

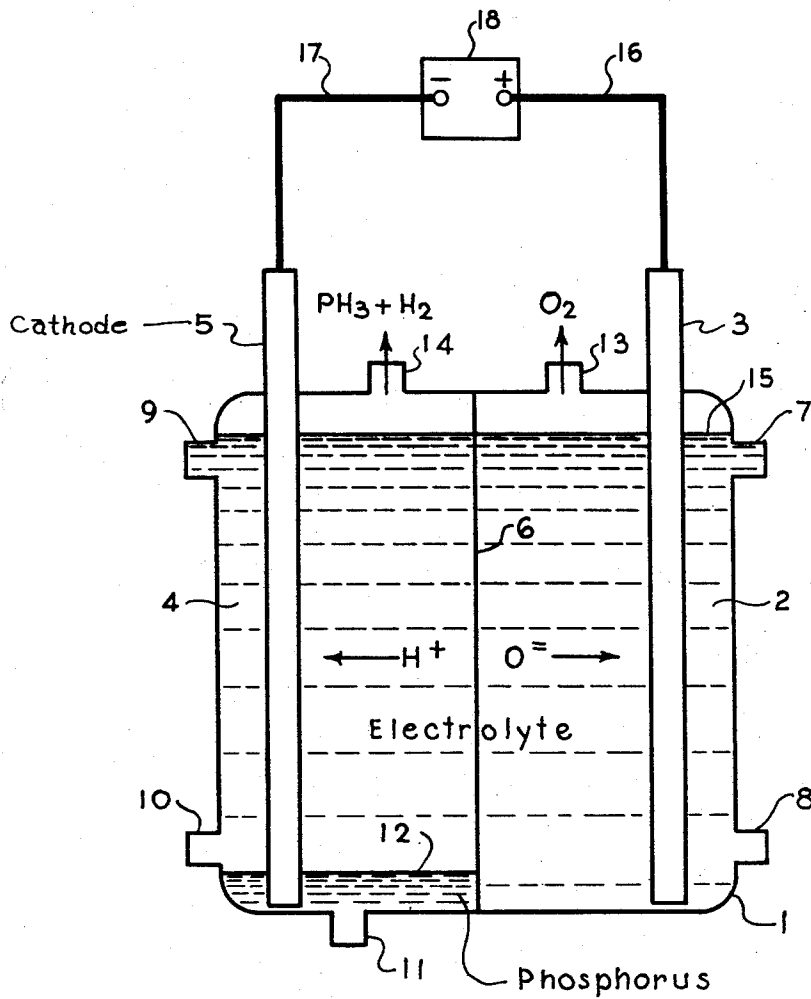
Nov. 5, 1963

G. T. MILLER ET AL

3,109,788

ELECTROLYTIC PRODUCTION OF PHOSPHINE

Filed July 27, 1960



1

3,109,788

ELECTROLYTIC PRODUCTION OF PHOSPHINE
George T. Miller, Lewiston, N.Y., and John Steingart,
St. Catharines, Ontario, Canada, assignors to Hooker
Chemical Corporation, Niagara Falls, N. Y., a corpo-
ration of New York

Filed July 27, 1960, Ser. No. 45,653

16 Claims. (Cl. 204-101)

This invention relates to the production of phosphine from molten phosphorus by electrolysis.

Numerous processes have been developed for the preparation of phosphine. For example, phosphine has been prepared by the reaction of metallic phosphides or phosphonium halides with water, and by the hydrolysis of elemental phosphorus. These techniques have various disadvantages, including low yield of phosphine, high contamination of the phosphine product and high production costs.

It is an object of this invention to provide a method for the production of phosphine from molten phosphorus by electrolysis.

Still another object of the invention is to provide a more economical method of preparing phosphine.

A further object of the invention is to provide a method of preparing phosphine in a form substantially free from phosphorus hydrides and other phosphorus impurities.

These and other objects of the invention will be apparent from the following detailed description of the invention.

