UNITED STATES PATENT OFFICE.

WILHELM PIP, OF DARMSTADT, GERMANY, ASSIGNOR TO THE FIRM OF E. MERCK, OF SAME PLACE.

PROCESS OF PRODUCING PIPERIDIN.

SPECIFICATION forming part of Letters Patent No. 680,543, dated August 13, 1901.

Application filed January 12, 1899. Serial No. 701,979. (No specimens.)

To all whom it may concern:

Be it known that I, WILHELM PIP, a subject of the Emperor of Germany, and a resident of Darmstadt, Germany, have invented a Process of Producing Piperidin, of which the following is a specification.

Attempts have heretofore been made to produce piperidin from pyridin by the electrolytic method, but without success. A definite process has already been proposed for this purpose—namely, to dissolve ten parts, by weight, of pyridin in one hundred parts, by weight, of ten per cent. sulfuric acid, and to subject this solution to the action of the electric current, lead plates being used as cathodes and any desired insoluble material for the anodes. Nevertheless, the process was not successful, and other experiments have so far remained without successful results. I have discovered, however, that piperidin can be successfully produced from pyridin by the electrolytic method if certain conditions simultaneously are observed. The conditions have more especial reference to, first, the quantity of the acid to be employed; second, the choice of the electrodes, and, third, the degrees of purity of the acids and the materials used in the operation.

I have found that when there is too small a quantity of sulfuric acid no piperidin is produced, but that the yield (when other necessary conditions are observed) will increase in proportion to the increase of the quantity of acid employed. For example, when one equivalent of pyridin to one equivalent of sulfuric acid (*i. e.*, such quantity of acid exactly sufficient to neutralize the pyridin) is employed no piperidin is produced. On the other hand, when, say, four or more equivalents of acid are used to one of pyridin the yield is a very good one. I therefore determined that in order that the reaction be satisfactory and the yield good the quantity of acid must be sufficient to leave a surplus or excess thereof throughout the duration of the reducing action.

Although sulfuric-acid solutions of pyridin are here described and in practice will no doubt be generally employed, nevertheless other acids, such as muriatic acid, may be used to produce piperidin when the other necessary conditions herein described are observed.

I have found that there is a choice of materials to be used for the anode and also for the cathode. Lead is found to be a suitable material for both electrodes. Furthermore, it is possible to use only certain other materials in this process of the electrodes, such as carbon, mercury, or silver. These materials are in this case equivalents to lead. I have also found that impure acids—*i. e.*, acids which contain other metals than those which may be used as electrodes in this process, or impure diaphragms, which yield to the solution salts of other metals than above mentioned—are injurious and interfere with the satisfactory working of the process. Therefore it is important to use pure materials. By "pure materials" may be understood any material whatever suitable for diaphragms. Consequently the invention is not limited to any particular substance. The material should not, however, contain any metals or metallic salts which can be brought into solution, thus impurifying the acid while the apparatus is in use. For instance, if clay diaphragms are used these should not contain any easily-decomposable silicates of iron or other easily-soluble iron salts, carbonates, &c., while at the same time the presence of undecomposable iron silicates is not considered injurious to the working of the process.

If pyridin is subjected to electrolytic reduction under the conditions described, a very good yield of piperidin will be obtained.

By way of example, the process may be carried out in the following manner: Ten kilograms of pyridin may be dissolved in one hundred and ten kilograms of water and twenty-five kilograms of sulfuric acid of 65° Baumé and electrolyzed with the use of lead electrodes in the cathodic cell of an electrolytic apparatus. The anodic cell is separated in a well-known manner from the cathodic cell by means of a diaphragm and contains a solution of five kilograms sulfuric acid of 66° Baumé in fifty kilograms of water. Also without any diaphragm a solution of ten kilograms of pyridin in one hundred and ten kilograms of water and twenty-five kilograms of

sulfuric acid of 66° Baumé may be subjected to the action of the electric current. Such method is, however, not so advantageous as in the use of anodic cells separated from the cathodic cells. In both cases the density of current is 4.5 amperes for each square decimeter cathodic surface; but the same can also be less or greater without any disadvantage.

Piperidin has heretofore been obtained by the reduction by means of sodium in alcoholic solution.

My process has the advantage of great simplicity, cheapness, and is technically easy and safe.

I claim as my invention—

1. The process herein described of producing piperidin from pyridin, consisting in dissolving the pyridin in such a quantity of pure acid that at least three equivalents of acid are used to one of pyridin, and passing an electric current through the solution with the aid of suitable electrodes, substantially as set forth.

2. The process herein described of producing piperidin from pyridin consisting in dissolving the pyridin in such a quantity of pure acid that at least three equivalents of acid are used to one of pyridin, putting this solution of pyridin in the cathodic cell of an electrolytic apparatus, separated from the anodic cell by a diaphragm of pure material, and passing a current of electricity through the solution with the aid of suitable electrodes, substantially as set forth.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

WILHELM PIP.

Witnesses:
DEAN B. MASON,
JEAN GRUND.