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ELECTROLYTIC HYDROGENATION PROCESS

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FIG 1.

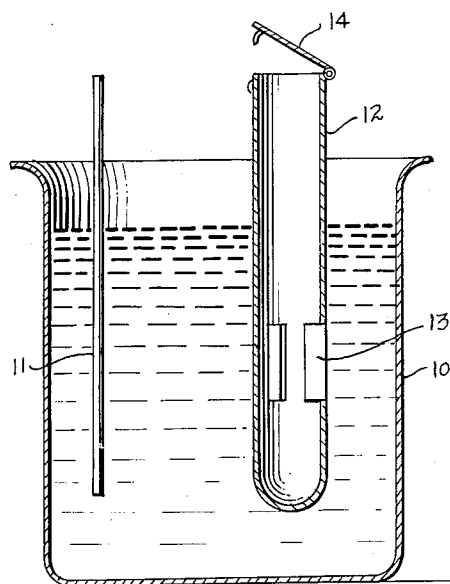
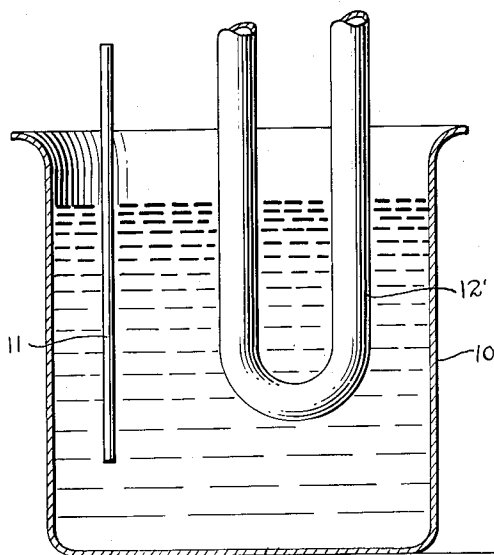


FIG 2.



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ELECTROLYTIC HYDROGENATION PROCESS

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8 Claims. (Cl. 204—73)

The present invention relates to the art of producing hydrogen and includes an improved hydrogenation process and apparatus therefor.

It is a well-known fact that hydrogen diffuses into some metals, but some uncertainty exists as to the mechanism of the process. In order to test the hypothesis that the process consists of a surface dissociation followed by a diffusion of the atomic hydrogen into the metal, the following preliminary experiments were first tried.

Palladium was made the cathode in an ordinary electrolytic sulfuric acid bath, and it was found that the hydrogen passed through the metal at room temperature and in appreciable quantities (as much as 1.5 cc. per cm.<sup>2</sup> per min.). The diffusion rate increased rapidly with the temperature. A palladium tube or chamber connected to a pressure gauge was next made the cathode in the bath, and a hydrogen pressure of 700 p. s. i. was built up in the tube. This is not the limiting pressure and the indications are that the pressure will continue to rise until the pressure dissociation on the exit surface causes an equilibrium to be established. This may run as high as several thousand pounds. The experiments were extended to a number of other metals and it was found that Ni, Nb, Ta and Mo all show a slight transmission. Iron and aluminum also transmit hydrogen. Indeed, evidence obtained in later experiments shows that most metals transmit hydrogen when made the cathode in an electrolytic bath. These experiments and in particular the experiments with the palladium tube or chamber demonstrated that the electrolytic method may be employed to produce high pressure, pure hydrogen. Wahlin, H. B., JI. Applied Physics 22, 1503 (1951).

Investigations of transmission through palladium chambers (2 inches long, 1/8 inch O. D. and with a 5 mil wall) were then continued and it was discovered that at currents below 0.25 amperes the transmission rate is independent of the temperature. The reason for this is that below 0.25 amperes all of the hydrogen liberated at the cathode (regardless of temperature) passes through the chamber and appears on the inside wall. The effect of temperature at various currents is shown below in Tables I and II.

