April 10, 1962 A. D. F. TOY ETAL 3,029,282

PROCESS FOR PRODUCING PHENYLPHOSPHONOUS DICHLORIDE

Filed Sept. 2, 1959 3 Sheets-Sheet 1

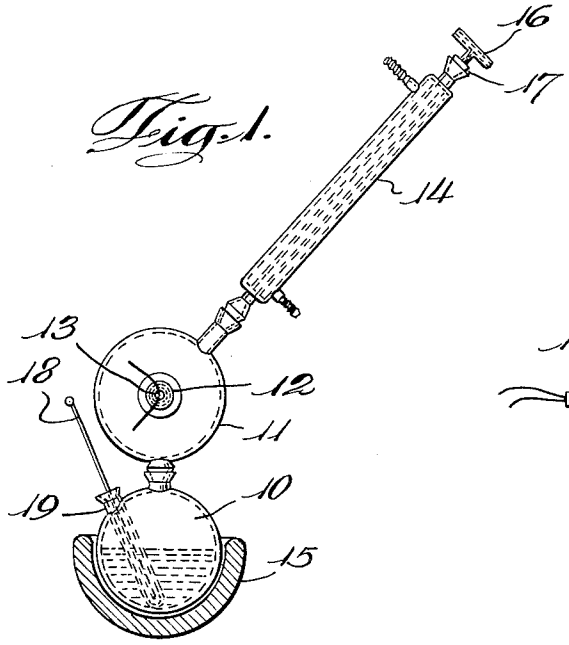


Fig. 1.

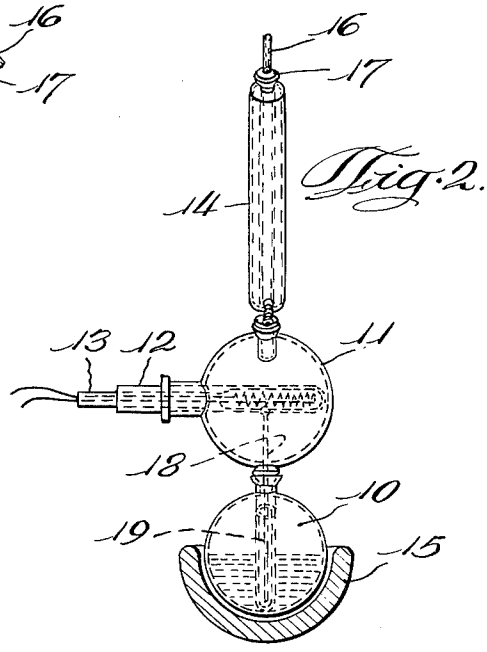


Fig. 2.

RATE OF FORMATION OF PHENYLPHOSPHONOUS DICHLORIDE VS. BENZENE CONCENTRATION AT VARIOUS CHLOROBENZENE CONCENTRATIONS TUBE TEMPERATURE ≅ 550° C.

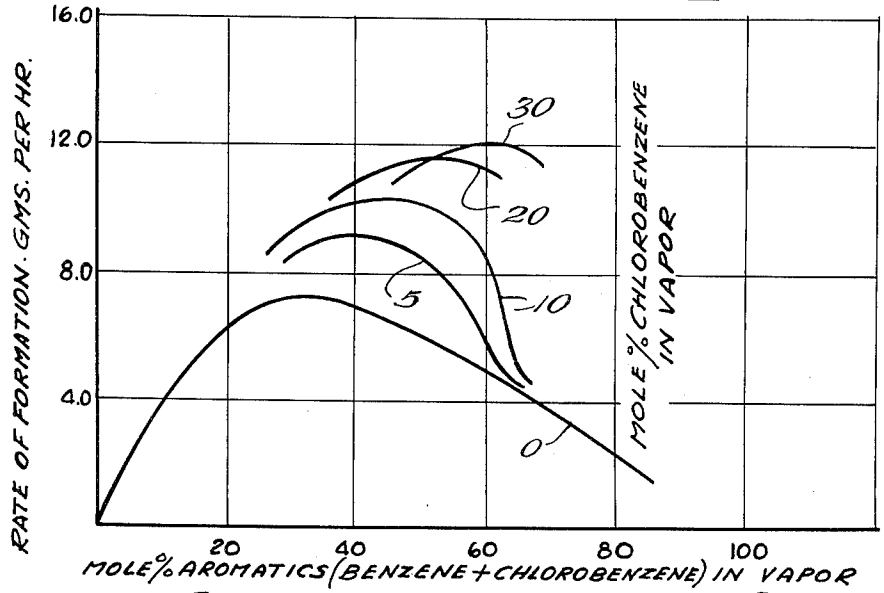


Fig. 3.

