

Production of Red Phosphorus by a Continuous Process

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A continuous process for the production of red phosphorus developed in the laboratories of the Tennessee Valley Authority shortens the time required for processing white phosphorus to red phosphorus from days to hours over the commercial batch process. During the war a pilot plant embodying the continuous process was built and operated to produce red phosphorus of high purity for the War Department. In this process liquid white phosphorus is maintained at its boiling point in a reaction vessel with a retention period of 5 to 6 hours, which converts from 30 to 50% of it to solid red phos-

FOR several years the Tennessee Valley Authority has been conducting laboratory studies on the formation and behavior of red phosphorus (4, 10). This work resulted in the invention of a process (9) for the continuous production of red phosphorus from liquid white phosphorus. Consequently, when the War Department asked TVA in 1944 to supply several tons of high-grade red phosphorus for experimental use, a pilot plant embodying the continuous process was built and operated to meet the request.

While continuous processes for red phosphorus production have been proposed (14, 15) it appears that none had been put into use prior to the present work. Commercial production of red phosphorus is carried out at present by a batch process (8) that apparently has changed very little since it was introduced more than 50 years ago. White phosphorus is heated in a converter for 3 to 5 days at a temperature of 465° F. (241° C.) or higher. The material is then removed, ground under water, and boiled with alkali to remove unconverted white phosphorus. Because conversion is incomplete, removal of material from the converter, usually by chipping, must be done with care to avoid fires. A continuous process would appear to offer possibilities of reduced cost, greater safety, closer control, and a product of improved physical characteristics.

The present paper describes a pilot plant for the continuous production of about 20 pounds of red phosphorus per hour from liquid white phosphorus and discusses the development of the process and the results obtained in pilot plant operation. The process consists essentially of (1) heating white phosphorus at its boiling point (536° F., 280° C.) to convert it to a fluid mixture containing 30 to 50% red phosphorus, (2) removing the unconverted white phosphorus from the mixture by vaporization to

phorus. The resulting slurry overflows continuously into a heated screw conveyer in which it is carried counter-current to a stream of hot inert gas. The white phosphorus is vaporized and carried to a condenser, to be collected and recycled. Red phosphorus is discharged as the product in the form of fine particles whose size can be controlled to a considerable degree, and which do not require treatment with boiling caustic or grinding, as in the batch process. An additional advantage of the continuous process is its suitability for making a product of high purity, needed in certain military applications.

leave red phosphorus, and (3) condensing and recycling the vaporized phosphorus.

The material produced for the War Department (Frankford Arsenal) had to meet stringent specifications (12) for particle size, purity, and stability toward oxidation. To meet these requirements, the red phosphorus obtained by the process outlined above was subjected to a sequence of operations developed at Frankford Arsenal and described by Silverstein and co-workers (9), which involved batchwise leaching with boiling dilute sulfuric acid, followed by coating of the individual particles with precipitated aluminum hydroxide. The present paper deals only with the conversion process, but mention is made of the ways in which the pilot plant design and operation were influenced by the specialized requirements for the product.

LABORATORY STUDIES

In a recent paper (4) DeWitt and Skolnik reported results of a study by TVA of the rate of conversion of liquid white phosphorus to red phosphorus in the temperature range of 482° to 662° F. (250° to 350° C.). The conversion was found to be a first-order reaction, the rate at any time being proportional to the amount of unconverted white phosphorus. From Figure 1, which shows the degree of conversion as a function of time for several temperatures, as calculated from the rate data, it is seen that the time required for 50% conversion is about 6.5 hours at 536° F. (280° C.) and decreases rapidly with increasing temperature.

It was found that the reaction mixture remained fluid until 50% conversion was reached and that the red phosphorus was present in the form of suspended particles large enough to settle rather rapidly on standing. On further reaction the mixture rapidly became viscous, passed through a plastic or mudlike stage, and finally solidified. This apparently resulted from the growing together of the red phosphorus particles to form an inter-

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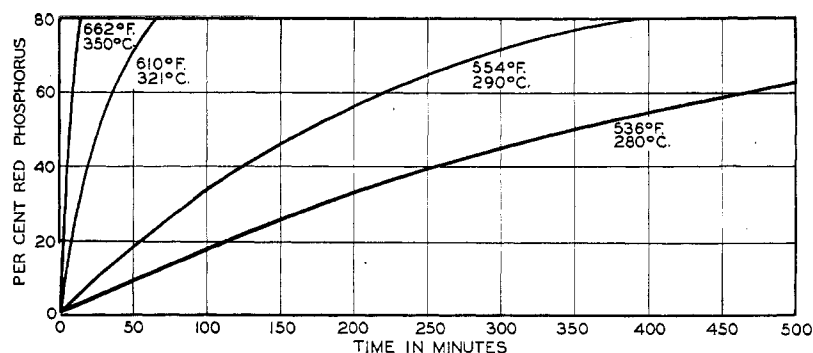


Figure 1. Conversion of Liquid White Phosphorus to Red Phosphorus without Catalyst

locking mass; calculations showed that with cubic packing of uniform spherical particles the spheres would touch at about 50% conversion.

The laboratory studies included exploration of methods of separating red and white phosphorus (unpublished results). The rapid settling of red phosphorus particles suggested the use of centrifuging for preliminary separation. However, this method was rejected when it was found that at a force of 2000 times gravity a maximum concentration of about 40% red phosphorus in the thickened phase was approached. Vacuum distillation was not satisfactory because of the difficulty of removing the last traces of white phosphorus. Samples of red phosphorus recovered by this method smoked or caught fire on exposure to the air. It was found that thorough sweeping with inert gas at temperatures above 392° F. (200° C.) effectively removed white phosphorus and resulted in stable red phosphorus. This operation was successfully carried out continuously by passing the mixture through a heated screw conveyor, made of glass, counter-current to a stream of heated nitrogen.

PILOT PLANT OPERATION

A diagrammatic flow sheet of the pilot plant is shown in Figure 2. The essential units were a reactor, a vaporizer, and a red phosphorus collecting system. Other equipment, of more or less standardized nature, included a white phosphorus feed system, an inert-gas heater, and a phosphorus condenser. Figure 3 is a photographic view of the plant, showing most of these units. Liquid white phosphorus was fed continuously to the reactor; a uniform mixture of liquid white phosphorus and solid red phosphorus particles overflowed continuously from the reactor into the lower end of the inclined screw conveyor-vaporizer. Hot carbon monoxide gas containing phosphorus vapor was discharged from this end of the vaporizer and passed to a water-spray condenser, in which liquid white phosphorus was collected for recycling to the feed tanks. Finely divided red phosphorus was discharged at the upper end of the vaporizer into a collecting system.