TABLE I  
Cc. of hydrogen per minute

| Temperature, °C. | Current in Amperes |     |     |     |     |     |
|------------------|--------------------|-----|-----|-----|-----|-----|
|                  | 0.25               | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| 32               | 1.5                | 2.5 | 3.0 | 3.5 | 3.5 | 3.5 |
| 48               | 1.5                | 3.0 | 4.5 | 5.0 | 5.5 | 6.0 |
| 61               | 1.5                | 3.1 | 5.5 | 6.5 | 7.5 | 8.5 |
| 75               | 1.5                | 3.2 | 6.0 | 7.5 | 8.5 | 9.5 |

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TABLE II  
Percent transmission

| Temperature, °C. | Current in Amperes |     |     |     |     |     |
|------------------|--------------------|-----|-----|-----|-----|-----|
|                  | 0.25               | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| 32               | 100                | 75  | 45  | 35  | 30  | 25  |
| 75               | 100                | 95  | 85  | 75  | 65  | 55  |

Before use the tubes or chambers employed in the above experiments were heated at about 900° C. for an hour and at 500° C. for about 14 hours. The inside of the tubes was then polished with #400 emery. The tubes, closed at one end, were connected to an inverted graduated tube so that the volume (cc.) of hydrogen transmitted could be measured. The figures given in the tables are approximate having been obtained by plotting the rate of transmission in cc. per minute and per cent hydrogen transmitted as a function of the current. In calculating percentage transmission the total hydrogen available was computed from the current and time. While the invention is not limited by theory of operation, it is believed that the increased transmission with temperature at the higher currents as shown in Table I is most probably due to the increased recombination of the atomic hydrogen to form molecular gas and the increased rate of the evaporation of this gas from the inner surface.

The next step was the investigation of the variation of the rate of transmission with the thickness of the tube or chamber wall. Three tubes with wall thickness of 5, 10 and 15 mils. were used and it was discovered that the transmission was independent of the wall thickness. This is also indicated by Table II for if the transmission depended on the wall thickness one would hardly expect 100% transmission even at low currents.

The role of the area of the tube or chamber surface exposed to the electrolyte was next investigated. The area of the surface was varied by painting the ends of the tube with lacquer. It was found that the area can be varied as much as 30% without changing the transmission rate. A tube was next annealed by the method described above and was used without polishing the inside. Due to migration of the Pd atoms along the surface the tube became thermally etched and had a considerably larger inside area than the polished tube. The outer surface of the tube was given the same cleaning treatment as was given to the tubes used before. It was discovered that this tube showed a 30% increase in transmission. The obvious conclusion is that the transmission is controlled primarily by the rate of escape of the hydrogen from the exit surface. The reason that the entrance surface is relatively unimportant is that the diffusion of the hydrogen through the palladium is so rapid and the migration of the hydrogen along the inner surface takes place so quickly that, even if the entrance surface has a small area, the entire tube becomes saturated with the gas and the exit surface controls the transmission. The above tables give representative data obtained with polished exit surfaces. When thermally etched surfaces are used, higher efficiencies are obtained.

Since the hydrogen appears on the inner surface of the palladium chamber or tube in the atomic form it should react readily with hydrogenatable materials. That it reacts with gaseous oxygen was initially confirmed. To investigate the reaction with other materials and spe-

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cifically organic hydrogenatable materials, a palladium tube (closed at one end) 4 inches long and  $\frac{3}{8}$  inches in diameter was used as the cathode. Cyclohexene was placed in the tube and an electrolytic current of 3 amperes applied. After 4 hours of running the cyclohexene was completely converted to cyclohexane. Reduction of cyclohexanone to cyclohexanol was also obtained. No change in the index of refraction was noted with benzene after 16 hours treatment. However, reduction of benzene did take place when the palladium tube or chamber was provided with a thin inner coating of platinum black catalyst. Liquids such as unsaturated vegetable oils may also be hydrogenated as well as gases such as ethylene and the like.

Continued investigations have shown the process of the present invention to provide a ready means for obtaining pure hydrogen including high pressure hydrogen, as well as the relatively very reactive atomic hydrogen. As heat is not necessary, the process may be readily carried out at room temperature or in the cold, e. g. 0°–10° C. or, indeed, at any temperature as long as the electrolytic bath remains conducting. This makes the process of special value in the reduction of unstable compounds where the present methods of high temperatures and pressures, due to degradation, etc., are not applicable. Difficult or "messy" separations encountered in electrochemical reductions are also avoided by the process of the present invention. Ordinarily, it is preferred to operate at about room temperature although optimum conditions may vary with the particular material undergoing treatment. Cooling or heating the palladium chamber, e. g. by cooling or heating the electrolytic bath, below or above room temperature accordingly may be resorted to where desired. Optimum conditions including currents to be employed can be readily determined by simple experimental tests.