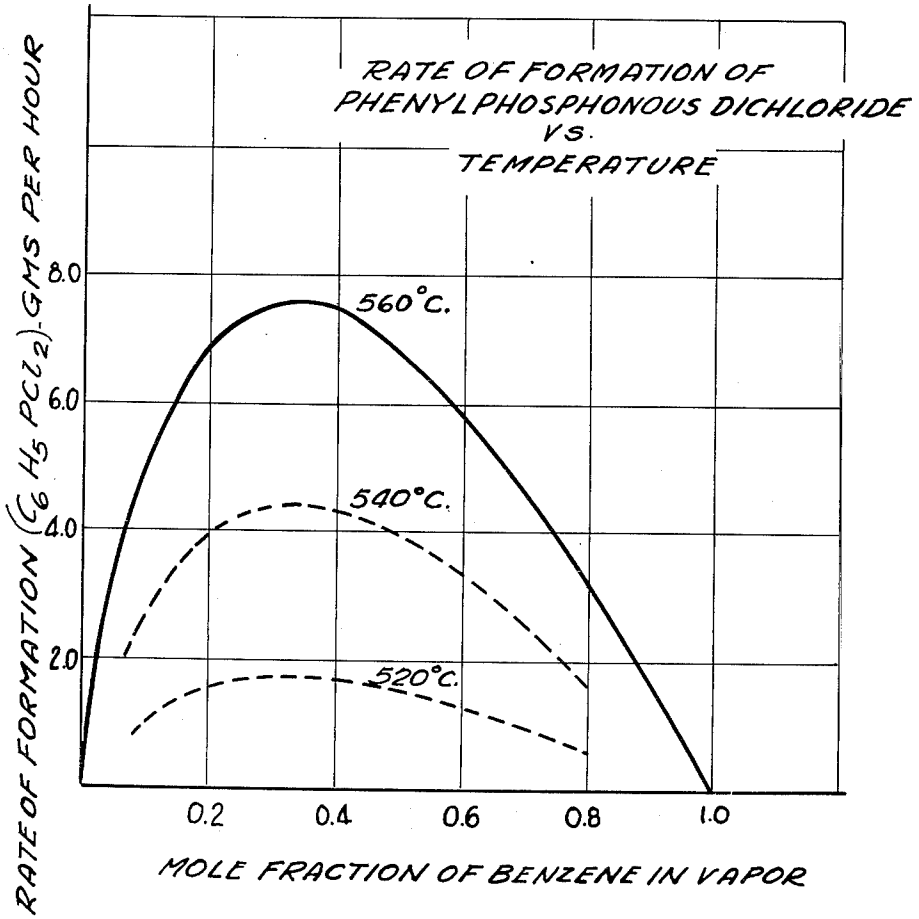
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Fig. 4.



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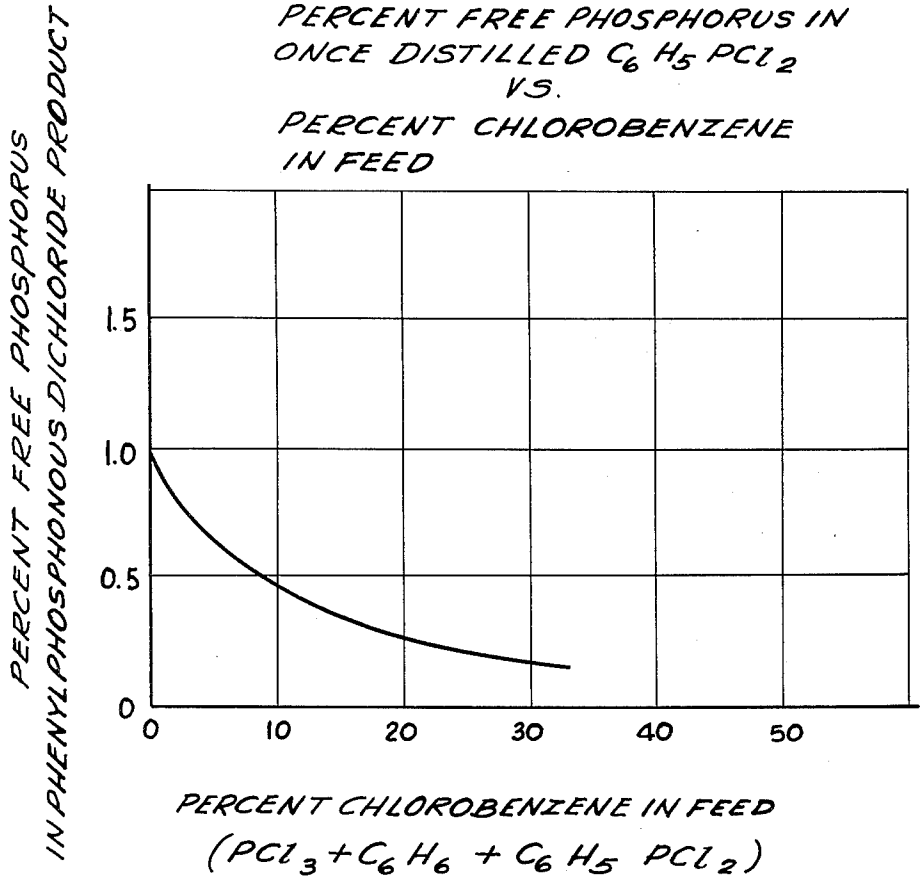


