Oct. 18, 1966 W. R. MUSTIAN, JR 3,279,526

CONCENTRATION OF PHOSPHORIC ACIDS

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FIG. 1

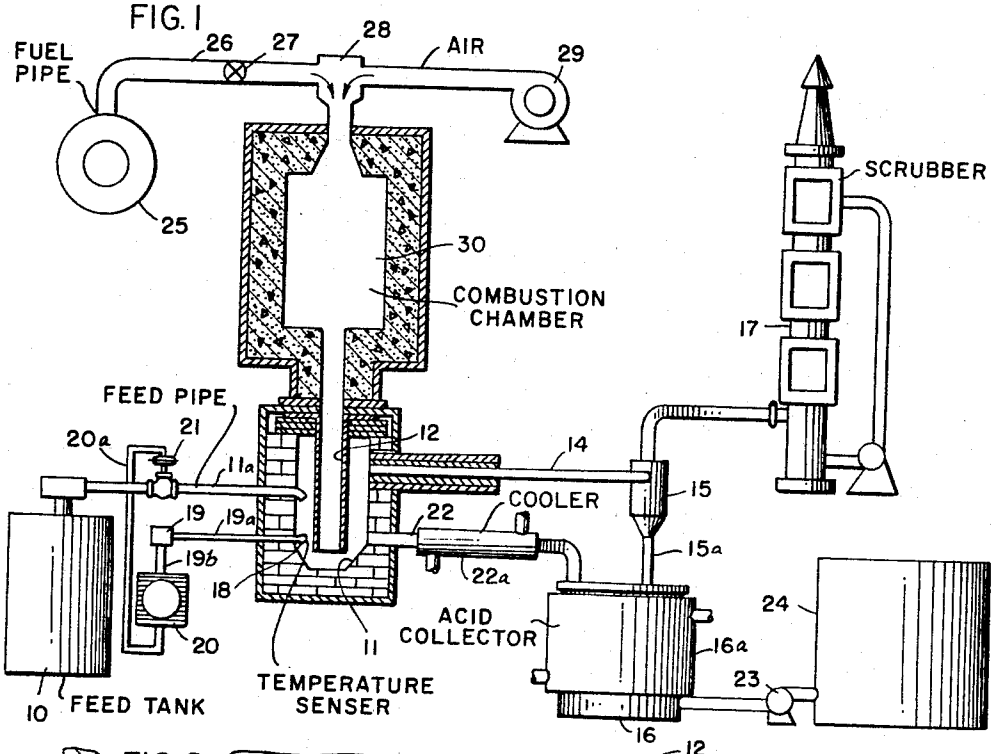
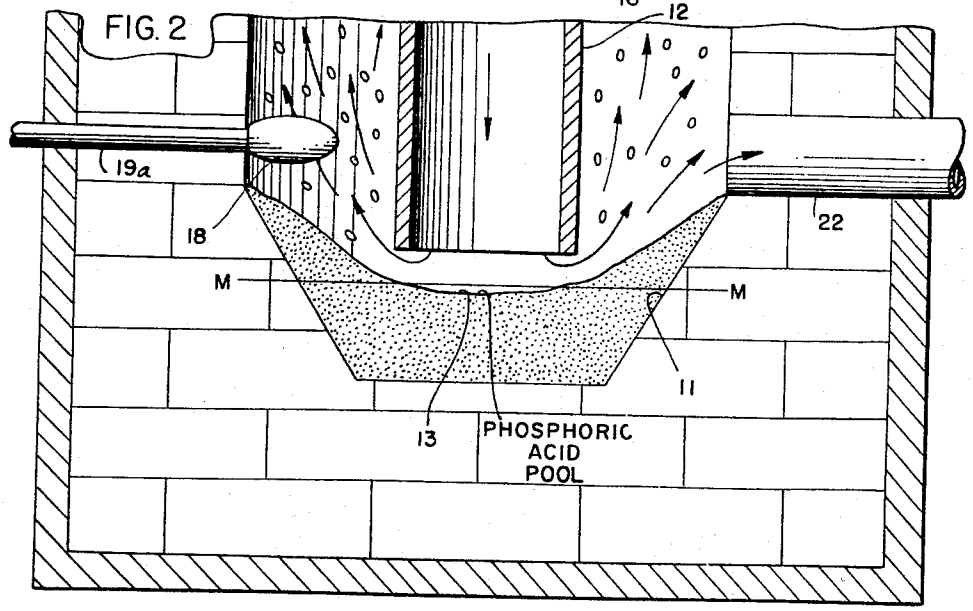


