

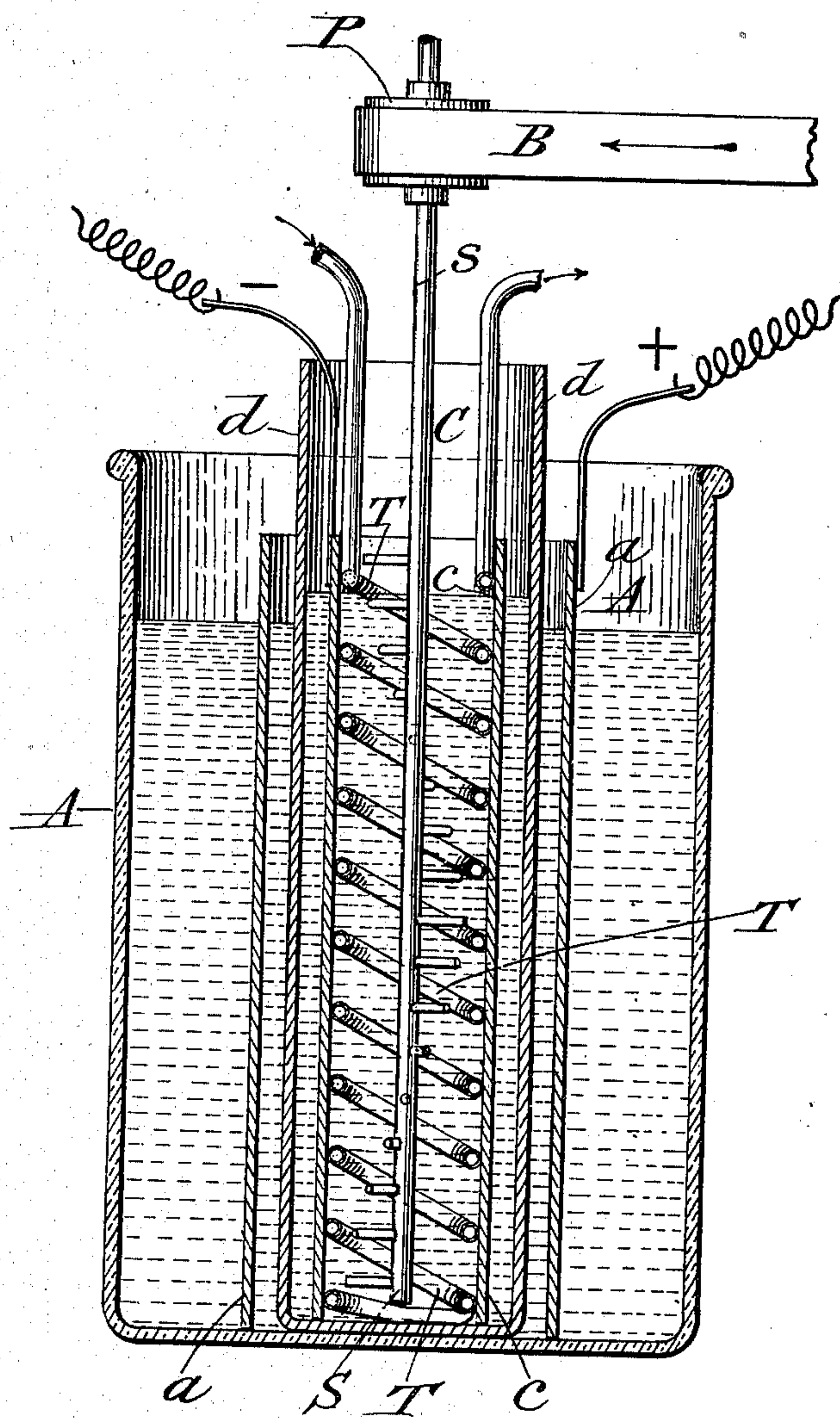
No. 736,206.

PATENTED AUG. 11. 1903.

M. BUCHNER.  
REDUCTION OF AROMATIC NITRO COMPOUNDS.

APPLICATION FILED DEC. 14. 1901.

NO MODEL.



Witnesses.

Bertie M. Murch.  
Anton D. Blatzner

Inventor :

Max Buchner,  
By George Massie,  
his Attorneys.



