SUBMERGED COMBUSTION APPARATUS FOR THE CONCENTRATION OF PHOSPHORIC ACIDS

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ABSTRACT OF THE DISCLOSURE

In the concentration of wet process phosphoric acid containing metal salts and other impurities, apparatus is provided for discharging combustion gases through a vertical and cylindrical dip pipe which extends downwardly into a frusto-conical chamber and is centered therein to bring about uniform flow of the combustion gases over the phosphoric acid and upwardly in the chamber. The chamber has a flat bottom aligned with the bottom of the dip pipe and has walls extending upwardly and outwardly at a continuous constant angle from the flat bottom and above the lower end of the dip pipe, the interrelationship of the dip pipe having at the lower end thereof a cross-sectional area less than that of the chamber bottom and terminating in a lower edge which is parallel and spaced from the bottom and on all sides thereof is equi-distant from the inclined walls.

This application is a continuation of my copending application Ser. No. 354,737, filed Mar. 25, 1964, now Patent No. 3,279,526.

This invention relates to the concentration of phosphoric acids, and more particularly to the concentration of wet process phosphoric acids containing metal salts and other impurities.

The maintenance of a uniform selected temperature for the production of a desired concentrated phosphoric acid from a wet process phosphoric acid feedstock has been found to be very important. Submerged heating through the use of hot gaseous products of combustion provides an efficient means for heating the feed acid, but, unfortunately, in the dehydration of wet process phosphoric acid, which may contain from 1 to 15 percent of impurities, such as metal salts, etc., there is a tendency for deposits to form in the dip pipe through which the combustion gases are introduced into the body of the liquid, and this results in a reduction in cross-sectional area and a back pressure which restrict the flow of combustion gases to the evaporator. The decrease of cross-sectional area increases the velocity of gases and therefore increases the pressure drop and restricts the flow of combustion gases to the evaporator. Further, there are conditions present in the operation which tend to dissolve the deposits, and as a result of the build-up and dissolution of the deposits, the back pressure may vary through wide limits, for example, between 4 to 30 inches water column, and extreme variations can result in flame failure at the burner.

I have discovered that by increasing the velocity of the gas within the dip pipe, it is possible to depress the top surface of the liquid pool so as to maintain it out of contact with the dip pipe, while at the same time withdrawing concentrated acid product from the top side area of the pool, and such procedure satisfactorily overcomes the problem of back pressure fluctuations heretofore experienced and enables one to maintain a uniform selected temperature for the acid pool. Further, the increase in velocity to the extent of maintaining the dip pipe out of contact with the liquid pool has other advantages in that the lower average retention time of the acid within the pool is made possible and a product lower in metaphosphate salts is obtained. Other advantages will appear as the specification proceeds.

A primary object, therefore, of the present invention is to provide a method and means for overcoming the problem of back pressure fluctuations while maintaining uniform selected temperatures in the dehydration zone.

A further object is to provide a method of dehydration in which a stream of combustion gases having a cross-section less than that of the pool of acids being dehydrated is impinged upon an area of the pool for depressing or dishing the surface of the pool so as to maintain the gas discharge pipe out of contact with the pool. Yet another object is to provide a method for the concentration of wet process phosphoric acid for the preparation of an improved uniform product. Other objects will appear as the specification proceeds.

The invention may be practiced in an illustrative embodiment, as shown by the accompanying drawing, in which—

FIGURE 1 is a side view in elevation, and partly in section, of apparatus in which the invention may be carried out; and FIG. 2, a broken, greatly enlarged, sectional view of a portion of the apparatus shown in FIG. 1.

In one embodiment of my invention, wet process phosphoric acid is supplied to an evaporator to provide a pool therein, and the acid pool is maintained at a desired temperature by gas heating, the gaseous products of combustion being directed onto the surface of the acid pool and at a velocity which depresses the central portion of the pool body. The pool temperature is maintained preferably by regulating the feed rate of fresh acid into the pool. The acid starting material may be any wet process phosphoric acid, such as, for example, the ordinary wet process phosphoric acid of commerce. Such acid may have a metal salt content of 1 to 15 percent, the usual range of such metal impurities being between 5 and 10 percent. For supplying heat to the process, I may provide a stream of hot gases resulting from the combustion of air and fuel, such as propane or other gaseous or liquid fuels. The combustion gases are preferably diluted with air to provide a final temperature of the gases entering the dehydration chamber of about 1500° to 1900° F.

As a specific illustration and referring more particularly to FIG. 1 of the drawings, phosphoric acid preferably of the range 27 to 64 weight percent phosphorus calculated as P₂O₅ equivalent is pumped from feed tank 10 through pipe 11a to evaporator 11, forming a pool in the frustoconical portion of the evaporator 11. The hot gases are directed through the dip pipe 12 to the lower portion of the reaction chamber. Here the gases at high velocity engage the liquid acids in the pool at the bottom of the evaporator, depressing the level of the liquid, as indicated best by the numeral 13 in FIG. 2. The moisture-laden gases which disengage from the acid in the space above the evaporator bottom are removed by duct 14 to the separator 15. Entrained acid droplets removed in the separator 15 are returned through duct 15a to the receiver 16. The gases continue to the floating bed scrubber 17, where condensable and water-soluble pollutants are removed.