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REACTOR. The reactor was a stainless steel (Type 316, 10-gage) vessel with a cylindrical section 20 inches in inside diameter by 40 inches high with a 45° cone bottom and a bolted gastight cover. Molten white phosphorus was fed continuously into the reactor, at a point near the top, by displacement with hot water from steel drums immersed in hot water tanks. The flow rate of displacement water was measured with a calibrated rotameter. The total amount of phosphorus removed from each feed drum also was determined from initial and final readings of a float level indicator. The reactor was heated externally by Calrod units (10 kw. total) wrapped around the cone and the cylindrical section below the overflow level, and this portion of the reactor was insulated with 2 inches of magnesia. Figure 4 is a photograph of the reactor with the insulation removed showing the Calrod heating elements. Energy input was controlled by means of Transtats. The cover and the wall above the overflow level were cooled with water sprays. A vertical centrally located Lightnin stirrer with two 7.5-inch propeller blades, driven at 1140 r.p.m. by a 1-h.p. motor, extended well down into the cone. The stirrer shaft entered the cover through a water-cooled packing gland, in which a graphite-asbestos packing (Garlock No. 230 or John Crane No. 896) was used. At first this packing gland required frequent re-packing, but by lengthening it to 6 inches, satisfactory service was obtained. A slurry of red and white phos-

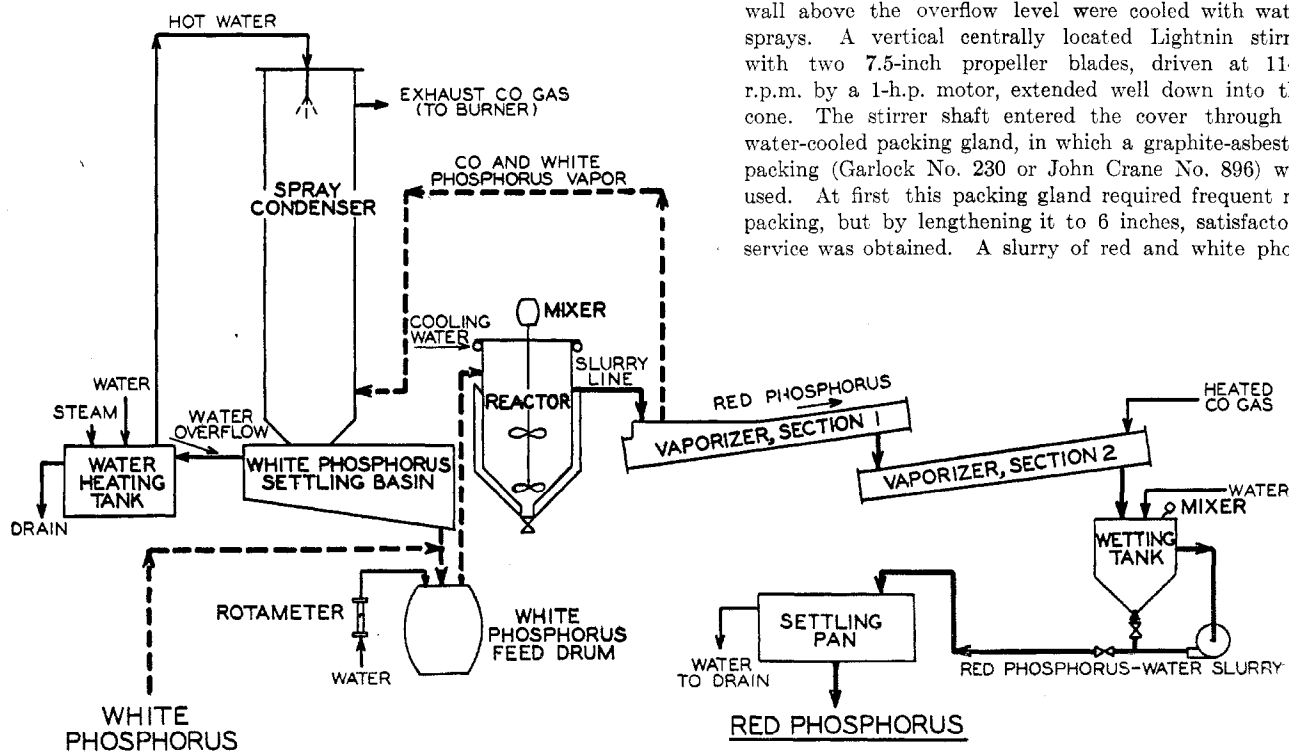


Figure 2. Flow Diagram of Pilot Plant for Continuous Production of Red Phosphorus

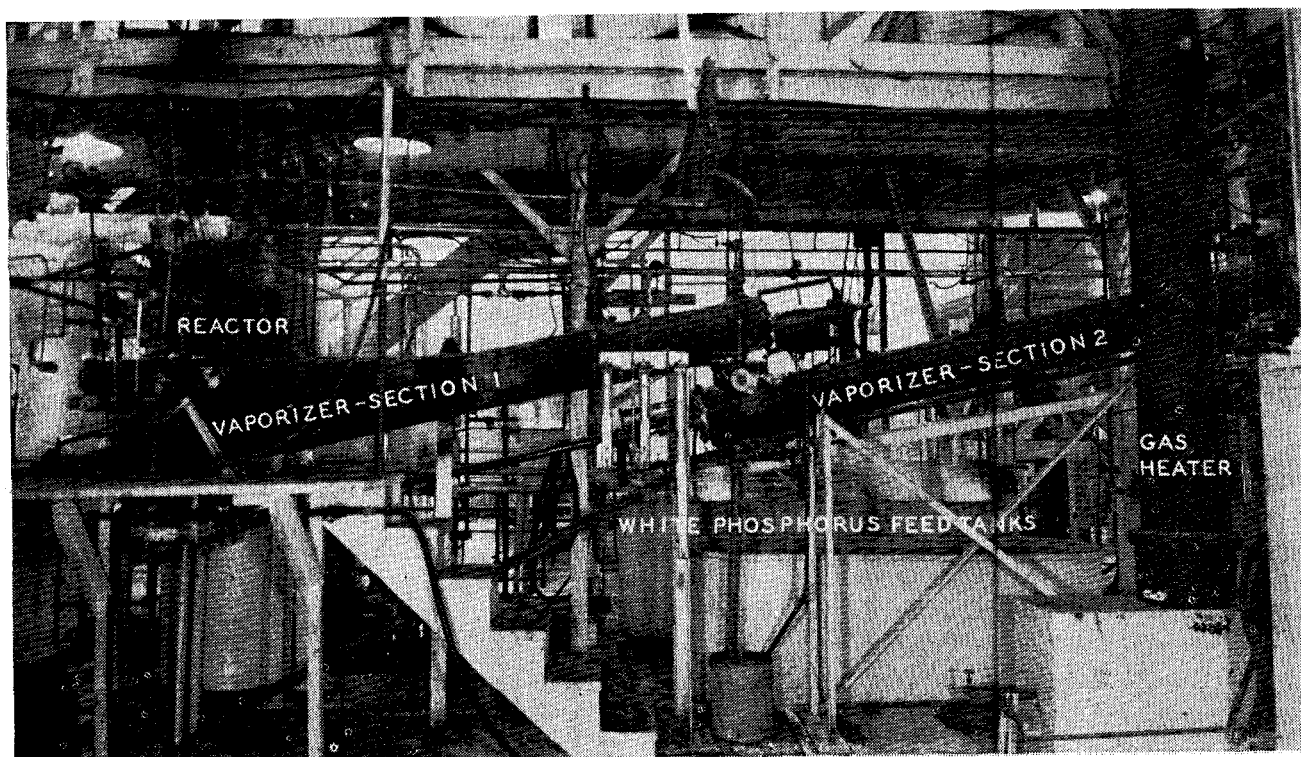


Figure 3. Red Phosphorus Pilot Plant

phorus overflowed continuously through a 2-inch line located 20 inches above the top of the cone. This line was equipped with 0.5-inch vertical and horizontal cleanout rods working through packing glands (see Figure 4), and by the occasional use of these rods, the overflow line was kept open without difficulty.

A sampling outlet for phosphorus slurry, equipped with cleanout rods, was provided in the side of the reactor. Temperatures were measured and recorded for four points on the reactor shell, two points in the slurry, and one in the vapor space, using iron-constantan thermocouples.

Calculations based on the dimensions of the reactor and the density of the phosphorus slurry indicated that the reactor should hold about 450 pounds of slurry up to the overflow. However, several measurements of the amount obtained by emptying the reactor completely after a period of steady-state operation indicated that it held only about 400 pounds of slurry. This difference is probably explained by the vortex created by the vigorous mechanical agitation, which was observed to be large in tests made with water. At a typical feed rate of 75 pounds per hour and a reactor charge of 400 pounds, the average retention time would be 5.33 hours (320 minutes), and at a temperature of 536° F. an average conversion of 47% of the white phosphorus to red phosphorus would be obtained (Figure 1).