It has now been discovered that when a solid vertical metallic surface is contacted with a pool of molten phosphorus, a thin layer of molten phosphorus forms on the metallic surface above the level of the molten phosphorus pool and contiguous with the molten phosphorus pool. Furthermore, when a vertical metal cathode is contacted with a pool of molten phosphorus in the cathode section of an electrolytic cell, in the presence of an aqueous electrolyte, and an electric current is caused to flow between the cathode and anode of the electrolytic cell, a phosphine-containing gas is produced in the cathode section in high yield and purity of phosphine.

The terms "wicking" and "wicking up" are used throughout the description and appended claims to describe the phenomenon in which molten phosphorus in contact with the lower portion of a vertical metallic surface rises above the level of the molten phosphorus pool and forms a thin layer on the metallic surface. The maximum height to which the phosphorus will climb up the vertical metallic surface is not known. When the lower portion of a porous lead sheet was contacted with a pool of molten phosphorus, the height of the thin phosphorus layer adhering to the surface of the porous lead was about twenty-two inches, and it appears that heights as high as five feet may be obtainable. While we do not wish to be limited by theory, it is believed that the wicking action is caused by surface tension effects.

The accompanying drawing is a schematic illustration of a suitable electrolytic cell for carrying out the novel process.

Referring to the drawing, there is shown a cell vessel 1, having an anode compartment 2, containing an anode 3, and a cathode compartment 4, containing a cathode 5. A porous diaphragm 6, separates the anode compartment 2 and the cathode compartment 4. Ports 7 and 8 permit the addition and removal of anolyte from the anode section 2. Ports 9 and 10 permit the addition and removal of catholyte from the cathode section 4. Port 11 permits the addition and removal of molten phosphorus from cathode section 4. Sufficient molten yellow phosphorus 12, is added to the cathode compartment 4, to contact the lower edge of cathode 5, thereby permitting wicking up

2

of the molten phosphorus onto the outer surface of the cathode. Anolyte gas discharge port 13 is provided in the top of the anode section to remove anolyte gas from the electrolytic cell. Catholyte discharge port 14 is provided in the top of cathode section 4 to remove catholyte gas.

The level of the anolyte and catholyte in the electrolytic cell is indicated as interface 15.

Anode electrical connector 16 and cathode electrical connector 17, are connected to the anode and cathode and to the positive and negative poles, respectively, of a source of direct current 18.

If desired, a heating source such as a constant temperature bath (not shown in the drawing), may be employed to maintain the catholyte and anolyte at the desired temperature.

Cell vessel 10 may be constructed of any material capable of resisting corrosion by the electrolyte and other materials employed in the cell. Typical examples of suitable materials of construction for cell vessel 10 include glass, glazed ceramics, tantalum, titanium, hard rubber, polyethylene, rigid materials coated with phenol-formaldehyde resin, and the like.

Diaphragm 6, which separates the anode section 2 from cathode section 4, may be a porous or semi-permeable material resistant to the cell environment and capable of maintaining the anode and cathode gases separate. Typical examples of suitable materials for use as a diaphragm include porous alundum, porous porcelain, sintered glass, glass fabric, resin impregnated wool felt, and the separators normally employed in lead storage batteries.

Any solid material having a hydrogen overvoltage as normally measured in the absence of phosphorus exceeding the hydrogen overvoltage of smooth platinum may be employed as the cathode. Typical cathodic materials include lead, lead mercury amalgam, cadmium, tin, aluminum, nickel, alloys of nickel, such as "Mumetal" (which is an alloy containing 77.2 percent nickel, 4.8 percent copper, 1.5 percent chromium and 14.9 percent iron), Monel, copper, silver, bismuth, and alloys thereof. For example, lead-tin, lead-bismuth, and tin-bismuth alloys may be employed. Various shapes of cathodes may be employed. For example, the cathode may be a plate as illustrated in the drawing. However, mats of metallic wool and porous metal sheets may also be employed if desired.