Fig. 5.

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PROCESS FOR PRODUCING PHENYLPHOSPHONOUS DICHLORIDE

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8 Claims. (Cl. 260—543)

This invention relates to a new and improved process of making phenylphosphonous dichloride.

This application is a continuation in part of our pending application Serial No. 682,176, filed September 5, 1957, now abandoned.

It has long been known that phenylphosphonous dichloride could be made by pyrolysis according to the following reaction:

$$PCl_3 + C_6H_6 \xrightarrow{\Delta} C_6H_5PCl_2 + HCl$$

More particularly, the above reaction was reported as early as 1873 by Michaelis, Ber. 6, 601, 816 (1873), and has been studied by a number of persons since this date. A variety of types of apparatus has been used, including red hot tubes through which the reactants were passed in vapor form and internally heated quartz tubes around which the gaseous reactants were passed. When using the above processes and various modifications thereof, the rates of reaction and product yields have never been very good. Furthermore, such processes cause the formation of a considerable amount of decomposition products. For example, these processes produce decomposition products such as free phosphorus, phosphine and various carbonaceous residues, which indicate that various side reactions take place.

In distinct contrast to the above referred to conventional reaction for producing phenylphosphonous dichloride, we have discovered a remarkable process that greatly reduces side reactions and the formation of decomposition products, and significantly increases the rate of formation of phenylphosphonous dichloride. Briefly, our process comprises reacting phosphorus trichloride and benzene in the presence of monochlorobenzene. Experience indicates that satisfactory results may be obtained with as low as about 1 mole percent monochlorobenzene in the vapor; however, in order to obtain commercially advantageous results, at least about 2–5 mole percent monochlorobenzene should be used in the vapor.

The process encompassed by our invention provides for the reaction of PCl_3 and benzene at elevated temperatures in the presence of monochlorobenzene. By the use of monochlorobenzene in this process, the rate of reaction may be increased by as much as 65–70%. At the same time, the decomposition products, including free phosphorus, are decreased and the quality of the product is improved. It is very important to obviate or reduce the level of the spontaneously ignitable free phosphorus, especially with benzene in the vicinity. FIGURE 5 shows that as the percentage of chlorobenzene in the feed (PCl_3, C_6H_6, and monochlorobenzene) increases above the zero level, the percentage of free phosphorus in the phenylphosphonous dichloride product correspondingly decreases. The level of phosphorus in the product shown

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in FIGURE 5 was determined by once distilling the product.

The exact mechanism by which the added monochlorobenzene improves the reaction rate is not known. It does not appear to be catalytic since increasing the amount of monochlorobenzene in the reacting vapors continues to increase the reaction rate even up to a level of approximately 30–35 mole percent monochlorobenzene.

To illustrate the process of this invention reference is made to the accompanying drawings wherein FIGURES 1 and 2 are front nad side views, respectively, of apparatus used to prepare phenylphosphonous dichloride.

Referring to the use of the apparatus shown in FIGURES 1 and 2, a mixture of phosphorus trichloride, benzene and monochlorobenzene is first charged into flask **10** which is heated by cup-shaped heater **15** so that the liquid is continually refluxing. The temperature of the charge in the flask **10** is determined by the thermometer **18** which is positioned in the well **19**. The vapors rise to reaction tube **12** which is heated by a heating unit such as the electric coil **13**. After passing through the reaction flask **11**, the vapors are condensed in condenser **14** and flow back down the side of flask **11** into flask **10**. An atmosphere of dry nitrogen is provided through entrance tube **16**, and HCl and by-product noncondensibles are removed through tube **17**.