FIG. 2



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CONCENTRATION OF PHOSPHORIC ACIDS

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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 feed stock 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 restricts 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 of 27 to 64 weight percent phosphorus calculated as P_2O_5 equivalent is pumped from feed tank **10** through pipe **11***a* to evaporator **11**, forming a pool in the frusto-conical 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 **15***a* 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 **19***a*, and the pressure transmitter **19** communicates similarly through conduit **19***b* with a recorder-controller **20** which is pre-set to the desired temperature and which pneumatically operates through conduit **20***a* the diaphragm control valve **21** in the feed acid line **10***a*. 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 **19***a*. 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 **22***a* to the receiving tank **16** which is provided with a cooling jacket **16***a*. 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 heretofore described. If desired, control elements, such as are shown in my copending application Serial No. 265,200, filed March 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** which serve to space the bottom end of the pipe from the liquid acid level.

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 heretofore employed and as described in my application Serial 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 heretofore 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 increases 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 dehydration 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 $\frac{1}{15}$, and preferably at least $\frac{1}{12}$, 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 $\frac{1}{8}$ of the liquid volume within the reaction chamber. I recommend that the ratio between the volume per minute of feed and volume of liquid within the reaction zone be from $\frac{1}{2}$ to $\frac{1}{12}$. 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** (28.3 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 bear a ratio to the cross-section 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 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-section area of 200 square inches, the ratio may be determined as follows:

$$\text{Ratio}\frac{\text{Dip pipe velocity (ft./min.)}}{\text{Annulus cross-section (in.}^2\text{)}}=\frac{1414\text{ ft./min.}}{200\text{ in.}^2}$$

$$=7.1\text{ ft./min./in.}^2$$

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

$$\text{Ratio}\frac{\text{Comb. gas volume (s.c.f.h.)}}{\text{Annulus cross-section (in.}^2\text{)}}=\frac{21{,}240}{200}$$

$$=106\text{ ft.}^3\text{/hr./in.}^2$$

The values expresesd 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 about 96. Variations of 2 to 3 percent of the values of these two ratios may also be expected with changes in feed composition, the percent of SO_3 in the feed, and also with the desired product composition as to P_2O_5 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 carried out in different forms of apparatus having quite different proportions, the velocities of the combustion gases being adjusted to give the result 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 conditon 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 **12** directly contact the thermocouple **18**.

The invention may be illustrated by the following specific example:

Example I

In a 10-gallon dehydrator as described in the foregoing specification, 54 percent wet process phosphoric acid feed was introduced into the chamber **11** 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 cylone separator **15**, 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 P_2O_5 content of 81.7. In comparison with the feed acid which contained 0.54 percent H_2O insolubles, the cyclone acid had only 0.35 percent H_2O insolubles. The product from the cyclone had only 0.2 percent Al_2O_3 and only 0.26 percent Fe_2O_3 as compared with 1.19 percent Al_2O_3 and 1.23 percent Fe_2O_3 in the feed acid. Further, the liquid product which was recovered in the draw-off line **22** had a P_2O_5 content of 81.05, but contained a greater amount of Al_2O_3, Fe_2O_3 and H_2O insolubles than did the product rcovered from the cyclone **15**.

From the foregoing, if it is desired to recover a product high in P_2O_5 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 **15** and less of the product through the draw-off **22**. 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 **22**.

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. In a process in which wet process phosphoric acid is concentrated in an evaporator chamber by heating a body of said acid through contact with hot combustion gases, the steps of directing said hot combustion gases downwardly in a generally vertical dip pipe which normally at zero gas velocity extends below the acid level and discharging said gases from the bottom of the dip pipe upon said wet process phosphoric acid at a velocity to press the top surface of said acid body away from the bottom of said dip pipe, and withdrawing concentrated acid product from the chamber, the velocity in feet per minute of the combustion gases in said pipe bearing a ratio to the annulus cross-sectional area in square inches between the bottom of the dip pipe and the nearest point of the evaporator chamber of in excess of 6.5.