No serious problems were encountered in the conversion step, and the performance agreed satisfactorily with the design data. The temperature remained slightly below the boiling point of 536° F.; it generally fell between 530° and 533° F. The difference did not seem to be caused by error in the thermocouple reading, since readings of 536° F. were sometimes obtained for short intervals. It seemed possible that, because of the vigorous agitation, surface evaporation of white phosphorus was sufficiently rapid to keep the reaction mixture from reaching the true boiling condition. The rate of heat input to the reactor required to hold the slurry at about 530° to 533° F. during continuous operation, at a feed rate of 115 pounds of white phosphorus per

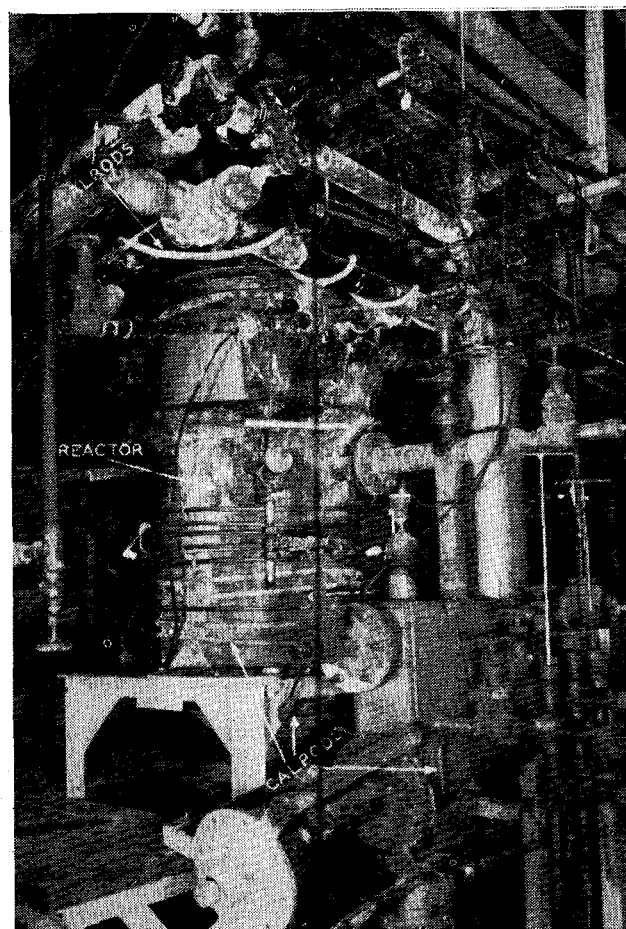


Figure 4. Reactor for Continuous Conversion of Liquid White Phosphorus to Red Phosphorus

Insulation removed to show Calrod heating elements. Feed end of vaporizer also shown

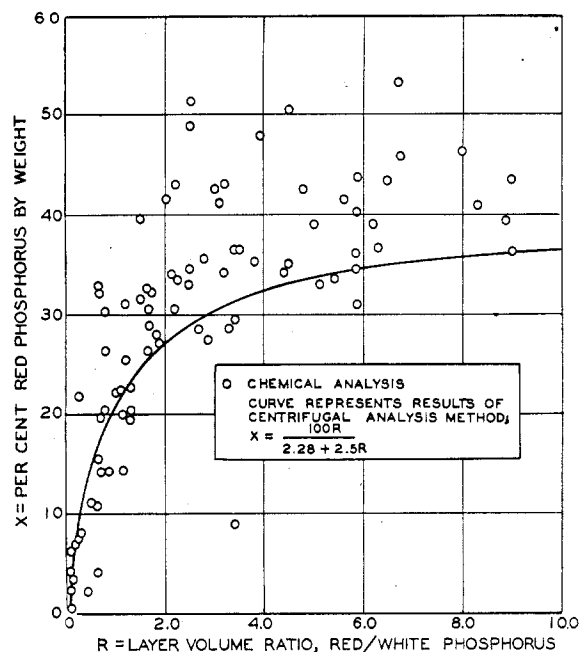


Figure 5. Red Phosphorus Content of Red Phosphorus-White Phosphorus Slurry

Centrifuging carried out at 2000 times gravity. Red phosphorus layer assumed to contain 60% white phosphorus by weight

hour, was about 330 watts. Increasing the heat input above this rate did not raise the temperature but only apparently increased the rate at which phosphorus was evaporated and refluxed, and sometimes a drop in the level of the phosphorus slurry below the overflow line was noticed when the heat input was high; this probably indicated that phosphorus vapor was being carried out of the reactor through the overflow line into the vaporizer because the evaporation rate had exceeded the condensing capacity in the refluxing section. The temperature in the vapor space of the reactor generally remained at about 140° F.

No tendency toward buildup of cake in the reactor was observed so long as vigorous agitation was maintained. However, the viscosity of the mixture evidently increased rapidly in the neighborhood of 40% red phosphorus concentration or above, so that a 0.5-h.p. stirrer motor originally installed sometimes became overheated and was therefore replaced by a 1-h.p. motor. On one or two occasions when the stirrer motor failed and no agitation could be provided for several hours, a hard cake built up, starting at the walls. This confirmed the behavior observed in exploratory tests made of a reactor of different design, in which the slurry was discharged from the bottom of the reactor and no agitation was provided; these tests invariably ended with a solid mass of red and white phosphorus in the reactor.

The degree of conversion obtained in the pilot plant reactor agreed well with predicted values based on Figure 1. Table I shows a comparison for a 200-hour period of continuous operation of the reactor during which the temperature of the slurry varied over a 15° range. While the actual concentration (40.1%) was substantially lower than the calculated value of 46.6%, closer agreement probably could not be expected in view of several uncertain factors, such as the size of the vortex. The agreement is in any case good enough to make the use of the theoretical data for design and control purposes satisfactory.

The red phosphorus content of the slurry, as reported in Table I, was determined by chemical analysis; however, for control purposes a rapid centrifugal method was used in which a small sample of the slurry, kept above the melting point of white

phosphorus, was centrifuged for 2 minutes at 2000 times gravity in a glass tube, and the respective heights of the red and white fractions were measured. From these measurements red phosphorus concentration was determined using the calibration chart shown in Figure 5; this chart is based on the empirical observation that, after centrifuging, the red phosphorus layer contained on the average 40% of red phosphorus by weight. Plotted also on the chart are a number of comparative values obtained by chemical analysis, and it is seen that the centrifugal results often deviated widely from the true value. However, the method proved adequate for control purposes.

It was difficult to maintain constant temperature when operating the reactor at temperatures substantially below boiling, such as 520° F., and since there was no particular advantage to such operation, this confirmed the desirability of operating as near the boiling point as possible.

VAPORIZER. From the reactor the slurry of red and white phosphorus overflowed continuously to a vaporizer in which it was heated and passed countercurrent to a stream of hot gas to remove the white phosphorus by evaporation. The vaporizer, which was made of stainless steel (Type 316 and Type 340), consisted of two sections of screw conveyer in series, each 10 feet 6 inches long by 6 inches in diameter (inside dimensions), with a slope of 1 to 5 (angle of inclination of 11° 20'). The screws were ribbons with a 6-inch pitch and were chain-driven from a countershaft driven by a 1.5-h.p. variable-speed drive (4.5 to 13.5 r.p.m.). The shells, made of 10-gage sheet, were externally heated by Calrod units (12 kw. on the first section; 8 kw. on the second section) controlled by Transtats and were insulated with 2 inches of magnesia. An enlargement was provided above the ribbon at the lower (feed) end of the first screw section (see Figure 4). Slurry entered continuously at this point through the 2-inch overflow line from the reactor. A considerable pool of slurry was maintained in the enlarged section. Sampling outlets were provided at three levels in the enlarged section of the vaporizer as a means of determining the approximate slurry level.

