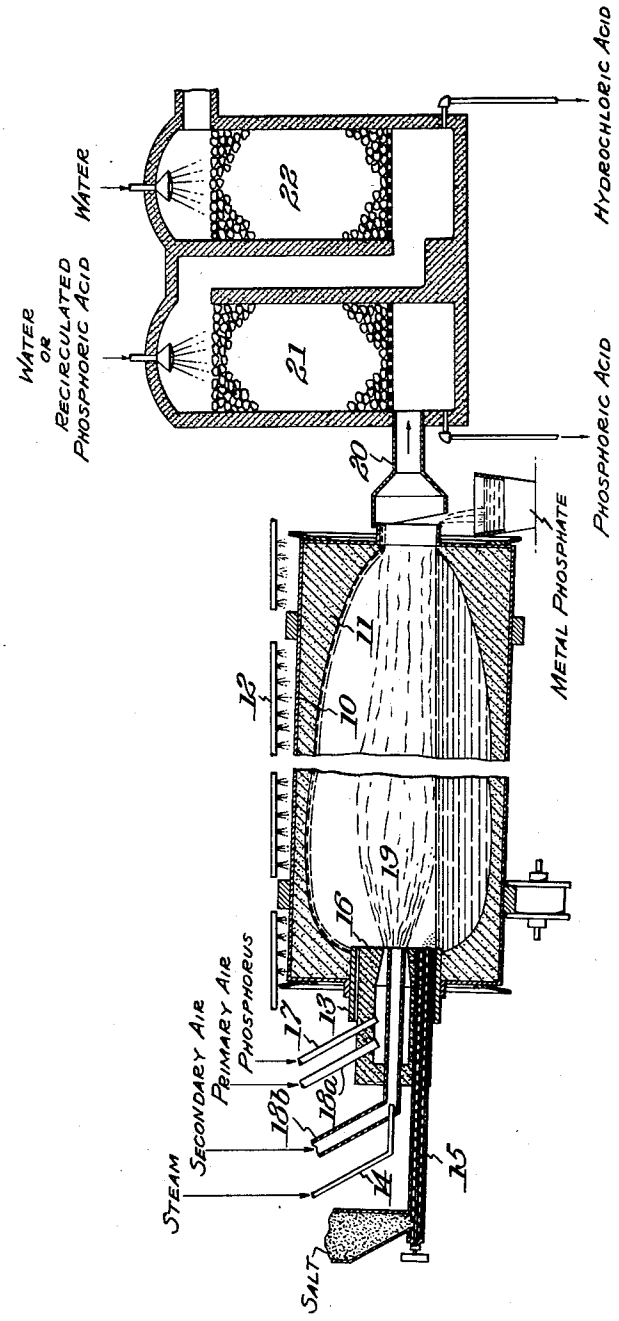
Jan. 3, 1939. F. P. KERSCHBAUM 2,142,944

PRODUCTION OF PHÓSPHATES

Filed May 21, 1937



Inventor:

Friedrich P. Kerschbaum

By Potter, Pierce & Scheffler

Attorneys.

Patented Jan. 3, 1939 2,142,944

UNITED STATES PATENT OFFICE

2,142,944

PRODUCTION OF PHOSPHATES

Friedrich P. Kerschbaum, Winter Haven, Fla., assignor to Harold T. Stowell, Washington, D. C.

Application May 21, 1937, Serial No. 144,069

6 Claims. (Cl. 23—106)

This invention relates to the production of salts and phosphoric acid and is particularly directed to the production of metal phosphates by the reaction of metal salts having volatile anions with the products of combustion of phosphorus.

It has been proposed to react the oxidation products of phosphorus with alkali metal chlorides to form alkali metal phosphates, but a number of heretofore unsurmounted difficulties have prevented the technical application of such a process. One of the most serious of the difficulties which has stood in the way of the utilization of such a process is the apparent impossibility of finding materials of construction which will withstand the combined effect of the highly oxidizing conditions, the high temperatures, and the extremely corrosive character of the products of the reaction at the temperatures necessarily employed. Metallic and ceramic materials are quickly disintegrated by molten alkali metal phosphates, while carbon is destroyed by oxidation.