Suitable anode materials include lead, platinum, lead peroxide, and other materials of construction capable of conducting current and resisting corrosion under the conditions of electrolysis employed. Any electrolyte which is non-reactive with molten phosphorus and which is capable of forming hydrogen ions under the electrolysis conditions employed, may be employed as the catholyte and anolyte. Typical examples of suitable compounds in aqueous solution, which may be employed as the electrolyte include hydrochloric acid, sodium chloride, lithium chloride, potassium chloride, sodium sulfate, potassium sulfate, monosodium phosphate, disodium phosphate, acetic acid, ammonium hydroxide, phosphoric acid, sulfuric acid, and mixtures thereof. The concentration of the compound in the aqueous electrolyte may vary between about five and about eighty percent by weight, and is preferably between about ten and about fifty percent by weight.

Improved results have been obtained when metallic ions are present in electrolyte in small proportions. For example, ions of metals such as antimony, bismuth, lead, tin, cadmium, mercury, silver, zinc, cobalt, calcium, barium, and mixtures thereof may be employed. The metal ions may be placed in the electrolyte by employing a consumable anode of the desired metal or metals such as a lead anode, whereby metal ions are formed in the

3

electrolyte and transferred to the area adjacent to the cathode. Salts or other compounds of the metals such as chlorides, phosphates, acetates and the like may be dissolved in the electrolyte if desired. In another embodiment finely divided metal in elemental form is dissolved in the electrolyte. Sufficient metal ion is added to the electrolyte to provide a metal in concentration between about 0.03 and about three percent by weight of the electrolyte. This embodiment of the invention is described in detail in copending application SN 45,554, filed of even date herewith.

During electrolysis the temperature of the catholyte and anolyte should be maintained above the melting point of phosphorus (about forty-four degrees centigrade), and below the boiling point of the electrolyte. Temperatures between about sixty degrees centigrade and one hundred and ten degrees centigrade are satisfactory, but optimum yields of phosphine appear to be obtained at temperatures between about seventy degrees centigrade and about one hundred degrees centigrade. When an electric current is passed through the cell, molten phosphorus on the surface of the cathode is consumed in the formation of the catholyte gas in the cathode section. The catholyte gas predominates in phosphine and contains some hydrogen. The anolyte gas depends on the over-voltages of the anions in the anolyte with reference to the anode material. Thus, for example, the anolyte gas predominates in oxygen if sulfuric acid or phosphoric acid is used with a platinum anode, whereas for the same anode, chlorine predominates if hydrochloric acid is used as anolyte. Thus, the co-production of anodic oxidation products may be carried out in the anode compartment of the cell of this invention without departing from the spirit of the invention.

As phosphorus is consumed on the surface of the cathode to yield phosphine, additional phosphorus, by the wicking action, passes from the molten pool to the vertical surface of the cathode. It is important to control the current density on the cathode so that the phosphorus is not consumed at a rate greater than it can be replenished on the cathode surface by wicking action from the molten pool of phosphorus. The cathodic current density necessary to give best results will vary with the cell design and the construction of the cathode. For example, when a porous lead cathode is employed, and the height of the phosphorus layer on the cathode is about five and one-half inches, the optimum cathodic current density appears to be between about six and about twelve amperes per square foot. However, any current density consistent with the economic production of phosphine, may be employed.

The phosphine-containing gas produced at the cathode has a relatively high concentration of phosphine, which may be as high as ninety percent phosphine by volume or higher. The catholyte gas is substantially free from other phosphorus hydrides, which are flammable when contacted with air.

In one embodiment of the invention a lead plate is employed as the cathode, and a tin-bismuth alloy (containing forty percent tin and sixty percent bismuth), is employed as the anode. Under these conditions it has been found that the wicking effect of the lead cathode is markedly improved by using the tin-bismuth alloy as the anode.