TABLE I. CONVERSION OF WHITE PHOSPHORUS TO RED PHOSPHORUS DURING CONTINUOUS OPERATION OF PILOT PLANT

Hours of continuous operation	200
Temperature, °F. ^a	
Average	533
Range	522-537
Feed rate, lb./hr.	
Average	68
Range	54-78
Retention time, min., average	353
Average conversion to red phosphorus, %	
Chemical analysis	40.1
Calculated from reaction rate data (4)	46.6

^a Temperature measurement for "reactor middle slurry."

Carbon monoxide gas (a by-product from operation of phosphate reduction electric furnaces, containing 88% carbon monoxide and about 1 mg. of phosphorus per liter) entered the discharge end of the second section of the vaporizer, flowed countercurrent to the phosphorus, and was discharged through an off-gas line near the slurry inlet. The gas was preheated to about 550° F. in a gas-fired tubular heater in which it passed through 28 feet of extra-heavy 0.5-inch pipe arranged in a hairpin; the heater was lined with a cylinder of 12-inch magnesia pipe insulation. The vaporizer off-gas line contained an initial 2-foot vertical section, 6 inches in diameter, to promote settling out of entrained phosphorus.

Temperatures were measured and recorded at a number of points along the vaporizer shell, in the vaporizer slurry, and in the vaporizer gas inlet and outlet, with iron-constantan thermocouples. Gas pressures at several points in the vaporizer, as well as in the condenser, the reactor, and the red phosphorus

collecting tank, were measured with mercury manometers. Most of the pressure lines could not be kept open very long at a time, but this proved to be of minor importance, since the maximum pressure in the system could be determined from the pressure required to introduce carbon monoxide gas into the gas heater.

The mixture of carbon monoxide and phosphorus vapor passed from the vaporizer to a condenser, which consisted of a steel cylinder 2 feet in diameter by 16 feet tall, into which hot water (130° F.) was sprayed at the rate of 10 gallons per minute. Condensed liquid white phosphorus was collected under water in a trough beneath the condenser and at intervals was drained into an empty feed drum. The stripped carbon monoxide leaving the condenser was burned.

Nearly all the white phosphorus was vaporized in the first section of the screw vaporizer, so that the product passing from the first unit to the second was red phosphorus in lump and powdered form. To ensure practically complete removal of the remaining white phosphorus in the second unit, three "breaker" plates (Figure 6), consisting of curved pieces fastened to the ribbon and having a clearance of $\frac{1}{16}$ to $\frac{1}{8}$ inch with the shell, were provided to break up the lumps. Samples of dry red phosphorus discharging from each section of the vaporizer could be taken with a thief operating through a packing gland and a quick-opening valve. Sight glasses also were provided at both of these points; however, their usefulness was limited by their tendency to become clouded over rather quickly.

The two critical factors of the vaporizer operation were the provision for breaking up the lumps and the control of the temperature. In initial tests without the breaker plates the red phosphorus delivered by the vaporizer contained a considerable proportion of lumps as large as 1 inch in size, which resulted from agglomeration of the fine particles (nearly all - 325 mesh) formed in the reactor. These lumps were friable but were inadequately free of white phosphorus; some burst into flame upon exposure to the air, while others were more stable but started to burn when they were crushed. It was not determined whether removal of white phosphorus from the lumps was limited by the rate of heat transfer into the lump or of diffusion of white phosphorus out of it, but it was apparent that the red phosphorus would have to be in finely divided form to obtain satisfactory removal of white phosphorus. The breaker plates provided a simple and effective means of breaking up the phosphorus agglomerates, and with their use no difficulty was experienced in ob-

taining a product essentially free of white phosphorus (less than 20 p.p.m.) and mainly broken up into its ultimate particles.

Tests made using breaker plates in the first vaporizer indicated that the plates acted as an obstruction for slurry reaching them, which eventually resulted in the accumulation of sufficient cake to plug the gas passage and cause a shutdown. Observation through the sight glass in the connecting pipe between the two vaporizer sections indicated that red phosphorus was no longer in the slurry condition when it reached this point. Indications were obtained that the slurry state generally did not extend very far up the first screw section, but in the absence of more specific information it was concluded that it was best to use no breaker plates in the first section. The use of breaker plates in only the second section proved satisfactory; however, further information on the optimum location of breaker plates is needed if the minimum size of the vaporizer is to be determined more closely than it was in the present work.

Several considerations determine the temperatures at which the vaporizer should be operated. Since the retention time of the slurry in the feed compartment of the vaporizer is appreciable (30 to 120 minutes), further formation of red phosphorus will take place there, and if this proceeds far enough, it will cause gelation. Occasional difficulty was caused by caking of red phosphorus on the wall of the slurry compartment, or by formation of hard lumps, which caused the screw to stall. Evaporation of white phosphorus from the slurry at this stage also contributes to increased concentration and to the danger of gelation and caking. It was found that this danger could be avoided by maintaining the slurry temperature at the feed compartment below 530° F. In other parts of the vaporizer higher temperatures were required to obtain the desired degree of removal of white phosphorus. It was not feasible in the pilot plant operation to determine the optimum temperature condition very closely; however, preliminary tests in a smaller unit consisting of a steel ribbon in a 2-inch glass cylinder indicated that it was necessary to heat the upper end of the vaporizer to at least 536° F. to reduce the white phosphorus content below 20 p.p.m. In these tests the superficial gas velocity was 0.75 foot per second (at 550° F.), and the retention time was about 12 minutes. The total retention time in the pilot plant vaporizer, excluding the feed compartment, was calculated to be 9 minutes, assuming no slippage. In the pilot plant vaporizer temperatures between 550° and 560° F. were satisfactory. There was some indication that optimum results might be obtained using somewhat different

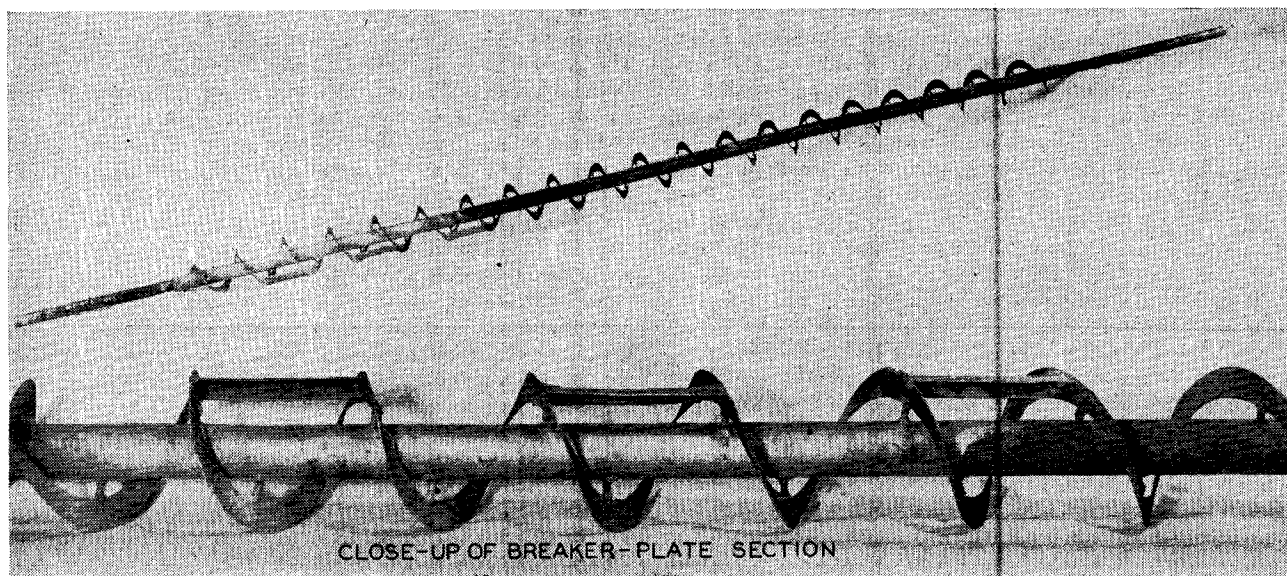


Figure 6. Screw Conveyor Used in Vaporizer Section 2

temperatures in the second screw section and in the upper part of the first, but this was not investigated.

