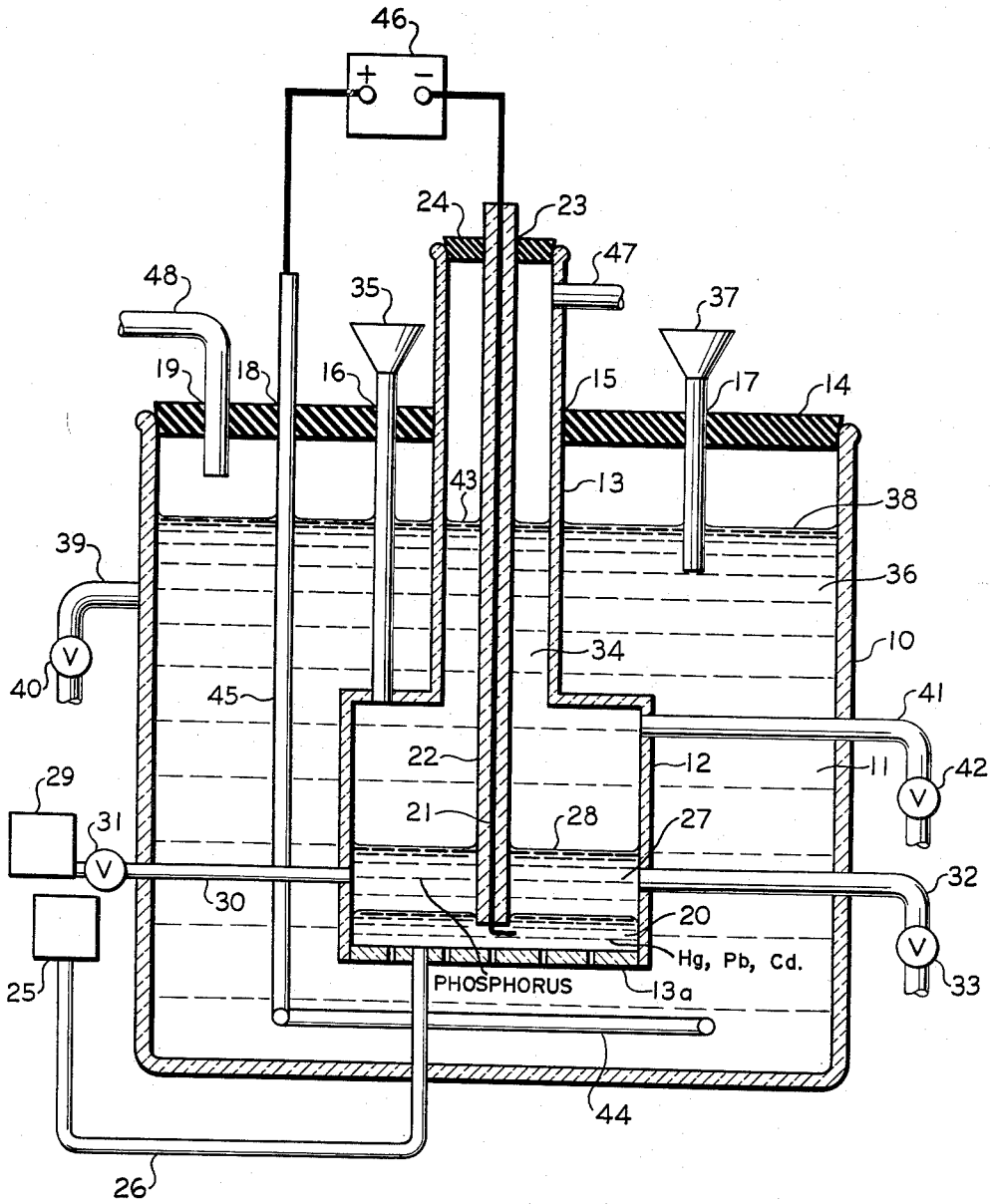


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G. T. MILLER ETAL  
PREPARATION OF PHOSPHINE

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**PREPARATION 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 corporation of New York

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This invention relates to a method and apparatus for producing phosphine from molten yellow 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 and a phosphonium halide with water and by the hydrolysis of elemental phosphorus. These methods have been unsatisfactory because of the high production costs and/or because the phosphine product is in an impure form.