In carrying out the technique of the instant novel process, it was observed that wicking action occurred prior to energizing the cell, that is, the thin layer of molten phosphorus formed on the outer surface of the vertical metallic cathode above the level of the molten pool of phosphorus before any current was impressed upon the system. As soon as a current is impressed upon the system, the wicking action became more rapid and was maintained more continuous. It was further observed that the rate of the wicking action was faster for some metals than others, and that the thickness of the

4

phosphorus layer on the metal surfaces was thicker on some metals than on others.

The following examples are presented to further define the invention without any intent of being limited thereby.

Example 1

A cell was constructed as follows: Into a three-liter beaker was placed an inverted beaker having seven openings through the inverted bottom. A first opening received electrolyte temperature recording means. A second opening received phosphorus temperature recording means. A third opening received the cathode current lead wire. A fourth opening received the initial nitrogen purge gas and later the molten phosphorus and electrolyte which were fed in periodically. Openings five and six were spaced on either side of said third opening and served to receive each of the lead wires to two anodes, one on either side of the cathode, and also to serve as outlets for the anode compartment gases (oxygen). And the seventh opening served as an outlet for the cathode compartment gases (PH_3 and H_2). Each of the anode compartments were constructed of glass containing an anode of porous lead peroxide with the side toward the cathode faced with a semi-porous diaphragm. The cathode was a sheet of commercial porous lead. The phosphorus was molten commercial yellow phosphorus and the electrolyte was a forty percent solution of H_3PO_4 .

In starting up the cell, the phosphoric acid was introduced into the cell. Then the current was turned on to make the cathode cathodic: this reduced oxides on the surface of the cathode. Next, the cell was purged with nitrogen, and enough molten yellow phosphorus was added to cover the bottom of the cell and to be in contact with the bottom edge of the cathode sheet; in this case five hundred and three grams were added.

Again the current was turned on. The phosphorus immediately began to wick up both sides of the cathode to the top, for a height of five and one-half inches. The dividing line on the cathode between the wicked and unwicked portion could be identified by the change in the appearance of the bubbles coming off the surfaces and also by the physical appearance of the surfaces. Oxygen was produced at the anode and phosphine began to be produced with hydrogen at the cathode. After a few hours the surfaces of the cathode were totally covered with phosphorus. The cathode gas analysis gradually enriched in PH_3 , and after about twenty-four hours of operation reached a maximum value of eighty percent PH_3 , at 2.9 volts and current density of 6.0 amperes per square foot at about one hundred degrees centigrade.

Example 2

An electrolytic cell was constructed from a two hundred cc. beaker having a rubber stopper in the top containing the other cell elements. The cell elements passing through the top stopper included a porous ceramic cylinder, which served as the anode section and diaphragm, a tin-bismuth alloy anode (one-eighth of an inch in diameter by eight inches long), the cylinder being adapted to convey oxygen gas from the anode section. Also inserted into the cell through the top stopper, were a thermometer, a tin-bismuth alloy cathode (one inch by three inches by one-eighth of an inch), and a tube adapted to convey the phosphine and hydrogen-containing gases from the cathode section of the cell (the portion of the cell outside the porous ceramic cylinder). Twenty grams of elemental white phosphorus were added to the cathode cross section and an electrolyte of forty percent phosphoric acid solution was added to the cathode and anode sections. The temperature of the cell was maintained at eighty degrees centigrade, and a direct current of 0.5 ampere was maintained at approximately 3.4 volts. After about twenty-four hours of operation, the tin-bismuth alloy anode was removed and replaced with a platinum wire anode. The phosphine concentration in

5

the cathode gas under these conditions increased from nine percent to 15.5 percent after six hours, and then decreased to six percent in two hours. After an additional nineteen hours, during which the phosphine concentration was six percent, the platinum anode was replaced with the tin-bismuth alloy anode. After 4.5 hours of operation, the alloy was replaced with the platinum anode. Sixteen hours after inserting the platinum anode, the cathode gas contained ninety-five percent phosphine by volume. After five days of operation under these conditions, during which time the phosphine concentration was greater than about ninety-two percent phosphine, the phosphine concentration decreased to about seventy percent due to depletion of molten phosphorus in the cathode section. After addition of phosphorus to the cathode section, the phosphine concentration in the cathode gas was greater than about ninety-two percent by volume for two additional days. The concentration then fluctuated in the seventy to eighty percent range for eighteen additional days. For the next sixteen days the cathode gas contained about fifty percent phosphine by volume.