## UNITED STATES PATENT OFFICE.

MAX BUCHNER, OF MANNHEIM, GERMANY, ASSIGNOR TO C. F. BOEHRINGER & SOEHNE, OF MANNHEIM-WALDHOF, BADEN, GERMANY, A FIRM.

## REDUCTION OF AROMATIC NITRO COMPOUNDS.

SPECIFICATION forming part of Letters Patent No. 736,206, dated August 11, 1903.

Application filed December 14, 1901. Serial No. 85,956. (No specimens.)

To all whom it may concern:

Be it known that I, MAX BUCHNER, a citizen of the German Empire, residing at Mannheim, Germany, (whose post-office address is Friedrichsring 46,) have invented a certain new and useful Improvement in the Reduction of Aromatic Nitro Compounds; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the art of reducing nitro compounds, its object being the reduction of such bodies to the corresponding amines. In this art it has hitherto been possible as a general thing to effect such reduction only when the nitro body to be reduced was suspended in an acid-bath. Only in some special instances where such reduction phase was aided by apparently constitutional conditions had it been possible to reduce a nitro body electrolytically to the corresponding amine in an alcoholic alkaline solution. (Elbs, *Zeitschrift für Electro-Chemie*, V, p. 113, and Rhode, *ibid.*, VII, pp. 328, 338.)

No general practically available process is, however, known at the present time whereby any nitro compound can be converted in sufficient quantity into the corresponding amine from an aqueous alkaline bath, which may be a solution or a suspension and irrespective of the constitution of the starting material to be reduced. I have found in my researches in this field that nitro bodies dissolved or suspended in alkaline baths or baths containing a salt, oxid, or other compound of an alkali may be reduced to the corresponding amines if a cathode, preferably one of copper, is employed, together with powdered copper. The process conducted on these lines, I find, will effect the desired reduction with all nitro bodies thus far examined. As an example I may state that with the aid of the same I have been enabled to readily reduce meta-nitraniline to meta-phenylene-diamine, although Elbs and Kopp were not able to obtain any diamine from the same according to their method. (*Zeitschrift für Electro-Chemie*, V, p. 108.)

Under my process the current energy is as a general thing almost entirely utilized in the work of reduction, the yield in the correspond-

ing amine being slightly less than quantitative. Only where the amine formed is chemically changed by the alkali is there any considerable loss of energy. The bases formed, particularly those existing in a liquid form, are isolated by very simple methods, which are so well known as to need no detailed description. The reaction takes place in the same manner if the solution or mixture of the nitro compound in the cathode-bath is facilitated by the addition of an indifferent organic solvent, such as alcohol. Moreover, the oxides or salts of the alkalis may be replaced by the corresponding compounds of the earthy alkalies, and these are therefore the equivalents of the former.

The electrolytic reduction of the nitro bodies above set forth out of baths containing salts or compounds of alkalis or earthy alkalies may be combined with the production of alkalis or earthy alkalies and chlorine, which involves a very considerable advantage over the reducing methods from acid solutions or baths as hitherto practiced. I have further found that the employment of a copper cathode, though preferable, is not indispensable in carrying out my process, but that instead cathodes of other cathode materials may be employed if copper or one of its salts or compounds be added to the electrolyte. All cathode materials which I have thus far investigated in connection with this process have answered and led to the reduction of the nitro bodies. It is therefore to be noted that my invention, broadly considered, involves the use of an alkaline bath for reducing nitro compounds to the corresponding amine in combination with copper or a salt or compound of copper added to the electrolyte.

By the term "alkaline bath" when employed in the claims I desire to cover either a bath of alkali or earthy alkali proper or a bath containing a salt or other compound of an alkali or earthy alkali or a mixture of such baths. My invention, moreover, involves such other steps, features, and methods as will be hereinafter set forth and pointed out in the claims.

In order to enable others to fully understand my invention, I will now give a detailed description of the same with the aid of a num-



ber of examples embodying what I consider the preferred method of carrying the same into effect.

