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MARTIN MOEST, HANS HERTLEIN, AND EHRLICH OPPERMANN, OF HÖCHST-ON-THE-MAIN, GERMANY, ASSIGNORS TO FARBWERKE, VORM. MEISTER, LUCIUS & BRÜNING, OF HÖCHST-ON-THE MAIN, GERMANY, A CORPORATION OF GERMANY.

ELECTROLYTIC REDUCTION OF ORGANIC COMPOUNDS BY MEANS OF TITANIUM COMPOUNDS.

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To all whom it may concern:

Be it known that we, MARTIN MOEST, Ph. D., HANS HERTLEIN, Ph. D., and EHRLICH OPPERMANN, Ph. D., citizens of the Empire of Germany, residing at Höchst-on-the-Main, Germany, have invented certain new and useful Improvements in the Reduction of Organic Substances by Means of Titanium Compounds in an Electrolytic Bath, of which the following is a specification.

It is known by the experiments of Knecht (*Ber. d. d. Chem. Ges.* 36, 166-169) that organic substances are most energetically reduced by titano salts. Thus titano chlorid reduces nitro compounds to amines, unsaturated acids to the corresponding saturated acids, azo bodies are decomposed, &c. The practical application of these compounds, however, has hitherto been impossible on account of their high price.

We now have found a process permitting a technical application of titano compounds for reducing purposes in a simple and cheap manner by conducting the reduction of organic substances by means of titano compounds in an electrolytic bath. Very small portions only of the respective titanium compound are requisite in the electrolyte, so that, in fact, the former is merely a carrier of the electrolytic hydrogen. As the electrolyte may be used again in many cases, the quantity of titanium salt requisite, as well as the technical loss, is very little. In a great number of cases the reduction may also occur without a diaphragm. This hitherto-unknown fact is based on the following observation:

If a titani solution—for instance, a solution of titani sulfate acidified with sulfuric acid—be electrolyzed in the absence of a diaphragm and with a lead cathode and platinum anode, then the whole of the hydrogen at the cathode is first used to reduce the titani salt, whereas the corresponding quantity of oxygen escapes at the anode. The yield in relation to the current is at first quantitative, but decreases in proportion as the contents of titano salt increases. Finally on the titano

salt having already become very considerable a kind of equilibrium sets in, when no further reduction occurs. At this stage of the process the proportion of titano to titani salt is unaltered even if the current continues to pass; but the proportion varies from the beginning, according to the conditions of the electrolysis. If, however, a substance capable of reduction is simultaneously introduced into this electrolytic cell—for instance, finely-divided azo-benzene—then the titano salt formed at the cathode is at once reoxidized by the conversion of the azo-benzene into benzidin, which is precipitated as sulfate. The organic substance serves, so to say, as "acceptor" (receiver) for the electrolytic hydrogen. In consequence of this the proportion of the titano salt compared with that of the titani salt remains very small, so that the yield in relation to the current is favorable, although no diaphragm is used.

We illustrate our process by the following examples:

Example I: A vessel lined with lead and serving as cathode contains diluted sulfuric acid, with any quantity of titani sulfate—for instance, two per cent.—dissolved in it. As anode may serve any first-class conductor which is not attacked. The circuit is then closed and a concentrated solution of ortho-nitro-para-cresol-ortho-sulfonate of sodium is preferably introduced, with stirring, at a moderate temperature. This introduction is best regulated in such a manner as to always leave some titano compound in the electrolyte. Part of the amido compound formed is directly precipitated. The remainder is obtained by concentrating the electrolyte. The whole is then filtered, and the electrolyte may be used for another operation.

Example II: The process of reduction may of course occur also in the presence of a diaphragm. This is particularly advantageous if a simultaneous production of chlorine is desired. In this case the operation is, for instance, as follows: Fifty liters of hydrochloric acid of three-per-cent. strength containing a solution of about one to two per cent. of titani-

um chlorid are introduced into the cathode-compartment of a cell, one kilo of nitrobenzene and six hundred cubic centimeters of alcohol being stirred into it. The anode-compartment contains an acidified solution of common salt. As electrodes may be used almost all first-class conductors which are not essentially attacked. The process occurs suitably with heating and a density of current of three to six amperes per square meter. As soon as somewhat more than the theoretical quantity of current is used the process is interrupted, and the anilin, which is obtained with excellent yield, is isolated in the usual manner.

Example III: The reduction of azo-benzene to benzidin may be carried out as follows: A vessel is used similar to that described in Example I. Lead, for instance, may be used as electrodes and a sulfuric-acid solution of sodium titanium sulfate as electrolyte. Finely-ground azo-benzene is then introduced into the liquid, heated to nearly the melting-point of the azo-benzene, and electrolyzed with a density of current of three to four amperes per square meter, the tension being three to four volts. Soon the benzidin sulfate is precipitated. On completion of the process it is filtered and converted into the free base in the usual manner, whereas the filtrate is re-conducted into the electrolyzer.

In the foregoing example for azo-benzene may be substituted azo-oxybenzene, which is also converted into benzidin. Like in Example II, a diaphragm may be used.

Example IV: If a quinone is to be reduced, the operation may occur as follows: The cathode-compartment of a cell is filled with a solution containing per liter twenty to thirty grams of hydrochloric acid, ten to twenty grams of titanium chlorid, and ten grams of benzo-quinone. The anode-compartment contains a solution of common salt. The

cathode is of lead, but may also consist of any other metal not essentially attacked. The process is conducted at ordinary temperature with a density of current of one to two amperes per square meter and interrupted as soon as the odor of quinone has disappeared or somewhat more than the theoretical quantity of current is used. The hydroquinone, obtained with a good yield, is isolated in the usual manner — for instance, with ether — whereupon the electrolyte may serve for another operation.

A great number of other organic substances may be reduced in a manner similar to that described in the above examples. Thus, for instance, from tetramethyldiamido-benzophenone may be obtained the corresponding hydrol. In a similar manner nitroso compounds — for instance, nitrosodimethylanilin, oximes, unsaturated acids, &c. — are converted into their respective products of reduction.

The temperature, the proportions of quantity, and current of the above examples may be varied within wide limits.

Having now described our invention, what we claim is —

The herein-described process for reducing organic substances by means of titanium compounds, which consists in conducting the reduction in an electrolytic bath in the presence of titanium compounds, substantially as set forth.

In testimony that we claim the foregoing as our invention we have signed our names in presence of two subscribing witnesses.

MARTIN MOEST.
HANS HERTLEIN.
EHRICH OPPERMAN.

Witnesses:

ALFRED BRISBOIS,
BERNHARD LYDECKER.