Example 3

In a cell similar to that employed in Example 1, one gram of cadmium acetate was added to the electrolyte. At seventy-five degrees centigrade, employing a current of 0.5 amperes and a voltage of 3.4 volts, a maximum of ninety-two percent phosphine was produced in the cathode gas. After three days of operation the cathode gas was found to contain between forty-eight and eighty-four percent phosphine.

It will be recognized by those skilled in the art that various modifications within the invention are possible, some of which are referred to above. Therefore, we do not wish to be limited, except as defined by the appended claims.

We claim:

1. A process for producing phosphine which comprises contacting an anode and a solid vertical cathode with an aqueous electrolyte, the lower portion of said cathode being in contact with a pool of molten yellow phosphorus, maintaining a thin layer of molten yellow phosphorus on the surface of said cathode above and contiguous with said pool of molten phosphorus, maintaining an electric current between said anode and said cathode through said electrolyte, whereby said phosphorus forms a phosphine containing gas at said cathode, and whereby phosphorus consumed from the thin layer on the surface of said cathode is replenished from said pool of molten phosphorus.

2. The process of claim 1 wherein said cathode is a material having a hydrogen overvoltage as normally measured in the absence of phosphorus exceeding the hydrogen overvoltage of smooth platinum.

3. The process of claim 1 wherein said cathode is lead.

6

4. The process of claim 1 wherein said cathode is an alloy of tin and bismuth.

5. The process of claim 1 wherein said cathode is cadmium.

6. The process of claim 1 wherein said cathode is tin.

7. The process of claim 1 wherein said cathode is an alloy of lead and tin.

8. The process of claim 1 wherein said electrolyte is an aqueous phosphoric acid solution.

9. A process for producing phosphine which comprises contacting an anode and a solid vertical cathode with an aqueous electrolyte, the lower portion of said cathode being in contact with a pool of molten yellow phosphorus, maintaining a thin layer of molten yellow phosphorus on the surface of said cathode above and contiguous with said pool of molten phosphorus, maintaining an electric current between said anode and said cathode through said electrolyte while maintaining metallic ions in said electrolyte, whereby said phosphorus forms a phosphine-containing gas at said cathode, and whereby phosphorus consumed from the thin layer on the surface of said cathode is replenished from said pool of molten phosphorus.

10. The process of claim 9 wherein said metallic ions are ions of a metal selected from the group consisting of lead, tin, bismuth, antimony, cadmium, zinc, mercury, barium, calcium, silver, copper and mixtures thereof.

11. The process of claim 9 wherein the concentration of metallic ions in said electrolyte is between about 0.03 percent and about three percent by weight.

12. The process of claim 9 wherein said metallic ions are lead ions.

13. The process of claim 9 wherein said metallic ions are cadmium ions.

14. The process of claim 9 wherein said metallic ions are bismuth ions.

15. The process of claim 9 wherein said metallic ions are tin ions.

16. The process of claim 9 wherein said metallic ions are mercury ions.

References Cited in the file of this patent

UNITED STATES PATENTS

791,194	Hoopes	May 30, 1905
1,040,379	Moest et al.	Oct. 8, 1912
1,375,819	Blumenberg	Apr. 26, 1921
2,867,568	Cunningham	Jan. 6, 1959
2,913,383	Topfer	Nov. 17, 1959

OTHER REFERENCES

Journal of Chemical Society, Volume 16 (1863), pages 263-72.

Ephraim: Inorganic Chemistry, 5th edition (1948), pages 617-22.

Pauling: College Chemistry (1955), pages 330-5,