Any type of electrolytic cell which generates hydrogen at the cathode may be employed in the process of the present invention as long as the palladium chamber or tube is maintained as the cathode. The standard cell comprises a container or compartment adaptable for holding the electrolytic bath, with an anode and cathode positioned therein. Various anodes and electrolytic baths may be employed, although the use of a platinum anode (or any metal which does not poison the cathode) and an aqueous sulfuric acid bath are of the preferred type as they work satisfactorily and are relatively inexpensive in operation. In the present invention, the cathode is preferably palladium and is in the form of a chamber or tube for holding the material to be hydrogenated. For batch operations the chamber or tube is closed at the bottom end with the upper or open end positioned above the surface of the bath to receive the material to be treated. The open end may be closed to permit hydrogenation under pressure. For continuous operations, a conduit type chamber or U-tube may be employed with means for introducing the material to be hydrogenated into one end and means for withdrawing the material after hydrogenation from the other end. The palladium forming the chamber or tube may be carried on an inert carrier and the chambers or tubes may be of various shapes. For optimum operations, however, a relatively large exit (inner) surface area should be provided. This may be accomplished by thermally etching the palladium surface or by otherwise providing relatively uneven (as distinguished from polished) large surface area for the inside of the palladium chamber or tube. The surface may also be extended by the use of fins, spongy palladium and the like. The inner surface of the chamber may also be provided with a thin coating of any of the hydro-

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genating catalysts to aid in hydrogenation. In the above description iron and aluminum may be used in place of palladium. Illustrative electrolytic cells for carrying out the processes of the present invention are shown in the following figures:

Fig. 1 is a side cross sectional view of one embodiment of the invention; and

Fig. 2 is a side cross sectional view of another embodiment of the invention.

Each cell comprises the standard type container or compartment 10 for holding the electrolyte with the anode 11 and cathode 12 positioned therein. In Fig. 1, the cathode 12 is in the form of a tube or chamber and is the type used for batch operations. This tube has been provided with fins 13 to extend or increase the inner surface area and also with closure member 14 which may be closed when desired to permit hydrogenation under pressure. In Fig. 2, the cathode 12' is in the form of a conduit type chamber or U-tube and is the type adaptable for carrying out continuous operations. Material to be hydrogenated, for example, may be introduced at one opening and, after passing through the conduit in contact with hydrogen, withdrawn at the other opening. This cathode like the cathode in Fig. 1 may also have the inner surface extended by the use of fins and the like, or by using thermally etched surfaces, a porous inner surface such as spongy palladium, etc.

I claim:

1. A method of electrolytically hydrogenating a hydrogenatable organic material which comprises reacting the material with cathodically-evolved hydrogen within a chamber in an electrolytic cell, said chamber being maintained as the cathode in said cell and the electrolyte being maintained in said cell exteriorly of the chamber, said hydrogen being thereby evolved at the outer surface of said chamber, said chamber being composed of a metal selected from the group consisting of palladium, iron and aluminum, said selected metal being capable of diffusing the evolved hydrogen to the inner surface of said chamber.

2. The method of claim 1 where the hydrogenatable material is passed through a conduit type chamber maintained as the cathode in the electrolytic cell.

3. The method of claim 1, where the hydrogenatable material is hydrogenated in the presence of a hydrogenation catalyst in the chamber maintained as the cathode in the electrolytic cell.

4. The method of claim 1 where the hydrogenatable material is hydrogenated under pressure in a closed chamber maintained as the cathode in the electrolytic cell.

5. The method of claim 1 where the chamber is cooled below room temperature.

6. The method of claim 1 where the chamber is heated above room temperature.

7. The method of claim 1 where the inside surface of the chamber is extended to provide a relatively large surface area.

8. The method of claim 1 where the chamber is annealed.

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