Ordinary Pyrex glass is used for this equipment with the exception of the reaction tube **12** which is preferably made of fused silica. Various corrosion-resistant metals such as stainless steels, Hastelloys, Inconels and nickel may also be used but are not generally as satisfactory as fused silica. The temperature of the reaction tube **12** is controlled by the current input after the tube has been calibrated by using a thermocouple pressed against the silica tube. Other means of temperature control, such as an optical pyrometer, may also be satisfactorily used.

The progress of the reaction is followed by the rise in boiling point of the liquid in flask **10**. As the concentration of the product phenylphosphonous dichloride (B.P., 224.6° C.) increases in the flask, the temperature slowly rises. The reaction rates referred to below, however, were calculated by recovering the product (i.e., phenylphosphonous dichloride) from the reactants and dividing this yield in grams by the number of hours duration of the run. This is illustrated in the example.

The raw materials suitable for use in our process are ordinary commercially available products. The benzene and chlorobenzene should be essentially anhydrous. If water is present in the commercially available products, they should be "topped" by distillation to remove the water.

The proportions of the reactants employed may be varied over a wide range. We have found, for example, that when only benzene and PCl_3 are reacted, the molar of ratio PCl_3 to benzene in the vapor may be varied from about 6:1 to 0.25:1. The preferred proportion is a ratio of PCl_3 to benzene of about 2:1, which corresponds to one chlorine atom for each hydrogen atom. When monochlorobenzene is added to this reaction mixture the ratio of PCl_3 to total aromatics (benzene plus chlorobenzene) shifts somewhat. The preferred molal vapor ratio in this case is more nearly between 1:1 and 1:1.5.

The amount of monochlorobenzene used may run as high as 30 to 35 mole percent of the entire vapor mixture. Thus, when the above mentioned ratios of PCl_3 to total aromatics are used, the monochlorobenzene present may be equivalent or in some cases even greater than the amount of benzene used. A preferred reaction vapor mixture for the process of this invention comprises approximately 40 mole percent PCl_3, 25 to 30 mole percent benzene, and 35 to 30 mole percent monochlorobenzene.

The following example illustrates the process of our invention.

EXAMPLE

137.4 gm. (1.0 mole) of phosphorus trichloride, 93.3 gm. (1.194 moles) of benzene, and 337.7 gm. (3.0 moles) of monochlorobenzene were charged into the boiling flask 10 equipped at shown in FIGURE 1. These quantities were calculated to give molal vapor concentrations of 39.1% PCl_3, 37.9% benzene and 23.0% chlorobenzene at a boiling point of approximately 100° C. The heating units were then turned on and the temperature of the reaction tube (fused silica) was raised to approximately 550° C. The vapors were allowed to reflux through the reaction flask 11 for 3.7 hours during which time the boiling point of the liquid rose from 100.7° C. to 107.0° C. 555.7 gm. of clear, dark amber reaction product was recovered; this product was distilled through a 14-inch Vigreux column. 505.6 gm. of low boiling reactants and 42.0 gm. of phenylphosphonous dichloride were recovered. This gives a rate of formation of 11.34 gm./hr. A percentage yield was calculated as follows:

568.4 gm. reactants charged
505.6 gm. reactants recovered

62.8 gm. reactants consumed
42.0 gm. product and 8.6 gm. equivalent HCl produced

$$\frac{42.0+8.6}{62.8}\times 100\% = 80.5\% \text{ yield}$$

Over 150 similar experiments were run in order to verify that the addition of monochlorobenzene increases the reaction rate over the best results obtained without monochlorobenzene. Yields in all cases were good and generally ran from 60 to 80%. As a check on purity of the product, occasional samples were hydrolyzed to phenylphosphonous acid, purified, and analysed. A typical example gave the following results:

	Analysis	Theory
P, percent	21.1	21.8
Total chlorine, do	0.2	0
Chloride ion, do	0.1	
Molecular weight by titration	145.0	142.1

Further, FIGURE 3 shows that the use of 5, 10, 20 and 30 mole percent monochlorobenzene in the vapor increases the rate of formation of phenylphosphonour dichloride, as compared with zero mole percent chlorobenzene. It can be seen from these data that if no monochlorobenzene is used, the rate of formation reaches a maximum at approximately 33% aromatics, i.e., a PCl_3 to benzene mole ratio of approximately 2:1 in the vapor.