5 I. *Reduction of Nitrobenzene* ( $C_6H_5.NO_2$ ) to *Anilin* ( $C_6H_5.NH_2$ ).

(a) *Employment of a copper cathode in aqueous suspension.*—An electrolytic cell is separated into an anode and a cathode chamber by a diaphragm. Into the former I pour a concentrated solution of salt, (sodium chlorid,) ordinary cooking-salt being advantageously employed, and use in connection with the same an anode of carbon or other indifferent material. The cathode-chamber is provided with a good stirring device and a coiled pipe, which may serve both for cooling or heating the cathode-bath, according to need. Into the cathode-chamber thus equipped I introduce the cathode-bath, as follows: I pour one thousand four hundred and forty parts, by weight, of a concentrated solution of sodium chlorid, fifty to one hundred parts, by weight, of powdered copper, and one hundred and twenty-three parts, by weight, of nitrobenzene. The latter is preferably added gradually. The cathode employed in this example is one of copper. When all the materials are added, the reduction is preferably carried out with a current density of about fifteen hundred amperes per square meter and a temperature of about  $80^\circ$  to  $100^\circ$  centigrade. The cathode-bath is stirred, so as to keep the ingredients well mixed. The tension of the bath will under those conditions amount to about five volts. The process is discontinued after the amount of current calculated for the complete reduction to anilin has passed through the cell. The greater portion of the anilin thus obtained may be directly drawn off, while the rest may be isolated by well-known methods.

(b) *Employment of a copper cathode in alcoholic solution.*—The cathode-chamber of the apparatus described under Example I<sup>a</sup> is charged with one thousand parts, by weight, of a four-per-cent. solution of caustic soda (NaHO), two hundred and fifty parts, by weight, of alcohol, and one hundred parts, by weight, of copper powder, and the anode-space with a twelve-per-cent. solution of caustic soda. To the cathode-bath so prepared there are added gradually one hundred and twenty-three parts, by weight, of nitrobenzene. The current density employed for the electrolysis is fifteen hundred amperes per square meter, and the temperature of the bath is from  $80^\circ$  to  $86^\circ$  centigrade. A copper cathode is employed.

(c) *Employment of a barium-chlorid bath.*—The cathode-chamber is charged with one hundred and twenty-three parts, by weight, of nitrobenzene, one thousand parts, by weight, of a thirty-per-cent. aqueous solution of barium chlorid, and one hundred parts, by weight, of powdered copper, and the anode-space with a thirty-per-cent. solution of barium chlorid. The current density employed is fifteen hun-

dred amperes to the square meter. The other conditions of the process are the same as in Example I<sup>a</sup>.

(d) *Employment of a platinum cathode in presence of powdered copper.*—The electrolytic cell is again subdivided into an anode and a cathode space by means of a diaphragm. Into the former, which is provided with a carbon or other indifferent electrode, a saturated solution of common salt (NaCl) is introduced. Into the cathode-space, which is equipped with a platinum electrode, an effective stirring device, and a platinum coiled pipe for cooling or heating the bath, there are introduced one thousand four hundred and forty parts, by weight, of saturated salt solution (NaCl), and about one hundred parts, by weight, of finely-divided copper powder. A current of a density of fifteen hundred to two thousand amperes per square meter of cathode-surface is now passed through the cell, and one hundred and twenty-three parts, by weight, of nitrobenzene are gradually introduced into the reduction-chamber. The electrolysis is preferably carried out at a temperature of from  $80^\circ$  to  $100^\circ$  centigrade, and the current is cut off after the quantity of current calculated to be required for the complete reduction has passed through the cell. The anilin thus obtained is then isolated and purified according to known methods. The yield is very good.

(e) *Employment of a tin cathode in presence of divided copper.*—The apparatus and conditions of process and proportions are the same as under the foregoing example, with the exception that instead of a platinum cathode one of tin is employed. The yield of anilin is very good.

(f) *Employment of a copper cathode in the presence of cuprous chlorid.*—The apparatus and conditions of process are the same as under Example I<sup>a</sup>, with the exception that instead of the copper powder about one hundred parts, by weight, of cuprous chlorid are added to the cathode-bath.

(g) *Employment of a nickel cathode in the presence of copper sulfate.*—The cathode-space is charged with one thousand four hundred and forty parts, by weight, of concentrated solution of common salt (NaCl) and one hundred parts, by weight, of sulfate of copper (blue vitriol) and equipped with a nickel cathode. In other respects the conditions of the process are the same as under Example I<sup>a</sup>.

II. *Reduction of Orthonitrotoluene* ( $C_6H_4.CH_3.NO_2$ ) to *Orthotoluidin* ( $C_6H_4.CH_3.NH_2$ ).

The apparatus for carrying out the process for this reduction is arranged as in the first example or Example I<sup>a</sup>. Into the cathode-space one thousand four hundred and forty parts, by weight, of saturated solution of ordinary salt, (sodium chlorid,) together with from fifty to one hundred parts, by weight, of powdered copper and one hundred and thirty-seven parts, by weight, of orthonitro-



toluene, are introduced. In other respects the process is the same as under Example I<sup>a</sup>. The resultant o-toluidin is isolated by known methods.

5 III. Reduction of Meta - Nitranilin ( $C_6H_4NO_2NH_2$ ) to Meta - Phenylene - Diamin ( $C_6H_4.2NH_2$ ).

10 The apparatus employed and steps and conditions of the process under this example are the same as under the first example—viz., I<sup>a</sup>—with the exception that the cathode-bath is to consist of one thousand four hundred and forty parts, by weight, of a concentrated so-  
15 lution of ordinary salt, fifty to one hundred parts, by weight, of comminuted copper, and one hundred and thirty-eight parts, by weight, of meta-nitranilin. The resulting meta-phenylene-diamin after completion of the elec-  
20 trolysis will be found to be partially dissolved and partially suspended in the alkaline electrolyte. It may be separated from such solution or suspension according to well-known methods. The yield is about eighty per cent.  
25 As seen from this example, a very good yield of the amin is obtained according to my method, which is contrary to theoretical views and the experiments made by Ebbs and Rhode, (*Zeitschrift für Electro-Chemie*, XXII, p. 340,  
30 1890,) which resulted in the formation of the azo compound.

35 IV. Reduction of Alpha - Nitronaphthalin ( $C_{10}H_7NO_2$ ) to Alpha - Naphthylamin ( $C_{10}H_7NH_2$ ).

Here again I proceed as under Example I<sup>a</sup>, introducing into the cathode-compartment a mixture of one thousand four hundred and forty parts, by weight, of concentrated salt  
40 (sodium chlorid) solution, from fifty to one hundred parts, by weight, of powdered copper, and one hundred and seventy-three parts, by weight, of alpha-nitronaphthalin. The resultant alpha-naphthylamin is isolated ac-  
45 cording to known methods.

It will be understood, of course, that in the above examples one cell or any desirable or suitable number of cells in a battery may be employed at one time and that any conven-  
50 ient and suitable electrolyzing apparatus may be used, it being manifest that the process claimed by me is not confined to any particular form of apparatus.

It will be noted that in all cases I use a bath  
55 containing copper, either free in the form of comminuted copper or combined as a copper salt or compound. In all cases, therefore, the electric current is passed through the bath, which may be a solution or a suspension in the  
60 presence of copper. The bath is in all cases an alkaline bath—that is to say, it contains a salt or a compound of an alkali metal or of a metal of the alkaline-earth series. These al-  
65 kaline-earth metals are for the purpose of this invention the full equivalents of the alkali metals. The fact that the electrolyte-bath

may contain either a compound of an alkali metal or of an alkaline-earth metal for the purposes of this invention is to be borne in mind in construing the claims forming part of  
70 this specification. It is to be noted also that the process embodying my invention is carried out in some instances when the ingredients of the cathode-bath are in solution and in others when they are partly suspended in  
75 the bath. These different conditions of the bath I express generically in the claims by stating that the substance to be reduced is "mixed with the electrolyte."

In the accompanying drawing I have rep-  
80 resented one out of the many possible forms of apparatus and electrolytic cells for carrying out the process involved in my invention.

In the drawing, A represents the anode-chamber, containing the anode electrolyte, and  
85 a the anode; C, the cathode-chamber, containing the cathode electrolyte, and c the cathode, while d represents a diaphragm of any suitable material for the separation of the two  
90 electrolytes, according to the usual manner.

S represents a suitable stirrer arranged within the cathode electrolyte, the spindle or  
shaft s of which may be connected with any suitable source of power by a belt and pulley  
95 B P, as shown, or in any preferred way.

The cooling of the cathode-compartment may be effected by a cooling-coil T, arranged within the said cathode-compartment, as  
100 shown, said coil serving for the circulation of any cooling fluid, such as cold water.

I claim—

1. The process of reduction which consists in passing an electric current through the sub-  
stance to be reduced in an electrolyte contain-  
105 ing a compound of an alkali metal or of an alkaline-earth metal, in the presence of copper.

2. The process of reduction which consists in passing an electric current through a nitro  
compound contained in an electrolyte con-  
110 taining a compound of an alkali metal or of an alkaline-earth metal, in the presence of copper.