A further difficulty arises from the fact that high temperatures and a large amount of heat are required to bring about the reaction of the alkali metal chloride, particularly when a substantially complete reaction is desired so that no substantial amount of chloride will be present in the alkali metal phosphate produced.

It has now been found that the necessary heat and temperature conditions may be obtained if the reaction is carried out, in or directly adjacent, to a zone of combustion of phosphorus. In order to obtain the desired temperature conditions, however, it is necessary that the phosphorus combustion zone be confined so as to concentrate the radiant heat of combustion upon the reactants. This condition, of course, intensifies the difficulty of finding materials of construction, but this difficulty has been solved by the present invention by using the solid alkali metal phosphate itself as the material for forming the chamber defining the combustion and reaction zone.

The invention therefore comprises the combustion of phosphorus and the reaction of the products of combustion with a metal salt particularly alkali metal chloride in a space exposed to direct radiation of heat from the combustion zone and confined within a solid shell of alkali metal phosphate.

By suitably proportioning the amount of alkali metal chloride supplied to the reaction zone, it is possible by the method of the present invention to produce different phosphate salts, such as metaphosphates, pyrophosphates and tri-alkali metal phosphates. In the production of tri-alkali metal phosphates, however, it has been found desirable to use an excess of alkali metal chloride.

The phosphorus supplied to the combustion zone may be substantially completely reacted by suitable adjustment of the reaction conditions. In general, completeness of reaction of the oxidized phosphorus is favored by decreasing the dilution of the combustion gases for example, by carrying out the combustion with oxygen or oxygen-enriched air. It is, however, usually advantageous to operate the process so as to permit the escape of a greater or less amount of phosphorus pentoxide or phosphoric acid from the reaction zone since this may readily be recovered as phosphoric acid of a high degree of purity. In practical operation, the conditions of reaction may readily be adjusted to result in the highest economy of production under prevailing market conditions.

Instead of, or in addition to, the use of oxygen-enriched air, the absorption of the oxidized phosphorus may be substantially increased by the use of preheated air. This is particularly advantageous in the production of alkali metal metaphosphates. The temperature to which the air is preheated will vary with the character of the product desired and with the type of furnace, much less preheat being necessary with furnaces designed to have comparatively low losses of heat by radiation. In a furnace producing sodium metaphosphate by the method of the invention and having a heat loss of about 50 to 70%, it has been found that highly satisfactory results may be obtained by preheating the air, not enriched in oxygen, to about 600°–800° C., for example.

In general, it is desirable to supply to the reaction zone sufficient water, preferably in the form of steam, to effect the conversion of all of the chlorine contained in the alkali metal chloride entering the reaction into hydrogen chloride. However, by omitting the supply of steam and suitably adjusting the supply of oxygen, the chlorine may be obtained in the uncombined state.

A method of operating the process of the invention and apparatus suitable for operating the process are illustrated in the accompanying drawing.

In the drawing 10 is the metal shell of a rotary furnace which may be rotated by conventional driving means, not shown. The interior of the metal shell is provided with a lining 11, of alkali metal phosphate, for example, sodium meta-

phosphate. This lining, which is a very important feature of the invention, may be provided by gradually building up the lining by melting the phosphate, for example, with the flame of an oil or gas burner while chilling the metal shell 10 with the water sprays 12. The lining may also be built up from solid blocks of phosphate fitted into place and welded into a unitary lining by melting the surface down with a burner until all of the cracks and joints are filled.

The lining may also advantageously be built up of a plurality of superposed layers, beginning preferably with sodium metaphosphate adjacent the furnace shell and then providing one or more layers of other phosphates of higher melting point.

When the phosphate lining has been provided, the operation of the process is started by burning phosphorus in burner 13, while supplying steam to the reaction zone through pipe 14 and sodium or potassium chloride through worm feed 15. The phosphorus burner shown in the drawing by way of example is a phosphorus vapor burner and consists of a hollow cylindrical carbon block having a narrowed nozzle 16 projecting into the furnace. Liquid phosphorus is supplied through pipe 17 which may be of carbon or quartz while a small portion of the air, air enriched with oxygen, or technical oxygen is supplied through pipe 18*a*. The oxidation of a portion of the phosphorus within the burner vaporizes the remaining phosphorus and the vaporus mixture passes out into the furnace where it burns with an intensely hot flame 19 together with the additional air or oxygen which is supplied around the outside of the burner or by means of an additional nozzle 18*b* which may be formed within the shell of burner 13. The shape and intensity of the flame may be regulated by adjusting the amount and the oxygen content of the two streams of the combustion supporting gases, and this in turn determines chiefly the size and shape of the more or less pear-shaped chamber formed in the phosphate lining 11.