FIGURE 3 is not intended to illustrate the total attainable rate of producing phenylphosphonous dichloride, but is intended to show the relative rates of phenylphosphonous dichloride produced with and without the use of monochlorobenzene using the same apparatus and reaction conditions. Large scale plant production and experience have shown that similar results are obtained when hundreds of pounds of phenylphosphonous dichloride are produced per day.

The data used in preparing FIGURE 3 were primarily obtained from a series of fourteen experiments, all of which were conducted in the same apparatus under conditions as nearly identical as possible. These data are shown in Table I, infra.

Table I

RATE OF FORMATION OF PHENYLPHOSPHONOUS DICHLORIDE AT VARIOUS CHLOROBENZENE CONCENTRATIONS vs. MOL PERCENT AROMATICS (BENZENE+CHLOROBENZENE) IN VAPOR AT 550° C.

Mol percent Chlorobenzene in Vapor	Mol percent Benzene in Vapor	Mol percent Aromatics in Vapor	Rate of Formation of Phenylphosphonous Dichloride, Gms./Hr.
5	47.0	52.0	8.3
5	27.5	31.5	8.6
5	59.0	64.0	4.3
10	44.5	54.5	10.0
10	24.8	34.8	9.8
10	56.0	66.0	4.4
15	42.0	57.0	10.9
15	23.5	38.5	10.5
15	53.0	68.0	4.6
20	39.3	59.3	11.5
20	22.0	42.0	11.0
25	37.0	62.0	11.9
25	21.0	46.0	11.2
30	34.5	64.5	12.1

The reaction rates in Table I, supra, were determined by recovering the phenylphosphonous dichloride from the reactants and dividing this yield (in grams) by the number of hours duration of the reaction or run. A steady rate of reaction was evidenced by a continued rise in the boiling point of the reaction mixture during the experiment.

The curve shown in FIGURE 3 that represents 0% chlorobenzene had been previously derived from a long series of experiments during which reaction temperatures and reactant ratios had been systematically varied over wide ranges. This curve thus represents a suitable base line for comparing the results of the chlorobenzene addition data referred to in Table I, supra.

Table I, supra, and FIGURE 3, together, clearly show that if no monochlorobenzene is used, the rate of formation of phenylphosphonous dichloride reaches a maximum at approximately 33% aromatics, i.e., a PCl_3 to benzene mole ratio of approximately 2:1 in the vapor. It can also be readily observed that by adding chlorobenzene to the reacting vapors the rate of formation steadily increases to a value approximately 1.7 times the maximum levels heretofore obtained using only benzene. It is also apparent that as the PCl_3 to total aromatics ratio becomes greater than 2 to 1 (i.e., less than 33% total aromatics), the addition of monochlorobenzene is of decreasing value. Thus, it is in the PCl_3 to aromatics ratio range of 2 to 1 down to about 0.25 to 1 (80% aromatics) that the addition of monochlorobenzene to the reaction mixture is most valuable. There is apparently no precise upper limit to the amount of monochlorobenzene which may be used to increase reaction rate. As the amount of monochlorobenzene used is increased above the preferred range of 30–35% (based on total vapors in the reaction mixture) monochlorobenzene, the reaction rate continues to increase but side reactions appear to take place which produce high boiling materials and reduce the yield of phenylphosphonous dichloride.

A run was made at 560° C. in which the rate of formation of phenylphosphonous dichloride was determined while using various concentrations of benzene in the vapor. These data are shown in Table II below and are graphed in FIGURE 4.

Table II

PREPARATION OF PHENYLPHOSPHONOUS DICHLORIDE AT 560° C.

Expt. No.	Avg. Mol percent Benzene in Vapor	Rate of Formation of $C_6H_5PCl_2$, gm./hr.
1	87	2.22
2	78.5	3.72
3	68	4.62
4	53	7.00
5	52	7.18
6	52	7.18
7	34	7.60
8	31	7.64
9	30	7.52
10	24	5.80
11	20	6.13
12	11	3.04

From the data shown in FIGURE 4, a family of curves were calculated and are identified by the 540° C. and 520° C. dotted lines in FIGURE 4, which give the maximum rate of formation of phenylphosphonous dichloride at a given temperature for a given mol fraction of benzene in the vapor. This information was then used to provide the data for the 0% monochlorobenzene which is in effect the base line of FIGURE 3. It can be readily seen that the base line of FIGURE 3 of the application corresponds to a curve similar to FIGURE 4, but is slightly flattened due to a reduction in the vertical scale.