If vaporizer shell temperatures were allowed to exceed 560° F. to any great extent, a decrease in the rate of production of red phosphorus was observed. This presumably resulted from the sublimation of some of the red phosphorus. Smits and Bokhorst (11) reported that the vapor pressure of red phosphorus increased from 50 mm. of mercury at 572° F. (300° C.) to 700 mm. at 752° F. (400° C.). These values may be too high, since Melville and Gray (6) using a different experimental procedure, obtained much lower values. While the pilot plant data were not such as to permit a close correlation between vaporizer temperature and decrease in production rate, it was fairly well established that 560° F. was a safe upper limit. It is also conceivable that sublimation occurring near the vaporizer discharge would increase the white phosphorus content of the product, and there was some evidence that this occurred.

Some difficulty was encountered through the entrainment of red phosphorus in the gas leaving the vaporizer. Such entrained red phosphorus gradually accumulated in the collecting basin of the phosphorus condenser and sometimes caused difficulty in draining the condensed white phosphorus from the condenser or in recycling the condensed phosphorus through the feed system to the reactor. Over extended periods of operation the red phosphorus content of the condensed white phosphorus amounted to about 1%, and in extreme cases it rose as high as 12%. The relation of red phosphorus entrainment to vaporizer operating conditions was not studied. Preliminary tests made in the small glass vaporizer mentioned above showed by direct observation that entrainment increased with gas velocity but was avoided if the velocity did not greatly exceed 0.75 foot per second (actual).

In the pilot plant a gas rate of 6 cubic feet per minute (S.T.P.) was generally used, which corresponded to a linear velocity of 1.0 foot per second (actual), and it appeared that most of the time entrainment was avoided but it did occur at irregular intervals. An attempt was made to obtain information on entrainment by inserting a section of Pyrex piping in the vapor line leading from the vaporizer to the condenser. This section failed rather quickly through mechanical strain, and its use was discontinued after several trials because of the hazard involved.

The limited observations indicated that with gas flows of 6 cubic feet per minute (S.T.P.), at an average operating temperature of 550° F., very little entrainment occurred during steady-state condition. The color of the phosphorus, which could be seen to condense in droplets and form rivulets, varied from slightly yellow to a light reddish orange; though occasionally surges of dark reddish-colored liquid phosphorus ran through the pipe at high velocity. It appeared that these surges were caused by sudden fluctuations in gas flow, caused in turn by fluctuations in pressure, and were independent of the nominal gas flow rate. It was concluded that the problem of entrainment should not be serious under the steady-state operation to be expected under nonexperimental conditions; however, to provide a solution to the problem of entrainment under the variable operating conditions of the pilot plant, the vapor line was heated electrically to a temperature above 900° F. in order to vaporize any entrained red phosphorus before it reached the condenser, and this procedure proved satisfactory.

A few tests were made in which the flow rate and temperature of the carbon monoxide entering the vaporizer were varied. These were not conclusive, but they indicated that a nonflammable product could not be obtained if the gas flow were eliminated completely and that flow rates above 4 cubic feet per minute (S.T.P.), equivalent to about 0.7 foot per second (actual) were probably desirable. On the other hand, stable red phosphorus was produced using an inlet gas temperature of 90° F.; this is not surprising, since the proportion of heat supplied by the heated gas for evaporation of white phosphorus was small compared with that supplied through the walls of the vaporizer.

While this indicated that gas preheating is not essential, it is probably beneficial.

Considerable work remains to be done to determine the effect of vaporizer temperature, gas flow rate and temperature, and retention time of red phosphorus in the vaporizer on the completeness of removal of white phosphorus. A limited study of these factors was included in the present investigation, but was handicapped by evident limitations in the analytical method used for determining white phosphorus in red phosphorus at the low concentrations involved (in the range of 0 to 100 p.p.m. of white phosphorus). Some attempt was made to correlate vaporizer conditions with stability of the red phosphorus as measured empirically by a modification of friction-firing test described by the Bureau of Mines (7); but these also proved unsuccessful, partly because the results of such tests were found to be influenced greatly by small amounts of moisture that were absorbed by samples of red phosphorus, even when they were kept in sealed bottles. There was little doubt that either the analytical method or the stability test could be developed sufficiently for the required purpose.

Originally it was planned to operate using nitrogen, recycled in a closed system, as the inert gas. However, in initial tests of such a system phosphine formed and accumulated in the recirculated gas, as evidenced by both the characteristic odor when gas leakage occurred and the mildly explosive behavior of the gas when allowed to escape to the atmosphere. While the literature contains little pertinent information of the conditions under which phosphine will form, it appeared likely that conditions for phosphine formation were favorable in the gas heater, since the gas recirculated from the phosphorus condenser to the heater was saturated with both water vapor and phosphorus vapor at about 130° F. It should be feasible to dry the gas at this stage and thus avoid phosphine formation or, if necessary, to provide a step in the cycle for the decomposition of phosphine, such as by contact with roasted iron pyrites (6), and the use of recycled gas would probably be desirable on a commercial scale. However, in view of the highly toxic character of phosphine and the lack of adequate methods for its quantitative determination in the gas, it proved expedient to use carbon monoxide in the pilot plant without recycling.

Some mechanical difficulty was at first encountered in the lower bearing of the first section of the vaporizer, which was generally below the slurry level. An inside bearing installed originally tended to freeze and stall the screw. This was corrected by placing the bearing, which was packed with Marfak grease, outside the packing gland. Similar difficulty was then encountered with the packing gland but was eliminated by making the gland a loose fit (approximately 0.0625 inch) and using a lantern ring for lubrication; the same type of packing was used in this packing gland as in the one for the reactor agitator.

Electrical heating of the vaporizer shells proved satisfactory, but it is probable that for commercial operation heating of both the reactor and vaporizer by means of gas or vapor would not only prove more economical but provide better temperature control. Division of the vaporizer into two sections had not only the mechanical advantage of shortening the length of the screw shaft on an individual drive, but the experimental advantage of making it convenient to obtain red phosphorus samples at an intermediate stage and to maintain different conditions in the two vaporizer sections. This arrangement is probably desirable in a commercial plant also.

RED PHOSPHORUS COLLECTOR. The collection of the red phosphorus, which was discharged from the vaporizer at a temperature above 500° F. and in a finely divided condition, presented both a technical problem and a hazard, since the red phosphorus was much more likely to be autoinflammable while hot. This was particularly true during the earlier stages of the investigation, when satisfactory control of the other steps of the process had not yet been established and the material discharged from

the vaporizer was therefore more variable in white phosphorus content and in stability. The presence of carbon monoxide naturally increased the hazard.

Two methods of collecting the red phosphorus were developed: the wet and the dry. The wet (under water) method was developed first and was used throughout most of the work. It had the advantages for the present work of being safer than the dry method, particularly during the more experimental stages, and of fitting in conveniently with the subsequent purification steps to which the red phosphorus was subjected, which were all carried out in an aqueous medium. It had the minor disadvantage that it was not convenient to measure accurately the weight of red phosphorus delivered from the vaporizer, except over relatively long periods. The dry collection method, apart from avoiding this latter shortcoming, has the obvious advantage from the viewpoint of commercial production that, where the red phosphorus is not to undergo further processing in a wet condition, the expense of dewatering and drying is avoided.

Wet System. Finely divided red phosphorus was discharged by gravity from the second screw through a 6-inch pipe into a cone-bottomed closed tank, 3 feet in diameter, almost completely filled with water (see Figure 2). A 0.25-h.p. Lightnin mixer kept the red phosphorus and water stirred into a uniform suspension. Fresh water was added continuously at a measured rate of about 65 gallons per hour, and red phosphorus-water slurry was removed through a side outlet by a centrifugal pump. Part of this slurry was recycled to the bottom of the collecting tank, serving as a means of additional agitation, while the remainder discharged into a rectangular settling pan 5 by 4 feet by 20 inches deep, where the red phosphorus settled out and the water overflowed to the drain. Less than 1% of the red phosphorus was lost in the overflow water, and this consisted of extremely fine, light-colored material, the removal of which was observed to improve the stability of the final product. The red phosphorus was dried in 1.5-inch layers in a vacuum dryer at 150° F. for 12 to 24 hours.

This system of collection, developed by successive trials of several similar arrangements, proved very satisfactory. Originally a water-jacketed screw conveyor 3 inches in diameter by 4 feet in length was installed between the vaporizer discharge and the collecting basin. This was removed after tests indicated that it gave no particular advantage and tended to aggravate the undesirable effects of pressure fluctuations in the system. However, the cooling screw was tried and abandoned before the wet collector had been developed to a completely satisfactory state so that the tests of its usefulness were probably inconclusive. General experience with collectors indicated that the volume of the gas space should be kept as small as possible to minimize the undesirable effects caused by the sudden increases in pressure which occurred occasionally in the vaporizer and caused phosphorus vapors to diffuse back into the red phosphorus collector. Minor difficulties were caused by hard, red, glassy lumps of material of undetermined origin that were infrequently discharged from the vaporizer and caused stoppages in the red phosphorus collector discharge line or pump.

Dry System. The dry collecting system was developed after several trials and consisted of a double-bell hopper, shown diagrammatically in Figure 7. Red phosphorus discharged directly from the vaporizer into the upper chamber of the hopper. The collector was operated on an hourly cycle, so that material was collected in the upper chamber over a 1-hour period before being discharged to the lower chamber, where it cooled for an hour, and was then discharged into a loosely covered stainless steel can. Both sections were closed by conical valves, which were controlled from an operating floor above the vaporizer through long shafts, one inside the other. The operation of the valves is evident from Figure 7. A small stream of nitrogen gas (less than 1 cubic foot per minute) was bled continuously into

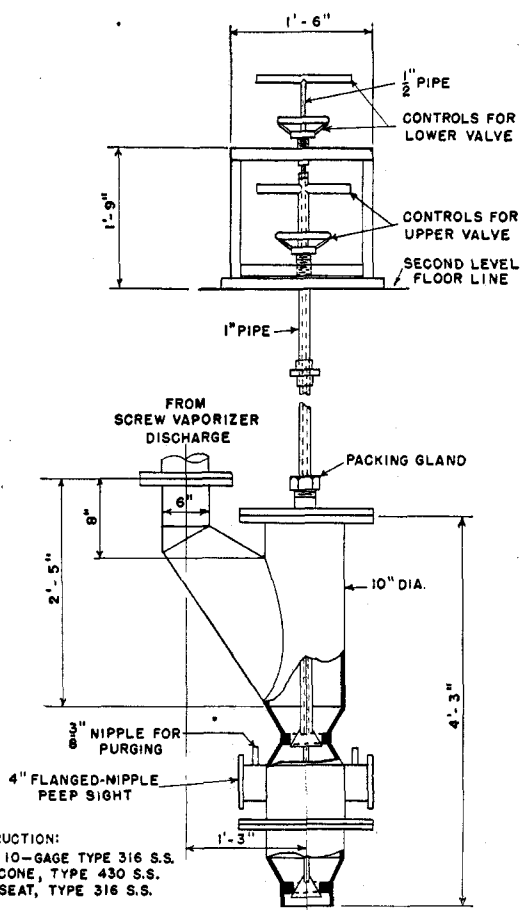


Figure 7. Double-Bell Dry Red Phosphorus Collector

the lower chamber of the hopper to maintain an outward flow of inert gas whenever either valve was opened.

The principal problem encountered in developing the dry collector was that of maintaining satisfactory valve operation. Slow leakage of air through the valves resulted in mild explosions. Originally both the valve cones and seats were made of Type 316 stainless steel and could not be kept gastight. A good seal was obtained by covering the valves with lead, but the covering wore out too rapidly to be practical. Successful operation was obtained by using Type 430 stainless steel valve cones, working against seats of Type 316 stainless steel. This use of dissimilar metals gave a satisfactory seal. In a test of this final arrangement, which was limited to 30 hours by extraneous circumstances, red phosphorus was discharged at hourly intervals with no sign of explosion or burning.

Continuous Operation. Following short periods of preliminary operation, during which the equipment modifications described above were developed, the pilot plant was operated continuously for 17 days. The shiftwise variation in the principal operating conditions for this period are shown in Figure 8. Much of the variation in plotted values for the rate of red phosphorus production and the rate of white phosphorus condensation is caused by limitations in the methods of measuring these values on a shiftwise basis. The average white phosphorus feed rate was 65 pounds per hour. Red phosphorus was produced at an average rate of 16 pounds per hour; the shift average varied from 10 to 20 pounds per hour. The reactor temperature remained fairly constant at about 533° F. The red phosphorus concentration in the reactor slurry fluctuated considerably and reached values slightly above 50%, but no evidence of caking was encountered. The gas flow rate was held at 4 cubic feet