Instead of a phosphorus vapor burner, any other form of burner may be used, such for example, as a spray type burner. It is also possible for the process to be operated satisfactorily with the phosphorus oxidation flame countercurrent to the flow of the alkali metal chloride and the alkali metal phosphate product through the furnace. Such operation will alter somewhat the shape of the reaction chamber formed in the phosphate lining from that shown in the drawing.

The lining is always cooled, by means of sprays or by cooling coils adjacent to or imbedded in the furnace shell or in the lining itself, so that the lining is maintained intact throughout the interior of the furnace. The reaction between the alkali metal chloride and the products of combustion of phosphorus is mainly effected in the surface of the pool of molten product in the lower part of the furnace and in the layer of molten product covering the inside of the lining, and to some extent in the pool itself. The constant rotation of the furnace during the operation of the process insures the maintenance of the lining in a uniform condition and also insures the constant presence of the layer of molten material on the interior of the lining.

The reaction of the materials supplied to the furnace is effected under the influence of the intense radiation from the zone of combustion of the phosphorus and to a large extent in the liquid layer lining the walls of the reaction chamber so that a very complete utilization of the alkali metal chloride may be obtained. The alkali metal phosphate produced is removed intermittently or continuously and worked up by known methods.

The hydrogen chloride produced in the reaction together with the unabsorbed phosphoric acid pass out of the furnace through conduit 20 into tower or electrical precipitator 21 where the phosphoric acid is condensed, while the hydrogen chloride and remaining gases of combustion pass to tower 22 wherein the hydrogen chloride is absorbed in water to form hydrochloric acid.

The amount of phosphorus absorbed in the reaction chamber is largely determined by the proportion of oxygen in the combustion supporting gases, although other factors such as the relative size and shape of the furnace have some effect. In an illustrative operation, using air as the combustion supporting gas, the absorption of phosphorus amounted to about 50%, while by increasing the proportion of oxygen in the gas, absorption of up to 85–90% of the phosphorus could be obtained. However, the use of a gas very rich in oxygen is not in general advantageous for combustion, apart from economic considerations, because the flame produced with pure oxygen would have a very small volume and the molten surfaces capable of affording a reaction zone would be correspondingly small. In general, it is desirable to provide carrier gases in the amount of at least 5% of the volume of oxygen, and a mixture of one volume of oxygen supplied as air and one volume of technical oxygen, giving a gas containing about 35% of oxygen, has been found very suitable. As previously pointed out, an increase in the absorption of the phosphorus oxidation products may also be effected by preheating the air used instead of enriching it with oxygen. Steam may be supplied to the reaction zone in such proportions as to act as a carrier gas as well as to facilitate the reaction with the alkali metal chloride as previously described.

As previously stated, the nature of the phosphate salt may be determined by the proportion of alkali metal chloride supplied to the reaction zone in relation to the amount of phosphorus absorbed therein. For example, for the production of sodium metaphosphate about two mols of sodium chloride is supplied to the reaction zone for each mol of P_2O_5 absorbed, while for the production of sodium pyrophosphate, double this proportion of sodium chloride is supplied. The amount of heat required for carrying out the process increases with the amount of alkali metal chloride used in proportion to the phosphorus burned.

It is sometimes advantageous to so operate the process that the alkali metal phosphate product coming from the furnace still contains a small proportion of unreacted alkali metal chloride which may thereafter be completely reacted by further heating. This may be effectively and economically accomplished by passing the molten product from the furnace directly into a second rotary furnace lined with alkali metal phosphates in which the necessary heat to complete the reaction of the residual alkali metal chloride is furnished, for example, by an oil or gas burner. It is desirable to supply steam in the second furnace to aid in completing the elimination of the alkali metal chloride. This may be advantageously supplied through the heating burner.