It should be noted that in the preceding discussion of FIGURE 3, molal vapor ratios have been used. As indicated in the example, when flask **10** is used as a batch reboiling flask the liquid composition is considerably different from the vapor concentration due to the different vapor pressures of the reactants. This fact of course must be taken into account when making up reaction charges. Our invention, however, also includes a continuous process using the same improved process.

When using a continuous process, flask **10** is simply used as a flash evaporator. The liquid fed to flask **10** is of the desired molal vapor concentration and is fed continuously and is totally evaporated. In this case, the liquid product from condenser **14** is simply conducted to a separate collection flask. In order to make the process completely continuous this collecting flask may be equipped with an efficient fractionating column which holds the phenylphosphonous dichloride in the flask and allows the low boiling material to return to the flask evaporator. It can easily be seen that the improved reaction rate caused by the presence of monochlorobenzene is present in either case.

The temperature range over which our reaction takes place is quite broad. We have indications that some reaction begins to take place as low as 350° C. We have also used temperatures as high as 890° C. without encountering excessive decomposition. Temperatures in this range are difficult to measure accurately and probably indicate the tube surface temperature rather than the temperature of the gases. However, it is thought that the reaction takes place primarily at the surface of the tube, consequently the actual reaction temperature is probably close to the actual tube temperature. Thus, the upper limit of the temperature range is more nearly dependent upon materials of construction than on the reaction mechanism. We have obtained our best results at temperatures in the range of 450° C. to 750° C.

The phenylphosphonous dichloride produced by our new process is a valuable chemical intermediate having many uses. It may be oxidized to benzenephosphorus oxydichloride in accordance with the process of U.S. Patent No. 2,482,810. This latter compound in turn may be used to make the plasticizers of U.S. Patent No. 2,471,483 and the resins of U.S. Patent No. 2,425,765. These resins in turn may be made into the copolymers of U.S. Patents Nos. 2,497,637; 2,453,167; 2,453,168; 2,583,810 and 2,586,885. Many other uses for this intermediate are well known in the art.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications will be obvious to those skilled in the art.

We claim:

1. A process for producing phenylphosphonous dichloride wich comprises reacting at at least about 350° C. an admixture of phosphorus trichloride and benzene in the presence of monochlorobenzene.

2. The process of claim 1 wherein the reaction temperature is about 450°–750° C.

3. A process for producing phenylphosphonous dichloride which comprises reacting a vapor mixture of phosphorus trichloride, benzene and monochlorobenzene, said monochlorobenzene being present in an amount of at least about 1 mole percent, at a temperature of at least about 350° C., and recovering phenylphosphonous dichloride from the reaction product.

4. The process of claim 3 wherein the vapor mixture contains at least about 2 mole percent monochlorobenzene.

5. The process of claim 3 wherein the reaction temperature is about 450°–750° C.

6. A process for producing phenylphosphonous dichloride, which comprises reacting phosphorus trichloride and benzene in a mole ratio of phosphorus trichloride to benzene of about 6:1 to 0.25:1 at temperatures of at least about 350° C. in the presence of monochlorobenzene.

7. A process for producing phenylphosphonous dichloride, which comprises reacting phosphorus trichloride and benzene in a mole ratio of about 6:1 to 0.25:1, respectively, at a temperature of at least about 350° C. in the presence of about 30–35 mole percent monochlorobenzene, and recovering phenylphosphonous dichloride from the reaction product.

8. A process for producing phenylphosphonous dichloride, which comprises reacting a vapor mixture of about 40 mole percent phosphorus trichloride and about 25–30 mole percent benzene in the presence of about 30–35 mole percent monochlorobenzene at a temperature of at least about 350° C., and recovering phenylphosphonous dichloride from the reaction product.

No references cited.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,029,282 April 10, 1962

Arthur Dock Fon Toy et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 11, for "nad" read -- and --; column 3, line 17, for "at" read -- as --; line 63, for "phenylphosphonour" read -- phenylphosphonous --; column 5, Table II, in the heading to the third column thereof, for "CtH_5PCl_2" read -- $C_6H_5PCl_2$ --; column 6, line 23, for "wich" read -- which --.

Signed and sealed this 14th day of August 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents