

UNITED STATES PATENT OFFICE.

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DIAMIDOFORMYL DIPHENYLAMIN AND PROCESS OF MAKING SAME.

No. 805,890.

Specification of Letters Patent.

Patented Nov. 28, 1905.

Application filed February 4, 1903. Serial No. 141,832. (Specimens.)

To all whom it may concern:

Be it known that I, OTTO SOHST, Ph. D., a citizen of the Empire of Germany, residing at Höchst-on-the-Main, Germany, have invented certain new and useful Improvements in Para-Para₁-Diamidoacidyl-diphenylamin and its Transformation into Diamidodiphenylamin, of which the following is a specification.

Para-para₁-diamidodiphenylamin has hitherto been obtained by reducing indamin; but as this process is inconvenient and the yield is not good a simpler and cheaper method for obtaining this technically-valuable base has been sought.

The para-para₁-dinitrodiphenylamin (*Zeitschrift f. angew. Chemie*, 1899, 1,051, and *Berichte*, XVI, 2,576) readily obtainable by the nitration of acidyl derivatives of diphenylamin and subsequent hydrolysis appears not to be suitable as parent material, for hitherto its reduction was only possible by use of the expensive stannous chlorid or zinc-dust and glacial acetic acid. (See above references.)

Nothing has been known hitherto about reducing the para-para₁-dinitrodiphenylamin with the comparatively cheap reducing agent, iron. Experiments have shown that it is possible to reduce the dinitro compound with iron; but the product cannot be separated in a pure state from the iron and in a rational manner, giving a good yield.

By operating, for instance, in the manner already described in *Berichte*, XXVIII, 2,969, for ortho-para-dinitrodiphenylamin the yield of pure base is very moderate, and as the para-para₁-diamidodiphenylamin is less soluble than the ortho-para-compound a large proportion of water is requisite to isolate the base from the reduced mass, and for this reason alone this mode of working is technically inapplicable.

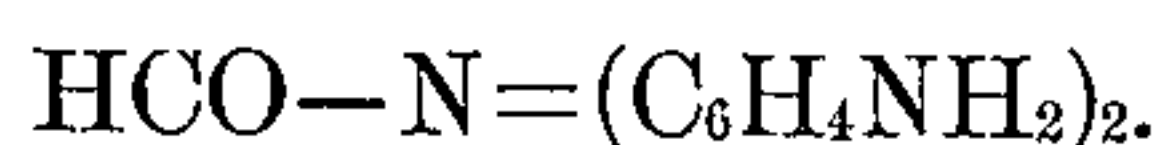
I have found that by using iron the reduction occurs more smoothly if for dinitrodiphenylamin the acidyl-dinitrodiphenylamin is used; but by this modification the process does not become available for industrial purposes, for it is just as difficult to isolate the acidyl-diamidodiphenylamin (melting-point 193° or 195° centigrade, respectively) from the reduced mass as the diamidodiphenylamin itself. I have further found that it is possible to extract the acidyl-diamidodiphenylamin from the reduced mass with hydrochlo-

ric or, better still, sulfuric acid without any decomposition or formation of color, as is the case, for instance, when operating with para-para₁- or ortho-para-dinitrodiphenylamin. The acidyl-para-para₁-diamidodiphenylamin, hitherto unknown, is readily obtained with a good yield by this process. It is easily hydrolyzed. When heated with an excess of sulfuric acid, it is transformed into para-para₁-diamidodiphenylamin. For this purpose it is not necessary to isolate the acidyl-para-para₁-diamidodiphenylamin; but the solution obtained by acidifying the reduced mass is treated with an excess of sulfuric acid and then heated. The readily-soluble sulfate of acidyl-para-para₁-diamidodiphenylamin is thus hydrolyzed, and the difficultly-soluble sulfate of para-para₁-diamidodiphenylamin crystallizes when the solution is cold.

The dinitroacidyl compounds used as parent material—namely, para-para₁-dinitroformyl-diphenylamin and para-para₁-dinitroacetyl-diphenylamin—may be obtained by dinitrating the formyldiphenylamin produced by the action of formic acid on diphenylamin (*Berichte*, VIII, 1,195) or the acetyldiphenylamin in a sulfuric-acid solution containing a mixture of nitric and sulfuric acid (*Ber.*, XIV, 2,366) in a similar manner as described in the *Zeitschrift f. angew. Chemie*, 1899, p.1,051. The nitrated mixture is then poured into ice-water and the precipitate of feeble-yellow color is filtered, washed, and dried.

According to the above observations the reduction and hydrolysis may be carried out, for instance, as follows: Fourteen kilograms of finely-ground dinitroformyldiphenylamin, mixed with water, are slowly introduced into a mixture of thirty kilograms of iron-filings, two hundred and fifty liters of water, and about one-half kilogram of sulfuric acid of 66° Baumé, specific gravity, heated to 60° to 90° centigrade. The whole is stirred at this temperature (about five hours) until the precipitate suspended in the reduced mass no longer appears brown, but black. The mass when cooled to 40° to 50° centigrade is then directly treated with 20–40 kilograms of sulfuric acid of fifty per cent. strength until an acid reaction sets in and hydrogen begins to be evolved. It is then filtered, and when cold the base is separated from the filtrate by adding sodium acetate. The diamidoformyldi-

phenylamin is thus obtained as small slightly-colored crystals having the formula



5 To obtain the para-para₁-diamidodiphenylamin, the filtrate, which is obtained by acidifying the reduced mass with sulfuric acid, may be treated with about ten kilograms of sulfuric acid of 66° Baumé, specific gravity, and
10 then boiled. When cold, the difficultly-soluble sulfate of para-para₁-diamidodiphenylamin then separates, forming a magma, while small proportions of isomeric bases remain in suspension.

15 If for dinitroformyldiphenylamin dinitroacetyldiphenylamin is used, the same products may be obtained. The hydrolysis, however, is somewhat slower.

20 The para-para₁-diamidoformyl-(acetyl)-diphenylamin is to serve for the manufacture of dyestuffs and diamidodiphenylamin.

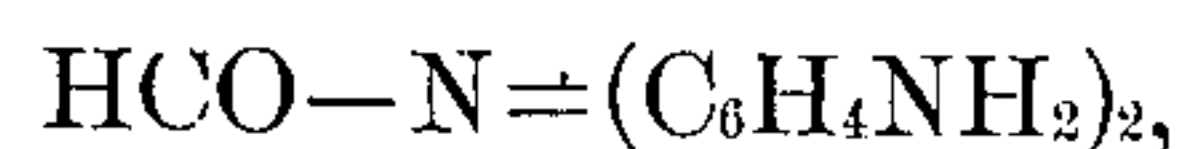
Having now described my invention, what I claim is—

25 1. The process of making diamidoformyldiphenylamin, which consists in reducing dinitro-

troformyldiphenylamin with iron in the presence of little acid, separating the base from the excess of iron by means of the easily-soluble sulfate and then isolating it with sodium acetate.

2. The process of making diamidodiphenylamin, which consists in reducing dinitroformyldiphenylamin with iron and then decomposing the diamidoformyldiphenylamin by heating it with acids.

3. As a new article of manufacture, the para-para₁-diamidoformyldiphenylamin having the formula



said product crystallizing from water in small crystals and being soluble in almost all solvents.

In testimony that I claim the foregoing as my invention I have signed my name in presence of two subscribing witnesses.

OTTO SOHST.

Witnesses:

ALFRED BRISBOIS,

BERNHARD LEYDECKER.