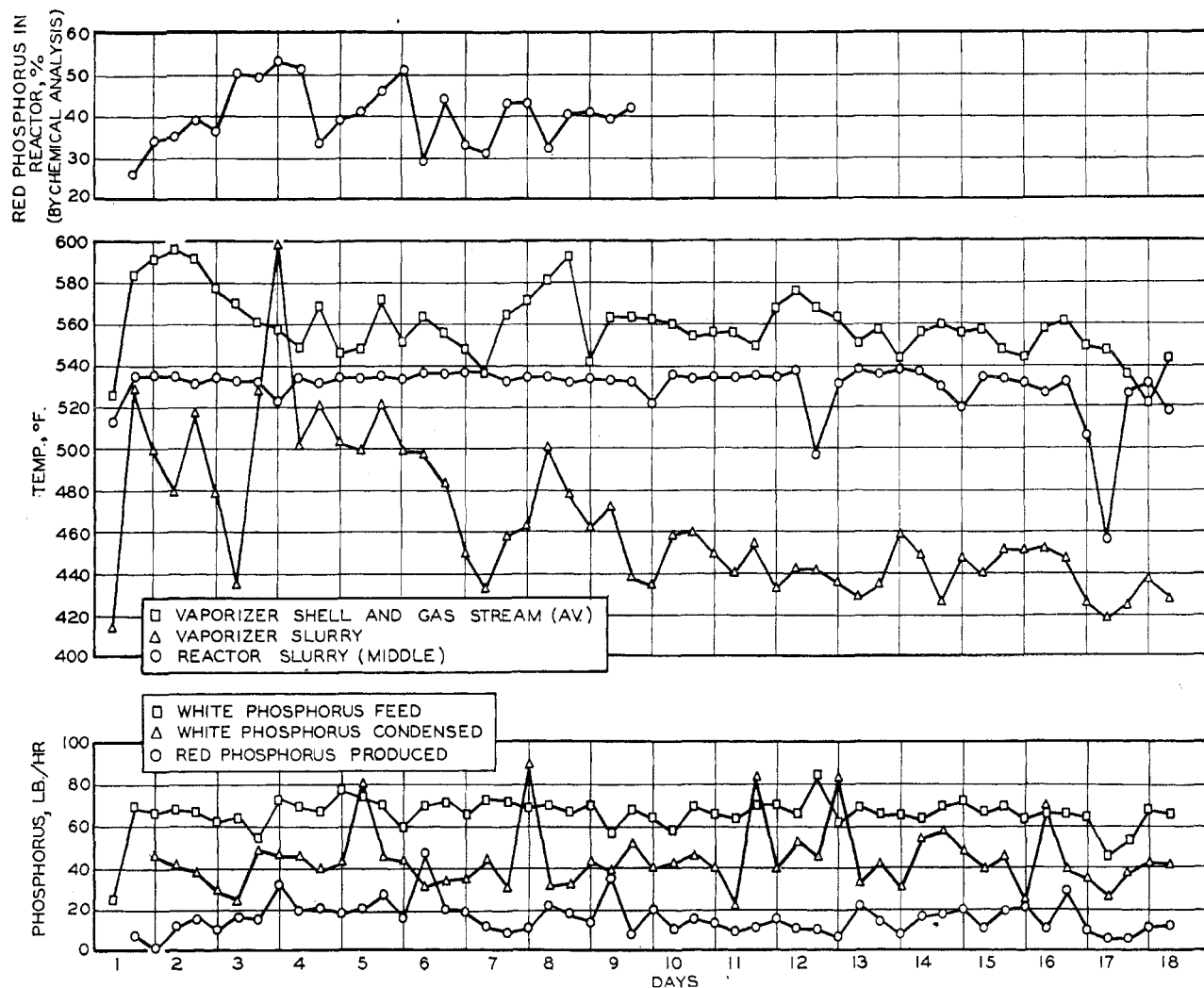


Figure 8. Shiftwise Variation of Operating Conditions during Continuous Operation

per minute (S.T.P.) throughout the run, which was equivalent to a superficial velocity of 0.7 foot per second (operating temperature). The vaporizer temperature was kept at about 560° F. most of the time but sometimes reached higher values for short periods. Operation was uninterrupted, and no serious difficulties were encountered. Some red phosphorus was entrained and was removed from the collecting basin of the condenser at the end of the run as a slurry of red and white phosphorus.

PURITY OF RED PHOSPHORUS

The chief established uses for red phosphorus are in the match industry, fireworks, and military pyrotechnics. While the specifications for red phosphorus used in the match industry were not ascertained, it is probable that the red phosphorus produced for this purpose meets Army-Navy Specification JAN-P-211 (13). This requires only that the total phosphorus content exceed 99.0%, the white phosphorus content be less than 0.02% (200 p.p.m.), the moisture content be less than 0.20%, and 98.0% pass a 100-mesh screen. The red phosphorus produced in the present work was subsequently processed to meet the more stringent specifications of Frankford Arsenal (12) for stabilized red phosphorus. In particular, these required that the iron and copper contents should not exceed 20 and 15 p.p.m., respectively. [These were tentative specifications; the specifications as finally issued (12) stated that the individual iron and

copper contents should not exceed 50 p.p.m. and that their product should not exceed 125.] The sulfuric acid treatment included in the purifying and stabilizing operations (9) to which the pilot plant product was subjected removed some of the iron impurity, but it was not practicable to remove any of the copper. It therefore was essential that the pilot plant product contain less than 15 p.p.m. of copper, and it was highly desirable that it contain less than 20 p.p.m. of iron. Rapid photometric methods used for the determination of iron and copper in red phosphorus at these low concentrations, with a precision of 2 p.p.m. for either component, were described recently by Brabson and co-workers (1).

The measures taken to obtain this purity, apart from care and cleanliness in the operation, were the elimination of copper, brass, and mild steel as materials of construction in the production and handling equipment and the use of white phosphorus of adequate purity. Fortunately, it was found that by exercising reasonable care an ample supply of selected white phosphorus containing not more than 20 p.p.m. of iron (15 p.p.m. average) and 5 p.p.m. of copper could be obtained directly from the electric-furnace phosphorus plant.

Figure 9 gives a shiftwise plot for the 17-day pilot plant run of the iron and copper contents of the white phosphorus feed and red phosphorus product. When due allowance is made for the holdup in the system, the correspondence between the copper contents of the white phosphorus and red phosphorus is rather

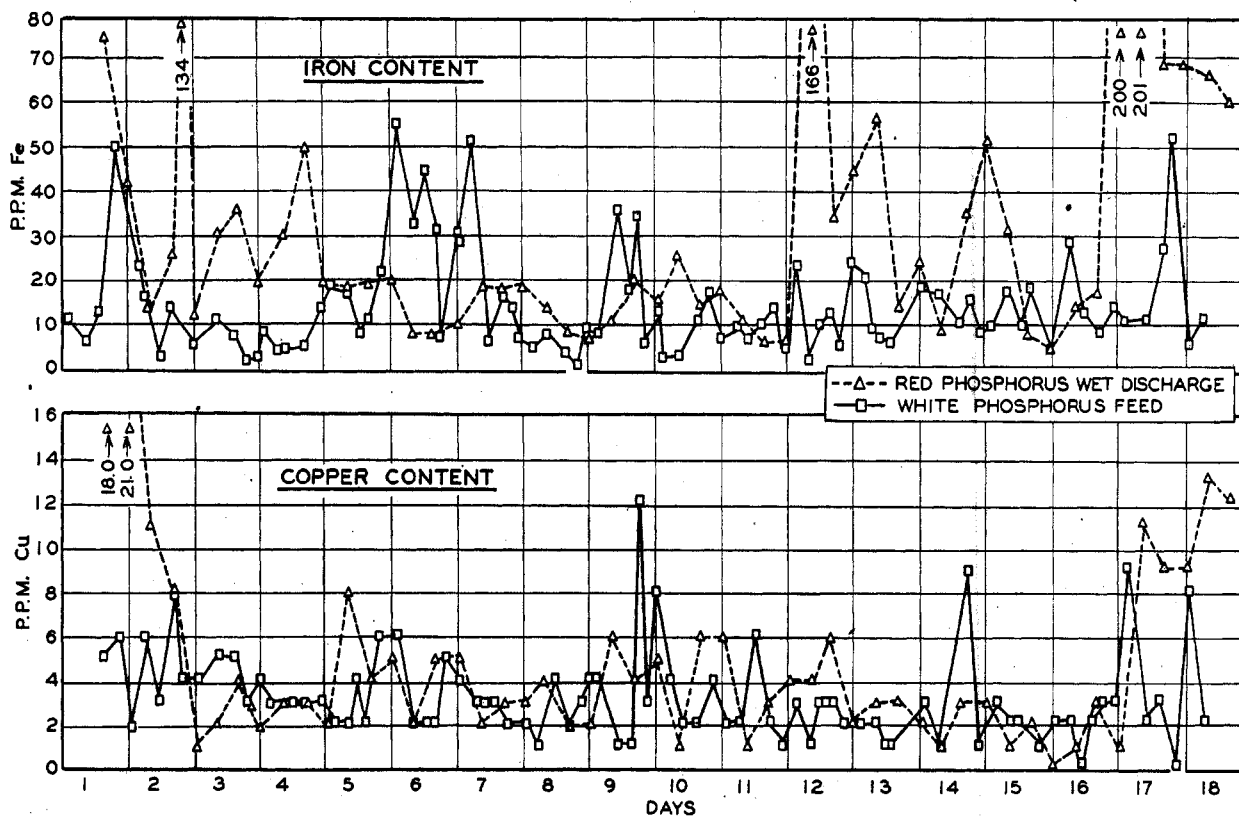


Figure 9. Iron and Copper Contents of White Phosphorus Feed and Red Phosphorus Product during Continuous Operation

good throughout the run. The comparison reveals a considerable increase in the iron content of the red phosphorus over that of the white phosphorus during much of the period. It was fairly well established that much of this contamination occurred when water accidentally got into the system, presumably reacting with phosphorus and causing corrosion; it was definitely observed that water got into the reactor (through the water-displacement phosphorus feed system) just before the sharp increase in iron content that occurred during the last 2 days of the run.

