UNITED STATES PATENT OFFICE.

OTTO DIEFFENBACH, OF DARMSTADT, GERMANY.

MANUFACTURE OF HYDROAZO DERIVATIVES.

No. 833,513. Specification of Letters Patent. Patented Oct. 16, 1906.

Application filed March 28, 1906. Serial No. 308,616.

To all whom it may concern:

Be it known that I, OTTO DIEFFENBACH, professor, a subject of the Grand Duke of Hesse, and a resident of Darmstadt, Grand Duchy of Hesse-Darmstadt, Germany, have invented new and useful Improvements in the Manufacture of Hydrazo Derivatives, of which the following is a full, clear, and complete specification.

The manufacture of hydrazo bodies, as hydrazobenzene and its homologues, by electrolytic reduction of the corresponding nitro, azoxy, or azo bodies suspended in the solution of an alkali or of an alkali salt according to the hitherto-known process (see, for instance, the German Patents No. 121,899, dated November 24, 1899, and No. 121,900, dated December 1, 1900) shows the inconvenience that during the process the reduction products are precipitated in a solid form and are apt to stick to the cathodes and diaphragms, so that they can only with difficulty be removed from the apparatus and at the expense of the durability of the latter. Besides, this coating or partial insulating of the cathode often causes a considerable rise of electric tension, and consequently a useless consumption of current.

I have now found that the manufacture of hydrazo bodies by electrolysis can be performed smoothly and with avoidance of the specified defects if convenient solvents for the reduction products, which, however, should not be itself soluble in water—as, for instance benzene, toluene, xylene, &c.—are added to the electrolytes. Inasmuch as such solvents take up the reduction products, they prevent the objectionable precipitations on the cathodes and diaphragms, and since at the end of the electrolysis they float on the electrolyte they can easily be removed from the cathode-compartment, together with the reduction products, without removing the electrolyte itself and without submitting the cathodes and diaphragms to a long cleaning noxious to their durability. A further advantage of additions of this kind is that they render it possible to remove in a simple manner the azoxy derivatives which are present, besides the hydrazo derivatives, from the latter and to return them to the electrolyte by adding directly to the benzene, toluene, or xylene solution the hydrochloric acid necessary to transform the hydrazo derivatives into the corresponding benzidine compounds. We thereby attain an aqueous solution of benzidine hydrochlorid (or of the hydrochlorid of another paradiamin of the benzidine series) which can easily be separated from the upper layer of benzene which contains the azoxy body in solution and can be introduced again into the cathode-compartment.

Example: The cathode-compartment of an electrolytic vat is charged with one thousand cubic centimeters of caustic-soda lye of three-per-cent. strength and one hundred grams of nitrobenzene, which are dissolved in three hundred grams of benzene, while the anode-compartment is charged with caustic-soda lye of five-per-cent. strength. The anodes and cathodes will be of metal and preferably of iron or nickel. The cathode liquid is strongly agitated, and electric current to the extent of about one hundred and fifty ampere-hours at current density of two to four amperes per square decimeter of cathode-surface is passed, whereby about eighty to eighty-five grams of nitrobenzene are thus converted into hydrazobenzene, while about 15–20 grams only are reduced to azoxy benzene. Both reduction products dissolve in the benzene, and when the reduction is completed they can be decanted easily from the surface of the cathode liquid. By adding the necessary quantity of hydrochloric acid to the solution in benzene the hydrazobenzene is converted into benzidine hydrochlorid, which is readily soluble in water, while the azoxy benzene remains dissolved in the benzene, and therefore can easily be separated from the aqueous solution of benzidine hydrochlorid. The solution of azoxy benzene in benzene is then returned to the cathode-compartment, together with a fresh portion of nitro benzene. Any other hydrazo derivative and the corresponding benzidine derivatives may be converted similarly into hydrazo benzene and benzidine in the above manner.

Instead of benzene other indifferent solvents, as toluene, xylene, ether, &c., may be employed, and instead of caustic soda the electrolyte may consist of caustic potash or of solutions of alkali salts—as, for instance, solution of common salt. Further, instead of dissolving the reduction products, as indicated in the example, in the nascent condition the indifferent solvent may be added during or

after the electrolysis and the reduction products extracted by mixing and stirring said solvent with the cathode liquid.

What I claim is—

The herein-described manufacture of hydrazo derivatives by the electrolytic reduction of the corresponding nitro, azoxy and azo bodies suspended in an aqueous alkaline solution, which consists in adding a convenient solvent insoluble in water to the electrolyte, in order to dissolve the reduction products obtained by the electrolysis, thereby preventing the said products from depositing in a solid form and facilitating their removal from the cathode-compartment.

In witness whereof I have hereunto signed my name, this 21st day of February, 1906, in the presence of two subscribing witnesses.

OTTO DIEFFENBACH.

Witnesses:

JEAN GRUND,

CARL GRUND.