UNITED STATES PATENT OFFICE.

BENNO HOMOLKA, OF HÖCHST-ON-THE-MAIN, GERMANY, ASSIGNOR TO THE FARBWERKE, VORMALS MEISTER, LUCIUS & BRÜNING, OF SAME PLACE.

PROCESS OF MAKING ROSANILINE DYES.

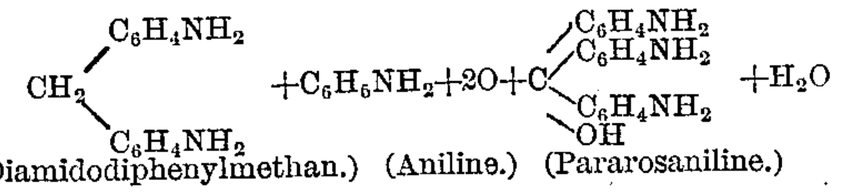
SPECIFICATION forming part of Letters Patent No. 471,638, dated March 29, 1892.

Application filed December 13, 1890. Serial No. 374,616. (No specimens.) Patented in England December 23, 1889, No. 20,678; in France December 23, 1889, No. 202,769; in Belgium December 31, 1889, No. 88,989, and in Italy April 3, 1890, XXIV, 27,054, LIII, 166.

To all whom it may concern:

Be it known that I, BENNO HOMOLKA, doctor of philosophy, a subject of the Emperor of Austria-Hungary, residing at Höchst-on-the-Main, in the Empire of Germany, have invented certain new and useful Improvements in the Production of Compounds of the Rosaniline Series, (for which I have received patents in England, No. 20,678, dated December 23, 1889; in France, No. 202,769, dated December 23, 1889; in Belgium, No. 88,989, dated December 31, 1889, and in Italy, XXIV, 27,054, LIII, 166, dated April 3, 1890;) 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 production of compounds of the rosaniline series by joint oxidation of compounds of the diphenylmethan group and aromatic amines, for example:



(Diamidodiphenylmethan.) (Aniline.) (Pararosaniline.)

The production may be effected by starting with the anhydroformaldehyde amines, $C_xH_yN=CH_2$, themselves causing the two stages of the operation to go on in the same vessel—that is to say, first, the formation of the compound of the diphenylmethan group, and, second, the oxidation. Also the formaldehyde may be introduced into the reaction mass, so that the operation may begin with the formation of the anhydroformaldehyde amine.

The process is more fully explained by the following examples:

EXAMPLE 1.

Ten parts, by weight, of anhydroformaldehyde aniline, fifty parts, by weight, of hydrochlorate of ortho-toluidine, ten parts, by weight, of aniline, twelve parts, by weight, of nitro-benzole, and one-half part, by weight, of iron filings or the eqivalent quantity of ferrous chloride are heated in an enameled vessel to about 170° centigrade for from two to three hours. Then the aniline and nitro-benzole are driven off by a current of steam and the magenta is precipitated from the solution by means of common salt.

EXAMPLE 2.

Ten parts, by weight, of diamidodiphenylmethan, thirty parts, by weight, of hydrochlorate of ortho-toluidine, eighteen parts, by weight, of ortho-toluidine, twelve parts, by weight, of orthonitrotoluol, and one-half part, by weight, of iron filings (or ferrous chloride) are treated as described in the preceding example. As oxidizing agents may be employed in the operations described nitro-benzole, orthonitrotoluol, paranitrotoluol, or a mixture of these compounds; also, nitroxylol, salts of oxide of iron, arsenical acid, azobenzole, and similar oxidizing agents.

EXAMPLE 3.

Production of triphenylrosaniline.—As raw material for the production of this body I employ the product resulting from the reaction between formaldehyde and diphenylamine in the presence of hydrochloric acid—the diphenyldiamido-diphenylmethan. Ten parts, by weight, of diphenyldiamido-diphenylmethan, fifty parts, by weight, of hydrochlorate of diphenylamine, twenty parts, by weight, of diphenylamine, five parts, by weight, of orthonitrotoluol, and three parts, by weight, of ferrous chloride (iron filings) are heated to 170° for three hours. The melt is treated hot with alcohol and filtered. From the filtrate on cooling the hydrochlorate of triphenylrosaniline is precipitated in the form of a crystalline mass, which is filtered and dried.

EXAMPLE 4.

Production of diphenylrosaniline.—Ten parts, by weight, of diphenyldiamido-diphenylmethan, fifty parts, by weight, of hydrochlorate of ortho-toluidine, twenty parts, by weight, of ortho-toluidine, five parts, by weight, of orthonitrotoluol, and three parts, by weight, of ferrous chloride (iron filings) are heated on an oil bath to 170° centigrade for three hours. The hot mass of the reaction is poured into diluted hydrochloric acid, boiled, and filtered. The residue is hydrochlorate of diphenylrosaniline, which is easily soluble in alcohol or

aniline and can be readily converted into sulphonic acids, available commercially as coloring-matters.

In the examples 3 and 4 there may be substituted for the diphenyldiamido-diphenylmethan any of the reaction products of formaldehyde with secondary aromatic bases—that is to say, ortho and para tolylphenylamine, ortho-ditolylamine, alpha and beta naphthylphenylamine, alpha and beta naphthyl-ortho-tolylamine, or mixtures of two of these bases.

For the diphenylamine mentioned in example 3 may be substituted any of the secondary bases enumerated above, and for the ortho-toluidine mentioned in example 4 may be substituted aniline or xylidine; also for the orthonitrotoluol of examples 3 and 4 may be substituted any of the oxidizing agents hereinbefore mentioned.

The compounds of the rosaniline series thus prepared are intended for use in dyeing and printing.

The coloring-matters are in the form of a crystalline powder with metallic-green luster. The alkalized, methylized, and ethylized coloring-matters are soluble in water and alcohol with red to violet coloring. The phenylized coloring-matters are insoluble in water, soluble in alcohol with blue tint. They are all insoluble in ether, chloroform, benzine, and other carburets of hydrogen. In concentrated mineral acids they dissolve with yellow to orange-yellow coloring.

What I claim as my invention, and wish to secure by Letters Patent, is—

The process herein described for the production of coloring-matters of the rosaniline series, which consists in treating diamidodiphenylmethan bodies with oxidizing agents in presence of hydrochlorates of aromatic amines, substantially as set forth.

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

BENNO HOMOLKA.

Witnesses:
JOSEF REVERDY,
HEINRICH HAHN.