A particularly valuable feature of the present invention is that the phosphate salts produced are free, or practically free, from arsenic which is usually contained in elemental phosphorus. This is due to the fact that under the conditions of the reaction the arsenic content of the prosphorus is converted into a volatile compound which passes out of the reaction zone with the unabsorbed gases. The elimination of arsenic may be more fully assured by supplying hydrochloric acid, either as gas or as aqueous acid, to or adjacent the zone of phosphorus combustion.

The method and apparatus of the invention may also be advantageously utilized for the production of other metal phosphates particularly phosphates of metals which may be melted at temperatures not greatly exceeding 1500° C., such as calcium, magnesium, zinc and lead.

The method and apparatus of the invention may further be used to advantage for the production of metal phosphates from phosphoric acid. It is especially suitable for the production of phosphates for fertilizer purposes from aqueous phosphoric acid such as is recovered in the refining of crude oil. For example, by the reaction of such recovered acid with potassium chloride to form a eutectic mixture of KCl and K_3PO_4 a very suitable fertilizer is obtained. In carrying out reactions of this type where the heat of combustion of the phosphorus is not available, heat must be supplied from another source, such as an oil or gas burner, or electrical energy.

Instead of a horizontal drum as described above by way of example, it is also possible to utilize a vertical vessel. In this case the interior of the vertical vessel is lined with solid salt which is maintained in solid condition by suitable cooling of the exterior of the vertical walls of the vessel. Instead of maintaining the lining by rotation of the vessel as in the case of the horizontal drum, this may be effected in the vertical vessel by flushing the walls with molten salt taken from the end product or any suitable intermediate stage by mechanical means, for example, a pneumatic lift.

This application is a continuation-in-part of my application Serial No. 105,605, filed October 14, 1936.

I claim:

1. A method of producing salts of phosphorus which comprises maintaining a continuous cylindrical solidified layer of the phosphate salt to be produced, establishing an incandescent combustion zone in the space confined by said cylindrical layer, supplying to said combustion zone oxidation products of phosphorus and a metal salt having an anion volatilizable by reaction with oxidation products, and reacting the same therein to form a phosphate salt.

2. A method of producing salts of phosphorus which comprises maintaining a continuous cylindrical solidified layer of the phosphate salt to be produced, establishing an incandescent combustion zone in the space confined by said cylindrical layer, supplying to said combustion zone oxidation products of phosphorus and a compound of a metal of the group consisting of alkali and alkaline earth metals capable of reacting with said oxidation products to form a phosphate salt, and reacting the same therein to form a phosphate salt.

3. A method of producing salts of phosphorus which comprises maintaining a continuous cylindrical solidified layer of the phosphate salt to be produced, establishing an incandescent combustion zone in the space confined by said cylindrical layer, supplying to said combustion zone oxidation products of phosphorus and an alkali metal chloride, and reacting the same therein to form a phosphate salt.

4. A method of producing salts of phosphorus which comprises maintaining a continuous cylindrical solidified layer of the phosphate salt to be produced, oxidizing elemental phosphorus in the space confined by said cylindrical layer to form an incandescent combustion zone, supplying to said combustion zone a metal salt having an anion volatilizable by reaction with oxidation products of phosphorus, and reacting the same therein to form a phosphate salt.

5. A method of producing salts of phosphorus which comprises maintaining a continuous cylindrical solidified layer of the phosphate salt to be produced, oxidizing elemental phosphorus in the space confined by said cylindrical layer to form an incandescent combustion zone, supplying to said combustion zone a compound of a metal of the group consisting of alkali and alkaline earth metals capable of reacting with oxidation products of phosphorus to form a phosphate salt, and reacting the same therein to form a phosphate salt.

6. A method of producing salts of phosphorus which comprises maintaining a continuous cylindrical solidified layer of the phosphate salt to be produced, oxidizing elemental phosphorus in the space confined by said cylindrical layer to form an incandescent combustion zone, supplying to said combustion zone an alkali metal chloride, and reacting the same therein to form a phosphate salt.

FRIEDRICH P. KERSCHBAUM.