More recently, processes and apparatus have been developed for the preparation of phosphine by the electrolysis of phosphorus. Phosphine can be produced in high yield and purity by the electrolysis of phosphorus. However, it has been observed that under certain conditions with continued operation of the cell for extended periods, the yield of phosphine in the catholyte gas gradually diminishes. Occasionally, spongy deposits form on the surface of the cathode, and the concentration of phosphine in the catholyte gas appears to decrease as the size of these spongy deposits increases. It is believed that the spongy deposits are formed by a deposit of metallic ions from either the electrolyte or the phosphorus, at or near the cathode. Profuse amounts of hydrogen bubbles are evolved from these deposits. While we do not wish to be limited by theory, it is believed that mono-atomic hydrogen forms at the cathode, and is prevented by these spongy deposits from combining with phosphorus to yield phosphine, and instead, the mono-atomic hydrogen combines with additional mono-atomic hydrogen to yield gaseous hydrogen. As a result, the hydrogen concentration in the catholyte gas increases and the phosphine concentration decreases.

It is an object of this invention to minimize or eliminate the harmful effects of spongy deposits in electrolytic cells for the production of phosphine.

It is a further object of the invention to provide an improved method for the reduction of phosphorus by electrolysis.

Still a further object of the invention is to provide an improved electrolytic cell for the production of phosphine by electrolysis.

Another object of the invention is to provide an improved cathode structure for use in electrolytic cells.

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

It has now been discovered that when a horizontal cathode is contacted with the top portion of a horizontal porous diaphragm and with the bottom portion of a pool of molten yellow phosphorus in an electrolytic cell, the formation of spongy deposits at or near the cathode is decreased or eliminated during electrolysis and the efficiency of the cell in the production of phosphine is markedly improved.

The accompanying drawing is a schematic illustration

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of the novel electrolytic cell which may be used in carrying out the process of the invention.

Referring to the drawing, there is shown cell vessel 10, having an anode section 11, and a cathode section 12, separated by a wall 13. The bottom horizontal wall portion 13a of wall 13 is porous, as discussed more fully below. A gas tight cover 14 having ports 15, 16, 17, 18 and 19, is secured to the top of cell vessel 10. Cathode section 12, which extends through port 15, is provided with cathode 20, which is positioned in contact with the top of bottom horizontal wall portion 13a. Cathode electrical connector 21, which may be insulated with a suitable insulator 22, extends from cathode 20 through port 23 in gas tight cover 24 of cathode section 12.

When a liquid cathode is employed, the liquid may be stored in cathode storage vessel 25, and fed through line 26 to the lower portion of cathode section 12.

A pool of molten phosphorus 27, is positioned above cathode 20, up to interface 28. If desired, circulation of the molten phosphorus may be effected by feeding molten phosphorus to the cathode section from phosphorus storage vessel 29, through line 30, having valve 31. The molten phosphorus may be removed from cathode section 12 through line 32, having valve 33. Catholyte 34 is added to catholyte section 12 by means of funnel 35, which extends through port 16.

Anolyte 36 is added to anolyte section 11 by means of funnel 37, which extends through port 17, up to anolyte level 38. Port 39, which is positioned in the side of cell vessel 10, below anolyte level 38, may be employed for removing anolyte if desired, by opening valve 40, which communicates with port 39. Line 41, having valve 42 communicates with cathode section 12, and extends through the side of cell vessel 10. Catholyte 34, which has an upper level 43, may be removed from catholyte section 12 by means of line 41 if desired. Anode 44 is positioned adjacent to or below cathode section 12, and is connected by means of anode electrical connector 45, which extends through port 18, to the positive pole of a source of direct current 46. Cathode electrical connector 21 is connected to the negative pole of a source of direct current 46.

When an electric current is impressed upon the system, phosphine-containing gas is generated in cathode section 12, and is discharged through catholyte gas discharge line 47, which is positioned in the upper portion of cathode section 12. At the same time the anolyte gas formed in the anode section 11 is discharged through anolyte gas discharge line 48, which extends through port 19.

It will be recognized by those skilled in the art that the design of the electrolytic cell shown in the drawing may be modified without departing from the spirit of the invention. For example, the cathode is shown in the drawing as a liquid, such as mercury, but a solid cathode may be used in place of the liquid cathode if desired.

Cell vessel 10 may be constructed of any impervious material of suitable corrosion resistance, such as glass, ceramics, rubber lined steel and the like.

Any 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 mercury, bismuth alloys which are liquid under

the temperature conditions employed, for example at temperatures between about sixty and one hundred degrees centigrade, lead, lead mercury amalgam, tin, cadmium, copper, bismuth, aluminum, zinc, brass, silver, nickel, gold and alloys thereof. For example, various tin-bismuth alloys, nickel alloys with such metals as iron, copper chromium and the like may be employed. Alloys of bismuth, tin, cadmium, indium, which are liquid under the temperature conditions employed, may also be used. Black phosphorus may also be employed as the cathode material.

The shape of the cathode may be varied if a solid cathode is employed. When the cathode is a solid, it must be so formed or shaped as to permit the gaseous products of electrolysis in the cathode section to rise through or around it, and must maintain a close physical relationship with the porous supporting diaphragm, so as to avoid an excessively thick electrically resistant layer of phosphorus between the cathode and the diaphragm. Metal fabricated as wool, shot, crimped sheet, porous sheet, fabric, screen and folded sheet or plate may be employed as a solid cathode. It is necessary to secure a porous diaphragm as bottom horizontal wall portion 13a, to the bottom of wall 13 to maintain the cathode separate from anode section 11. The porous diaphragm may be constructed of any suitable porous material such as sintered glass, porous aluminum, ion-exchange membranes, plastic cloth and the like.

Suitable anode materials include lead, lead-antimony alloys, lead dioxide, platinum, graphite, stainless steel and the like.

Either basic or acidic aqueous solutions may be employed as the anolyte and catholyte. Typical examples of suitable compounds in aqueous solution which may be employed as the electrolyte, (catholyte and/or anolyte) include phosphoric acid, sulfuric acid, hydrochloric acid, sodium chloride, lithium chloride, potassium chloride, sodium sulfate, potassium sulfate, monosodium phosphate, disodium phosphate, acetic acid, ammonium hydroxide and mixtures thereof. The concentration of the compound in the electrolyte may vary between about 0.1 percent and about seventy-five percent by weight of the electrolyte, and is preferably between about five and about fifty percent by weight.

A heating means, such as a constant temperature bath (not shown in the drawing), is employed to maintain the temperature of the electrolyte between about forty-four degrees centigrade and about the boiling point of the electrolyte, and preferably between about sixty degrees centigrade and about one hundred degrees centigrade during electrolysis.

Optimum current and current density depend upon the cell design employed. However, any conditions of operation that yield phosphine at a rate and of a purity consistent with economic operations may be employed. For example, a cathodic current density between about one and about two hundred amperes per square foot, and a voltage drop across the system between about two and about twenty-five volts will normally yield phosphine at a rate and of a purity which is economically feasible.

When a solid cathode in particulate form is employed, some of the molten yellow phosphorus seeps below the particles of the cathode onto the top of the porous diaphragm. Molten phosphorus does not readily conduct electricity and thus, when a thick layer of phosphorus is between the cathode and the porous diaphragm, the efficiency of the cell is markedly reduced. Therefore, it is desirable to maintain the thickness of this layer of phosphorus, which may contain some metallic phosphides, at less than about one-eighth of an inch and preferably less than about one-thirty-second of an inch. Current can be passed through this lower phosphorus layer if the thickness is maintained within the above mentioned range.

In another embodiment of this invention there is provided a novel cathode structure comprising a horizontal

metallic cathode and a housing therefor. The under portion of said cathode is adapted to be in communication with electrolyte and an electrolytic current passing there-through. The upper portion of said cathode is adapted to be covered by a liquid material reactive with a product of electrolysis. And the cathode is adapted to permit passage of product of electrolysis from the under portion to the upper portion of said cathode. The housing for said cathode has a lower end adapted to receive or contain said cathode and be in communication with electrolyte and an electrolytic current passing therethrough, and has its upper end adapted to collect and remove electrolyte and gaseous products of electrolysis, and is adapted to receive electrical means connected with said cathode.

This cathode structure can be used especially in the electrolysis of molten phosphorus to produce phosphine, wherein the cathode structure is placed in the upper part of a cell container, and an anode is positioned in said container and adapted to produce and separately recover a gaseous product of electrolysis. This can be done in several ways. The anode can be in the shape of an annular ring circumferentially outside a cathode structure, where the cathode area is circular. Where the cathode area is rectangular, the anodes can be in the form of alternate parallel rods or blocks.

In the operation of the above described cell, gas bubbles form at the lower portion of the cathode and rise through and/or around the cathode, through the layer of molten phosphorus into the electrolyte and are discharged through the catholyte discharge port. Circulation and agitation of the molten phosphorus, and of the cathode, when the cathode is a liquid, by these gas bubbles, causes the "sponge-forming" metallic compounds to be suspended in the molten phosphorus (and the liquid cathode, if one is used), thereby inhibiting or minimizing the formation of spongy deposits on the surfaces of the cathode, and thereby markedly extending the operating time of the cell. If desired, when the concentration of impurities builds up in the molten phosphorus, it can be removed through line 32 and replaced with fresh molten phosphorus through line 30.

In another embodiment of the invention circulation and agitation of the molten phosphorus (and liquid cathode, when one is used), can be effected by gas bubbles as described above, in combination with circulation of the electrolyte up through the porous diaphragm. This circulation and agitation can be effected in a cell of the following design:

A cell vessel, similar to that shown in the drawing, is provided with a cathode section similar to cathode section 12 in the drawing, except that the cathode section is closed at the top. A catholyte discharge tube is positioned vertically adjacent to the cathode section, the top portion of the tube extending out of the cell vessel and being adapted to discharge catholyte gas. The bottom of the catholyte discharge tube communicates with a phosphorus storage vessel. An upper conduit communicates between the cathode section and the lower portion of the catholyte discharge tube, preferably sloping upwardly from the cathode section. A lower conduit communicates between the phosphorus storage vessel and the cathode section, connecting with the cathode section below the upper conduit and above the phosphorus level in the cathode section. The lower conduit connects with the storage vessel at a point about midway between the upper and lower level of phosphorus in the phosphorus storage vessel and slopes upwardly from the phosphorus storage vessel.

The cathode section is provided with a porous diaphragm at the bottom, a horizontal cathode such as mercury above the diaphragm, and a layer of molten phosphorus above the cathode. An anode is positioned below or adjacent to the diaphragm as in the drawing. Electrolyte fills the anode section to a level substantially above the level of electrolyte in the cathode section and in the

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catholyte gas discharge tube. An intermediate conduit communicates with the catholyte gas discharge tube at a point below the electrolyte level and above the phosphorus level in the phosphorus storage vessel. The other end of the intermediate conduit communicates with a suitable pump such as a gas-lift pump, which conveys electrolyte from the catholyte gas discharge tube to the anolyte section.

In the operation of a cell of the latter type, after the cell is energized, gas bubbles form at the bottom of the cathode and rise up through the cathode and molten phosphorus. In addition, because the height of the electrolyte in the anode section is greater than the height of the electrolyte in the cathode section, electrolyte is forced by hydrostatic pressure up through the porous diaphragm, through the cathode and phosphorus. The gas bubbles and electrolyte effect circulation of the phosphorus (and liquid cathode, if used). In addition, the circulating electrolyte and gas bubbles carry droplets of molten phosphorus, which contain sponge forming impurities, up to and through the upper conduit into the catholyte gas discharge tube. The gas bubbles separate and rise up through the tube. The phosphorus droplets settle to the bottom of the phosphorus storage vessel. Sponge forming impurities in the phosphorus appear to collect in the bottom and top of the phosphorus layer, while the somewhat purified phosphorus flows by hydrostatic pressure through the lower conduit back to the cathode section and drops through the electrolyte into the phosphorus layer of the cathode section. Electrolyte in the catholyte gas discharge tube is conveyed by hydrostatic pressure through the intermediate conduit to the pump where it is recirculated to the anolyte section. Means may be provided at the top of the cell vessel for collecting the anolyte gas.

The following example is given to further illustrate the invention without any intention of being limited thereby.

#### Example 1

An electrolytic cell was constructed as follows: an inverted Buchner funnel having its top cut off near the fritted glass disk was used as the cathode compartment. A layer of mercury was introduced into the compartment through the inlet neck. The area of the mercury was 4.5 square inches. A glass tube having therein a platinum cathode lead wire was inserted through the neck to contact the pool of mercury. The glass served to shield the wire from being in contact with the other materials in the compartment. This funnel was suspended inside a large glass beaker. The neck of the funnel had an outlet for removal of gases and an electrolyte level equalizer outlet.

An annular ring of platinum wire anode was suspended near the level of the fritted glass and positioned so that the ring diameter was entirely outside the outer edge of the funnel to permit separate recovery of evolved anode gaseous products. A glass tube having therein a platinum anode lead wire, shielded the anode lead wire from the cell liquids and gases.

