

PATENT SPECIFICATION

617,990



Convention Date: (France): Aug. 16, 1944.

Application Date (in United Kingdom): July 22, 1946. No. 21863/46.

Complete Specification Accepted: Feb. 15, 1949.

(Under Section 6 (1) (a) of the Patents &c. (Emergency) Act, 1939 the proviso to Section 91 (4) of the Patents and Designs Acts, 1907 to 1946 became operative on July 22, 1946.

Index at Acceptance:—Class 1(ii), E3b.

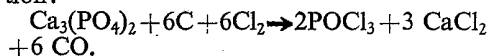
COMPLETE SPECIFICATION

An Improved Process for the Manufacture of Phosphorus Oxychloride

We, SOCIÉTÉ ANONYME DES MANUFACTURES DES GLACES ET PRODUITS CHIMIQUES DE SAINT-GOBAIN, CHAUNY & CIREY, a Company organised under the laws of the French Republic, of 1 bis, Place des Saussaies, Paris 8e, France, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

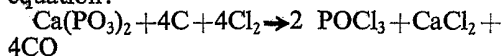
This invention relates to the manufacture of phosphorus oxychloride by the known process which consists in subjecting the orthophosphates or metaphosphates of calcium to the action of chlorine in the presence of a reducing agent such as, for example, carbon.

For calcium orthophosphate the reaction may be expressed by the following equation:—



The process is generally carried out at a relatively high temperature, of the order of 300°C., and in some cases it is even recommended that the temperatures employed lie between 500° and 750°C. in order to cause partial fusion of the calcium chloride formed which, if allowed to remain in the solid state, slows up the reaction between the chlorine and the phosphate.

It is also known that, if the orthophosphate be replaced by calcium metaphosphate, the reaction then being expressed by the following equation:—



the quantity of chlorine consumed in producing a given quantity of phosphorus oxychloride is only two-thirds of that which is required when starting from tri-calcium phosphate. Hence, operating in accordance with this reaction may be more advantageous.

The present invention consists in an improved process for the manufacture of phosphorus oxychloride, when operating in accordance with either of the reactions indi-

cated above, wherein, once the reaction has been initiated, heat for maintaining them as in reaction at a suitable temperature is generated by passing an electric current through the calcium chloride formed.

As a preliminary step, in order to initiate the reaction, the temperature in the reaction chamber is raised to about 800°C., by the aid of any suitable auxiliary heating means, so that the calcium chloride formed passes into the liquid state and accumulates at the bottom of the reaction chamber which latter, as will be understood, is provided at this level with current-supply means.

Since the reaction which results in the formation of phosphorus oxychloride is exothermic, a relatively low rate of generation of heat in the heating resistance thus constituted by the calcium chloride is sufficient to compensate for the heat losses and to maintain the temperature at about 800°C.

It is of advantage to cause the phosphatic ores to become immersed, at least in part, in the fused calcium chloride in order to ensure a good transmission of heat to the mass in reaction, this expedient not checking the course of the reaction because the presence of fused calcium chloride in contact with the ores does not impede the action of the chlorine on these latter.

The electrical heating process according to the invention enables a precise and substantially uniform temperature to be maintained throughout the mass which is immersed in the fused calcium chloride, and, in consequence, makes it possible to operate at a temperature substantially higher than those usually employed. The mean temperature may thus be brought close to the maximum temperature compatible with the continued resistance of the refractory walls of the reaction chamber to the action of the reducing mixture of chlorine and carbon. There is considerable advantage in being able to operate at a temperature much higher than those generally employed in these reactions because both the yield and the speed of these

[Price 2/-]

latter increase with rise in temperature. At 800°C. the yield reaches 97% of that theoretically possible.