The temperature of the liquid acids within the reaction chamber is maintained at a substantially constant value by a control circuit. The filled bulb 18 communicates with the pneumatic transmitter 19 through conduit 19a, and the pressure transmitter 19 communicates through conduit 19b with a recorder-controller 20 which is pre-set to the desired temperature and which pneumatically operates through conduit 20a the diaphragm.
control valve 21 in the feed acid line 10. In operation, the filled bulb 18 senses the acid temperature and records the same by means of transmitter 19 with recorder-controller 20 which is preset to the desired temperature, the signal from the bulb to the transmitter being by pressure through the gas-filled conduit 19a. The recorder-controller in operation adjusts the diaphragm control valve 21 so as to increase or decrease the amount of feed as required to maintain the acid at predetermined temperature. The effect of this system is to decrease the feed rate with increasing water content of the feed acid, and to increase the feed rate when the water content of the acid decreases.

The dehydrated acid product is removed from the evaporator 11 through liquid overflow line 22, which is preferably cooled by water jacket 22a to the receiving tank 16 which is provided with a cooling jacket 16a. From the receiver 16, the product is passed by pump 23 to the product tank 24.

A fuel gas, such as propane, is passed from fuel tank 25 through conduit 26 controlled by valve 27 to the vortex burner 28 where it is mixed with air (preferably an excess of air) from blower 29. Combustion takes place within the chamber 30, and the combustion gases are delivered through the dip pipe 12 as hereinafter described.

If desired, control elements, such as are shown in my copending application Ser. No. 265,200, filed Mar. 14, 1963, may be employed for maintaining a substantially constant rate of fuel gas input. Such control apparatus, however, need not be employed because of the advantages flowing from the increased velocities of the pipe 12 as will be hereinafter described.

The overflow pipe 22 is located at a point on the evaporator which is generally in line with the elevated outer portion of the liquid pool, as shown best in FIG. 2. In the submerged heating operations hereinafter employed and as described in my application Ser. No. 265,200, the dip pipe extends below the level of the acid pool and the products of combustion are discharged into the body of the pool. I have found that by increasing the normal velocities hereinafter employed in such submerged heating by from 10 to 15 percent, the pool liquid is blown away from contact with the bottom of the discharge pipe 12 so that the pipe is no longer submerged, thus eliminating variations in back pressure. If desired, the velocities may be increased to a greater extent, but best results are obtained where the velocity increase is in the range of about 10 to 15 percent. By maintaining the surface of the pool in the dished or concave form illustrated best in FIG. 2, I find that not only is very effective heating brought about, but also vaporization takes place readily, with some entrainment of liquid particles and with some return to the liquid body so that the reaction of dehydration takes place readily.

To provide for the quick removal of the dehydrated acids from the reaction zone, the rate of introduction of feed acids should be related to the volume of the acids within the reaction zone so that the acids will be passed through the reaction chamber in a certain minimum time. I find it desirable to use a feed acid rate in volume per minute which is at least 1/2g, and preferably at least 1/2g, of the volume of the liquid within the reaction chamber.

Best results have been obtained when the volume of the liquid fed per minute is at least 1/2g of the liquid volume within the reaction chamber. I recommend that the ratio between the volume of feed acid per minute and volume of liquid within the reaction zone be from 1/2g to 1/2g. From the foregoing, it will be seen that with a contemplated feed rate of 4 gallons of wet process phosphoric acid per minute, the reaction chamber should be designed so as to contain from 8 to 48 gallons of acids which will provide an average retention time of the acids within the reaction chamber of 2 to 12 minutes. By way of illustration, in the structure shown in FIG. 2, a volume of 10 gallons is provided by the frusto-conical bottom portion of the evaporator in which the cone is 10 inches high, with a diameter of 23 inches at the top of the cone, and with the liquid draw-off pipe 22 at a point 10 inches above the flat bottom of the evaporator.

The pool temperatures may range from 400° to 750° F., or higher, if desired. The temperature obtained by the liquid acids through contact with the hot gaseous products of combustion should preferably be the boiling point of the acid in the desired product composition which has the lowest boiling point.

In the above illustrative design shown in FIG. 1, the median pool cross-sectional area (226.9 sq. in.) bears with the cross-sectional area of the dip pipe 12 (23.8 sq. in.) the ratio of 8 to 1. The median pool cross-sectional area is indicated in FIG. 2 by the line M-M. I prefer that the median pool cross-sectional area should have a ratio to the cross-sectional area of the dip pipe of at least 5.5 to 1. In any event, the ratio should be such as to permit combustion gas velocity rates which are sufficiently high to depress the central area of the acid pool, as illustrated in FIG. 2, so as to maintain the pool level out of direct contact with the bottom portion of the pipe 12.