In starting up the cell, phosphoric acid of forty percent concentration was introduced into the beaker and funnel to a level above that of the equalizer, and maintained at a temperature of sixty-five degrees centigrade. The cathode compartment funnel was purged with nitrogen, and enough commercial molten yellow phosphorus was added through the inlet to cover the mercury surface.

When a voltage of 7.0 volts was impressed across the electrodes, 5.0 amperes of current flowed, giving a cathode current density of about one hundred and sixty amperes per square foot. Oxygen was generated at the platinum wire anode and rose up externally to the funnel. Within the cathode compartment funnel, it was observed that bubbles of phosphine and hydrogen were rising at the outer edge of and through the phosphorus layer. The cathode gas recovered was analyzed with alkaline NaOBr solution and contained sixty-five percent phosphine.

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#### Example 2

The procedure of Example 1 was repeated employing the apparatus of Example 1. After about thirty hours of operation the phosphine concentration in the cathode gas was about eighty-three percent by volume. After about seven days of further operation, (during which time the phosphine concentration was above eighty percent), the concentration decreased to about seventy percent and the current decreased from about five amperes at six volts to about one ampere at seven volts. At this point, 0.214 gram of powdered cadmium was added to the mercury (which comprised about one hundred and ninety-three grams). Shortly thereafter, the phosphine concentration increased to about eighty-one percent and the current returned to five amperes at six volts.

#### Example 3

A cell vessel similar to that of Example 1 was employed with the exception that the mercury cathode was replaced with a coil of lead strip which was eight and one-half inches long by one inch wide by one-sixteenth of an inch thick, and which had been ground flat on the bottom to obtain maximum contact between the bottom of the coil and the diaphragm. Employing a current of about one ampere at about 5.5 volts, at seventy-five degrees centigrade, analyses showed that the catholyte gas was about twenty-five percent phosphine by volume for about four days, and reached concentrations as high as forty-two percent during that time.

Further improvement in cell operation can be obtained by incorporating metallic ions in the electrolyte as described in copending application SN 45,554, filed of even date herewith. In this application there is disclosed the technique of incorporating metallic ions of metals such as lead, tin, bismuth, antimony, cadmium, zinc, mercury, barium, calcium, silver, cobalt and mixtures thereof in the electrolyte in a proportion between about 0.03 and about three percent by weight of the electrolyte, whereby improved cell operation is obtained.

It will be obvious to those skilled in the art that various modifications of 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 the production of phosphine in an electrolytic cell which comprises contacting an anode and a horizontal cathode with an aqueous electrolyte, separating said anode and said cathode by means of a horizontal porous diaphragm, contacting said cathode with said diaphragm and with molten yellow phosphorus, passing an electric current between said anode and said cathode through said electrolyte, and recovering a phosphine-containing gas produced at the cathode.

2. The process of claim 1 wherein said molten phosphorus is circulated by means of gas bubbles formed in said cathode during electrolysis.

3. The process of claim 1 wherein said molten phosphorus is circulated, and the electrolyte is forced up through the diaphragm through the cathode into said molten phosphorus.

4. 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.

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

6. The process of claim 1 wherein said cathode is mercury-cadmium amalgam.

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

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

9. The process of claim 1 wherein said electrolyte is an aqueous solution of sulfuric acid.

(References on following page)

3,109,789

**7**

**References Cited in the file of this patent**

**UNITED STATES PATENTS**

363,411	Molloy	May 24, 1887	2,427,433
641,360	Barricks	Jan. 16, 1900	2,502,888
1,264,535	McElroy	Apr. 30, 1918	2,545,376
1,368,955	Matsushima	Feb. 15, 1921	2,688,594
1,375,819	Blumenberg	Apr. 26, 1921	2,717,237
1,981,498	Engelhardt et al.	Nov. 20, 1934	2,898,282
2,150,775	Messner	Mar. 14, 1939	2,992,170
2,328,484	Oosterhuis	Aug. 31, 1943	
2,338,713	Ewing	Jan. 11, 1944	

5

10

309,316  
1,130,548

**8**

Winslow et al.	Sept. 16, 1947
Ravenscroft	Apr. 4, 1950
Ornhjelm	Mar. 13, 1951
Oosterman	Sept. 7, 1954
Rempel	Sept. 6, 1955
Flook et al.	Aug. 4, 1959
Robinson	July 11, 1961

**FOREIGN PATENTS**

Great Britain	Apr. 11, 1929
France	Oct. 1, 1956