Using the heating method of the invention, with the consequent easy and precise control of operations, and by employing as the refractories compact silico-aluminous products obtained by fusion in an electric furnace, the present Applicants have been able to operate the process at 800°C., at which temperature all the calcium chloride passes into the liquid state and flows freely since the fusion temperature of pure calcium chloride is in the region of 770°C. The controlled removal of the calcium chloride is thus made easy and may be effected, for example, by means of a siphon arranged to maintain the liquid bath at a constant level.

The invention may be carried into practical effect by using as the reaction chamber, by way of a specific example, a vertical furnace of the type illustrated in vertical section on the accompanying drawing.

This furnace comprises a vat 1, preferably of sheet steel, provided with a heat-insulating covering 2 and of a height which is large compared with its other dimensions so that total absorption of the chlorine may be ensured. The furnace has a lining 3 preferably formed from fused and compacted refractory materials such as, for example, a refractory with a base of silica and alumina obtained by fusion in the electric furnace.

The upper end of the furnace 1 is hermetically closed by a cover 4 which has its inner face provided with a refractory lining 5 and which may be provided with a hopper (not shown) through which a mixture of phosphate and carbon is introduced in amounts corresponding to the progress of the reaction. The charging device is such, in all cases, that no gases can escape through the hopper at any time. The cover 4 is provided with an exhaust pipe 6 for the evacuation of the gases.

The mixture of phosphate and carbon is supported on a grid 7 beneath which open nozzles 8 each delivering a current of chlorine which passes through the grid to react with the mixture. These nozzles are made from a material, such as nickel, which is but slightly attacked by chlorine.

The current-supply electrodes 9 are mounted close to the bottom 10 of the furnace into which opens a pipe 11 for the drawing off of the molten calcium chloride 12 under the control of a siphon.

In order to initiate the reaction, the temperature is raised to 800°C. by the aid of any suitable auxiliary heating means. When molten calcium chloride 12 has accumulated at the bottom of the vat, electric current is passed through its mass and the auxiliary heating means is rendered inoperative. The temperature of the bath 12 is thus main-

tained at a suitable value by the heat generated in the calcium chloride. The siphon regulating the drawing off of the liquid from the bath 12 is so arranged that the liquid rises above the grid 7 and immerses part of the mixture of phosphate and carbon.

So that the reaction may proceed favourably, the phosphate and carbon may be mixed together as intimately as possible, this necessitating very fine subdivision of the materials. However as, on the other hand, it is necessary to allow the chlorine to circulate through the mass, it is advantageous to make balls or briquettes (for example, by pressure) from a ground mixture of natural tricalcium phosphate and wood charcoal. Only the minimum quantity of wood charcoal necessary to ensure reaction with the phosphate should be employed and the formation of the balls may be facilitated by adding ammonium phosphate which, as is known, acts as a binder.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the manufacture of phosphorus oxychloride by the action of chlorine on a calcium phosphate in the presence of carbon, wherein once the reaction has been initiated heat for maintaining the mass in reaction at a suitable temperature is generated by passing an electric current through the calcium chloride formed.

2. A process according to claim 1, wherein the reaction is initiated by the aid of an auxiliary heating means which is kept in operation until the calcium chloride formed in the reaction passes into the liquid state.

3. A process according to claim 1 or 2, wherein the phosphatic ores and the carbon are so arranged as to be partially or completely immersed in the bath of fused calcium chloride.

4. A process according to claim 1, 2 or 3, wherein the reaction is carried out at a temperature of about 800°C.

5. A process according to any of the preceding claims, wherein the reaction is carried out in a furnace comprising a reaction space having near its lower end a grid or the equivalent for supporting the phosphatic ores and the carbon, means for supplying chlorine beneath the grid or the like, and means for supplying electric current to the zone beneath the grid or the like in which accumulates the calcium chloride formed.

6. A process as claimed in claim 1, substantially as herein described.

Dated this 22nd day of July, 1946.

For the Applicants:
RAWORTH, MOSS & COOK,
 75, Victoria Street, London, S.W.1.
 Chartered Patent Agents.

[This Drawing is a reproduction of the Original on a reduced scale.]