There are critical proportions which make the difference between the liquid being pressed away from the bottom of the dip pipe and the dip pipe being submerged. Considering the cross-sectional annular area between the bottom of the dip pipe and the adjacent nearest point of the evaporator 11, I find that the ratio of the dip pipe velocity to this annulus cross-section should be about 7.1 feet per minute as the velocity to the area of the cross-section in square inches.

For example, with a dip pipe velocity of 1414 feet per minute and with the annulus cross-sectional area of 200 square inches, the ratio may be determined as follows:

\[
\text{Ratio} = \frac{1414 \text{ ft./min.}}{200 \text{ in.}^2} = 7.1 \text{ ft./min./in.}^2.
\]

The ratio may also be expressed in terms of cubic feet per hour velocity to the area of annulus in square inches as follows:

\[
\text{Ratio} = \frac{121940}{200} = 606 \text{ ft.}^3/\text{hr./in.}^2.
\]

The values expressed in these two ratios are those which bring out the condition of displacing the liquid from the bottom of the dip pipe.

If these rates of gas flow are decreased by the order of 10 to 15 percent, no longer will the liquid be removed from the bottom of the dip pipe and the operation will revert to submerged dip pipe conditions. If the gas input or velocity is raised above 10 to 15 percent, successful results can be obtained, but the efficiency of the operation will be decreased. From the above, it will be seen that for effective operation, the ratio in the first equation should be at least about 6.5 and in the second equation above should be at least 93. Variations of 2 to 3 percent of the value of these two ratios may also be expected with changes in feed composition, the percent of SO₃ in the feed, and also with the desired product composition as to P₂O₅ concentration.

While I have in the foregoing description referred to a specific type of apparatus having specific proportions, it will be understood that the operation can be expected to give the results in which the top level of the acid pool is dished and the pool is spaced from the bottom of
the pipe, while at the same time liquid product can be withdrawn at a level above the bottom of the pipe, and this condition can be observed in various ways, as, for example, by watching the temperature of the thermocouple which will indicate the condition where the dip pipe is no longer submerged and where the hot gases passing under the free end of the pipe directly contact the thermocouple.

The invention may be illustrated by the following specific example:

**Example 1**

In a 10-gallon dehydrator as described in the foregoing specification, 54 percent wet process phosphoric acid feed was introduced into the chamber at a feed rate of 1.6 gallons per minute. With total air of 20,140 s.c.f.h., consisting of secondary air of 8520 s.c.f.h., primary air of 11,620 s.c.f.h., and propane gas 450 s.c.f.h., the dip pipe gas velocity was 1414 feet per minute. The acid pool was maintained at a temperature of about 690°F. The average retention time in the evaporator was about 8 minutes. The product withdrawal rate was about 0.9 gallon per minute. The temperature of the effluent liquid product was about 640°F, and was collected in the product receiver, the temperature of which was maintained at about 450°F. The moisture-laden gases, which disengaged in the space above the acid pool, were at about 765°F, and were removed through a duct to the cyclone separator, as shown in the drawing. Product acid in excess of 1 percent was recovered in the cyclone, and this was returned to the product receiver. Such a product had a P₂O₅ content of 81.7. In comparison with the feed acid which contained 0.54 percent H₂O insolubles, the cyclone acid had only 0.35 percent H₂O insolubles. The product from the cyclone had only 0.2 percent Al₂O₃ and only 0.26 percent Fe₂O₃ as compared with 1.19 percent Al₂O₃ and 1.23 percent Fe₂O₃ in the feed acid. Further, the liquid product which was recovered in the draw-off line had a P₂O₅ content of 81.05, but contained a greater amount of Al₂O₃, Fe₂O₃ and H₂O insolubles than did the product recovered from the cyclone.

From the foregoing, if it is desired to recover a product high in P₂O₅ and with a greatly reduced amount of metal and other impurities, it is advantageous to recover more of the acid product from the cyclone separator and less of the product through the draw-off. If there is no objection to the amount of the impurities in the liquid product, the process can be operated for the recovery of the product mainly through the liquid draw-off line.

While in the foregoing specification I have set forth specific structure and specific process steps in considerable detail for the purpose of illustrating my invention, it will be understood that such detail or details may be varied widely by those skilled in the art without departing from the spirit of my invention.

I claim:

1. Apparatus for concentrating wet process phosphoric acid, comprising a closed evaporator vessel, aperture at its top to receive a dip pipe, a vertically extending cylindrical dip pipe extending sealingly through said aperture and into the lower portion of said vessel, a combustion chamber for supplying combustion gases to the upper end of said dip pipe, vapor and gas outlet means in the upper portion of said vessel, means for feeding phosphoric acid into said vessel, and means in the lower portion of said vessel for withdrawing liquid product, said vessel in its lower portion providing a chamber in the shape of an inverted cone provided with a flat bottom and inclined walls extending upwardly and outwardly at a continuous constant angle from said flat bottom and to above the lower end of said dip pipe, the interior passage of said dip pipe having at the lower end thereof a cross-sectional area less than that of said chamber bottom and terminating in a lower edge which is parallel with and spaced from said bottom, said lower edge being circular and equi-distant on all sides from said inclined walls.

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