For 7 consecutive days (January 8 through 14) the product as made consistently met the specifications for iron and copper. In this period a total of 3000 pounds of red phosphorus with a weighted average analysis of 14.0 p.p.m. of iron and 3.9 p.p.m. of copper was obtained. It is believed that these results establish the feasibility of producing directly, in stainless steel equipment, red phosphorus meeting the purity requirements for stabilized red phosphorus.

Samples of dry red phosphorus taken from the vaporizer discharge frequently contained somewhat more iron than the wet product. It has been suggested that some of this iron was in the form of surface contamination, resulting from the evaporation of white phosphorus and from equipment erosion, and that this was readily removed by the water in the collecting system. Analysis of a single sample of water overflowing from the red phosphorus settling pan showed 2 p.p.m. of iron and 92 p.p.m. of phosphorus pentoxide. The tap water contained 0.05 p.p.m. of iron (and 0.01 p.p.m. of copper). These figures are of the right order of magnitude to account for the difference in iron content between the dry and wet phosphorus, and the phosphorus pentoxide content of the overflow water would account for its dissolving action. A decrease in copper content between the dry and wet red phosphorus was also observed, although its magnitude was less than for iron.

The pilot plant was operated for a short preliminary period using a vaporizer and wet product collector made of plain steel.

The red phosphorus removed from the wet collecting system generally contained several hundred parts per million of iron. However, four samples removed in the dry condition from the vaporizer discharge ranged in iron content from 34 to 176 p.p.m. Since this equipment was not operated long enough to establish steady-state conditions, these results are considered to indicate that there is some possibility of producing red phosphorus containing less than 20 p.p.m. using mild steel for the equipment not exposed to water; the possibility would improve with increase in the scale of operation.

Analysis of the red phosphorus during continuous operation indicated that the white phosphorus content was less than 90 p.p.m. (0.0090%) for all but three shifts and generally ran below 20 p.p.m. Detailed results are not reported here because the reliability of the analytical method, an adaptation of the standard benzene-extraction method (2), is questionable at such low white phosphorus concentrations. Occasionally, a batch of red phosphorus started to burn while being screened or being transferred from one container to another. There was no indication this behavior was related either to the white phosphorus content or to any other measured chemical or physical properties. (This statement is not meant to apply to cases of gross contamination with white phosphorus, in the order of 0.1% or more, in which cases the material smoked and generally caught fire during drying.) Spontaneous combustion of commercial red phosphorus is a frequent occurrence, particularly when shipping containers are opened.

PARTICLE SIZE OF RED PHOSPHORUS

Previous studies in the TVA laboratory, reported by Skolnik, Tarbutton, and Bergman (10), showed that the particle size of red phosphorus produced by the continuous process was a function of the degree of conversion of white phosphorus in the reactor. A comparison is made in Figure 10 between the particle size of the

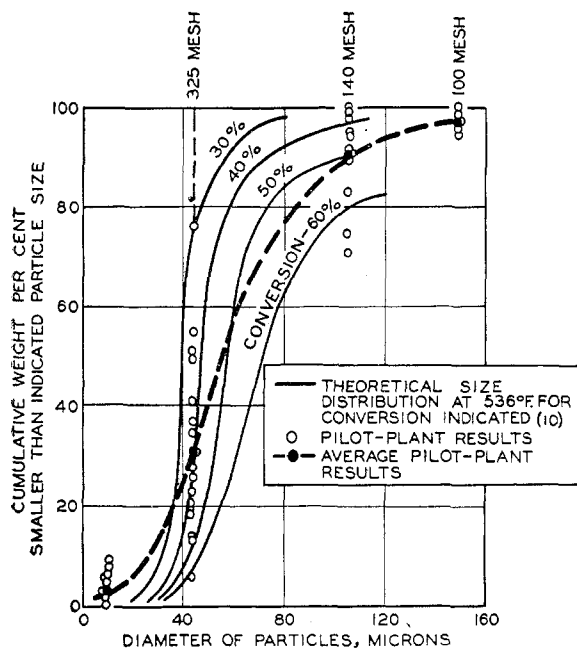


Figure 10. Particle-Size Distribution of Red Phosphorus Produced by Conversion of White Phosphorus

pilot plant product and the data obtained in the laboratory studies. Each set of points represents a batch of about 280 pounds of red phosphorus, and data are given for all the 21 batches for which data are available. Accurate information—by chemical analysis—on the concentration of red phosphorus in the reactor was obtained only for the first 7 days of operation (see Figure 8); during this time it varied considerably but averaged about 40%. The average value for the -325-mesh fraction in the pilot plant red phosphorus falls close to the theoretical curve for 40% conversion, as does the average value for the -100-mesh fraction. However, the value for the -140-mesh fraction falls close to the curve for 50% conversion. The average content of -10-micron particles is higher than predicted; however, the accuracy of the sedimentation method (12) used to determine the -10-micron fraction has been found to be low in this range. (The other particle sizes were determined by standard wet screen analysis.)

The following tabulation compares the average values for the pilot plant red phosphorus as produced with those called for by the Frankford Arsenal specifications (12).

U. S. Standard Sieve No.	Cumulative Per Cent Through	
	TVA product	Specifications
100	97	98.0 minimum
140	91	85.0 minimum
325	31	60(±15)
-10 micron	3	1 maximum

The average pilot plant product was somewhat coarser than that specified, principally in the deficiency of -325-mesh particles. However, after screening out, crushing, and reblending a small amount of oversize material and removing a small amount of fines by simple water decantation, most of the batches were made to meet the specifications. From Figure 10 it is seen that operation at slightly higher than 30% conversion should give a product meeting all these requirements. In recent operation at lower average conversion a finer product has been obtained.

CONCLUSIONS

The work described in this paper demonstrated on a substantial scale the feasibility of a continuous process for producing red phosphorus from liquid white phosphorus and the suitability of the type of equipment used in the pilot plant for a large plant.

Although further work is needed to define more closely the optimum operating conditions, in particular for the vaporizing operation, the following conditions give satisfactory operation. The reactor is operated at the boiling temperature (536° F.) and at a red phosphorus concentration of 30 to 40%; the vaporizer temperature is kept below 530° F. in the feed compartment to avoid gelation of the slurry and below 560° F. in the remainder of the vaporizer to avoid sublimation. Some mechanical provision in the vaporizer, such as the breaker plates used in the present work, is essential for breaking up the red phosphorus agglomerates. Heated inert gas should be circulated through the vaporizer at an actual linear velocity not exceeding 1 foot per second; both carbon monoxide and nitrogen are satisfactory for this purpose. The gas probably could be recycled if provision were made for freeing it of moisture and phosphine during each cycle. The product can be collected either in water or in the dry condition; in either case the stability of the dry product is comparable, and there is some indication that it is superior, to that of commercial red phosphorus.

The continuous process has particular advantages for the production of stabilized red phosphorus (to meet Army Specification 50-11-137), use of which appears to be growing. By carrying the conversion of white phosphorus to about 30% in the reactor, a product is obtained that meets the particle-size specifications directly or with very little adjustment, whereas the commercial process requires grinding of the product followed by separation of a substantial proportion of fines. By the exercise of suitable and feasible precautions to avoid contamination, a product containing less than 20 p.p.m. of iron and 5 p.p.m. of copper is obtained by the continuous process, making an acid treatment to remove iron unnecessary. On the other hand, analysis of eight samples of red phosphorus obtained from six different suppliers showed iron contents ranging from 100 to 300 p.p.m. and copper contents ranging from 5 to 20 p.p.m.

Because of the lack of information on the commercial method for red phosphorus manufacture, it has not been feasible to make a cost comparison between the two processes. However, it appears that the production cost would be substantially less for the continuous process, since this process should require less labor, smaller equipment, no grinding, and no treatment with caustic to remove white phosphorus, and it can also dispense with drying.

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