3. The process of reduction which consists in passing an electric current through the sub-  
stance to be reduced in an alkaline electro-  
115 lyte in the presence of copper.

4. The process of reduction which consists in passing an electric current through a nitro  
compound in an alkaline electrolyte in the  
120 presence of copper.

5. The process of reduction which consists in passing an electric current through a nitro  
compound of the aromatic series contained in an electrolyte containing a compound of an  
125 alkali metal or of an alkaline-earth metal, in the presence of copper, until the corresponding amin is produced.

6. The process of reduction which consists in mixing the substance to be reduced with  
an alkaline electrolyte containing copper, and  
130 passing the electric current through the same.

7. The process of reduction which consists



in mixing a nitro compound with an electrolyte containing a compound of an alkali metal or of an alkaline-earth metal, and copper, and passing the electric current therethrough.

5 8. The process of reduction which consists in mixing a nitro compound of the aromatic series with an electrolyte containing a compound of an alkali metal or of an alkaline-earth metal, and copper, and passing the electric current therethrough.

10 9. The process of reduction which consists in mixing a nitro compound of the aromatic series with an alkaline electrolyte containing copper, and passing the electric current there-  
15 through.

10. The process of reduction which consists in mixing a nitro compound with cathode-bath, containing a compound of an alkali metal or of an alkaline-earth metal, and pass-  
20 ing an electric current therethrough in the presence of a copper cathode.

11. The process of reduction which consists in mixing a nitro compound with an alkaline cathode-bath and passing an electric current  
25 therethrough in the presence of a copper cathode.

12. The process of reduction which consists in mixing the compound to be reduced with an electrolyte containing a compound of an al-  
30 kali metal or of an alkaline-earth metal, and copper and passing an electric current there- through.

13. The process of reduction which consists in mixing the compound to be reduced with an  
35 alkaline electrolyte containing copper, and passing an electric current therethrough.

14. The process of reduction which consists in mixing the compound to be reduced with an electrolyte containing a compound of an al-  
40 kali metal or of an alkaline-earth metal, and finely-divided metallic copper, and passing an electric current therethrough.

15. The process of reduction which consists in mixing the compound to be reduced with a  
45 cathode-bath containing a compound of an alkali metal or of an alkaline-earth metal and copper, and passing the electric current there- through in the presence of a copper cathode.

16. The process of reduction which consists  
50 in mixing the compound to be reduced with a cathode-bath containing a compound of an alkali metal or of an alkaline-earth metal, and finely-divided metallic copper, and passing

an electric current therethrough in the pres-  
ence of a copper cathode.

17. The process of reduction which consists in mixing a nitro compound with an electro-  
lyte containing an alkali compound and cop-  
per, and passing an electric current there-  
through.

18. The process of reduction which consists in mixing a nitro compound with an electro-  
lyte containing a compound of an alkali metal  
or of an alkaline-earth metal, and finely-di-  
vided metallic copper, and passing an electric  
current therethrough.

19. The process of reduction which consists in mixing a nitro compound with a cathode-  
bath containing a compound of an alkali metal  
or of an alkaline-earth metal, and copper, and  
passing the electric current therethrough in  
the presence of a copper cathode.

20. The process of reduction which consists in mixing a nitro compound with a cathode-  
bath containing a compound of an alkali metal  
or of an alkaline-earth metal, and finely-di-  
vided metallic copper, and passing an electric  
current therethrough in the presence of a cop-  
per cathode.

21. The process of reduction which consists  
80 in mixing a nitro compound of the aromatic series with an electrolyte containing a com-  
pound of an alkali metal or of an alkaline-  
earth metal, and finely-divided metallic cop-  
per, and passing an electric current there-  
through.

22. The process of reduction which consists in mixing a nitro compound of the aromatic  
series with a cathode-bath containing a com-  
pound of an alkali metal or of an alkaline-  
earth metal, and copper, and passing the elec-  
tric current therethrough in the presence of  
a copper cathode.

23. The process of reduction which consists  
95 in mixing a nitro compound of the aromatic series with a cathode-bath containing a com-  
pound of an alkali metal or of an alkaline-  
earth metal, and finely-divided metallic cop-  
per, and passing an electric current there-  
through in the presence of a copper cathode.

In testimony whereof I affix my signature  
in presence of two witnesses.

MAX BUCHNER.

Witnesses:

EDWARD KÖBNER,  
JACOB ADRIAN.