2. The process of claim 1 in which said ratio is in excess of 7.1.

3. In a process in which wet process phosphoric acid is concentrated in an evaporator chamber by heating a body of said acid through contact with hot combustion gases, the steps of directing said hot combustion gases downwardly in a generally vertical dip pipe which normally at zero gas velocity extends below the acid level and discharging said gases from the bottom of the dip pipe upon said wet phosphoric acid at a velocity to press the top surface of said acid body away from the bottom of said dip pipe, and withdrawing concentrated acid product from the chamber, the combustion gas volumetric rate in cubic feet per hour bearing a ratio to the annulus cross-sectional area in square inches between the bottom of the dip pipe and the nearest point of the evaporator chamber of in excess of 96.

4. The process of claim **3** in which said ratio is in excess of 106.

5. In a process in which wet process phosphoric acid is concentrated in an evaporator chamber by heating a body of said acid through contact with hot combustion gases, the steps of directing said hot combustion gases downwardly in a generally vertical dip pipe which normally at zero gas velocity extends below the acid level and discharging said gases from the bottom of the dip pipe upon said wet process phosphoric acid at a velocity to press the surface of said acid body away from the bottom of said dip pipe, and withdrawing concentrated acid product from the chamber, the velocity in feet per minute of the combustion gases in said pipe bearing a ratio to the annulus cross-sectional area in square inches between the bottom of the dip pipe and the nearest point of the evaporator chamber of in excess of 7.1 and the combustion gas volumetric rate in cubic feet per hour bearing a ratio to the annulus cross-sectional area in square inches between the bottom of the dip pipe and the nearest point of the evaporator chamber of in excess of 106.

6. In a process in which wet process phosphoric acid is concentrated in an evaporator chamber by heating a pool of said acid through contact with hot combustion gases, the steps of directing said hot combustion gases downwardly in a generally vertical dip pipe which normally at zero gas velocity extends below the acid level and discharging said gases from the bottom of said dip pipe upon said wet process phosphoric acid at a velocity to press the top surface of said acid pool away from the bottom of said dip pipe, the median pool cross-sectional area bearing a ratio to the cross-sectional area of the dip pipe of at least 5.5 to 1, and withdrawing concentrated acid product from the chamber.

7. In a process in which wet process phosphoric acid is concentrated in an evaportion chamber by directing hot combustion gases downwardly in a generally vertical dip pipe and discharging the gases from the bottom of the dip pipe upon said wet process phosphoric acid, the steps of feeding liquid wet process phosphoric acids into said chamber, withdrawing liquid concentrated acid product from said chamber while maintaining within said chamber a body of liquid acid which at zero gas velocity would submerge the bottom of said dip pipe, discharging combustion gases from the bottom of said dip pipe and through the area of the annulus between the bottom of said dip pipe and the closest points on said chamber at a velocity which is increased to the point that under the conditions of the process the gases press the top surface of said body of liquid acids into dish-shaped form and laterally away from the bottom of said pipe and pass freely between the top surface of said liquid and the lowermost edges of said dip pipe, passing said gases along with liquid particles from said acid body upwardly into the space within said chamber above said acid body, and returning liquid particles disengaged from said gases to said body.

8. In a process in which wet process phosphoric acid is concentrated in an evaporator chamber by directing hot combustion gases downwardly in a generally vertical dip pipe and discharging the gases from the bottom of the dip pipe upon said acid, the steps of feeding liquid wet process phosphoric acids into said chamber, withdrawing liquid concentrated acid product from said chamber while maintaining within said chamber a body of liquid acids which at zero gas velocity would submerge the bottom of said dip pipe, passing combustion gases from the bottom of said dip pipe and through the area of the annulus between the bottom of said dip pipe and the nearest points of said chamber at a velocity to press the top surface of said liquid body below the bottom edges of said dip pipe while directing displaced portions of said acid body away from the bottom edge of said dip pipe along an inclined path upwardly and outwardly through contact of said gases with said liquid body.

9. In a process in which wet process phosphoric acid is concentrated in an evaporator chamber by directing hot combustion gases downwardly in a generally vertical dip pipe and discharging the gases from the bottom of the dip pipe upon said wet process phosphoric acid, the steps

of feeding wet process phosphoric acid to be concentrated into said chamber and withdrawing concentrated acid from said chamber, said feeding and withdrawal rates being such that at zero gas velocity the acid body would submerge the bottom of said dip pipe, discharging said combustion gases from said dip pipe at a velocity which is increased to press the top surface of said acid body into a generally smooth dish-shaped surface out of contact with said dip pipe, thus providing a free and open gas passage around said dip pipe bottom, and withdrawing concentrated acid product from said chamber.

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