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OTTO NICODEMUS AND WALTER SCHMIDT, OF FRANKFORT-ON-THE-MAIN-HOCHST, GERMANY, ASSIGNORS TO I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, OF FRANKFORT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY

PROCESS OF PREPARING SECONDARY AND TERTIARY ALIPHATIC AMINES FROM PRIMARY ALIPHATIC BASES

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The present invention relates to process of preparing secondary and tertiary aliphatic amines from primary aliphatic bases.

The manufacture of secondary aliphatic bases from primary amines by catalytic elimination of ammonia in the gaseous phase has already often been the subject of investigations. These trials have, however, not led to the desired result because the elimination of ammonia was always accompanied by a dehydrogenation of the aliphatic bases and with a decomposition of the products of dehydrogenation.

We have now found that primary aliphatic amines in the gaseous phase can be converted catalytically in an easy manner, with elimination of ammonia, into secondary and tertiary bases without accompanying decomposition into hydrocarbons or dehydrogenation to nitriles, if case is taken that the working temperatures are below 300° C. As suitable catalysts for this purpose are the metals which are known to have hydrogenating or dehydrogenating action, such as, for instance, copper, cobalt, nickel or platinum. According to the character of the metal used the temperature at which the desired change occurs and the yield of converted primary bases vary; in most cases the temperature is about 200° C.; when copper is used, it is somewhat higher, about 260° C.–280° C. Only above the optimum working temperatures do the metals determine dehydrogenation and decomposition.

The preferred mode of operating consists in passing the aliphatic primary base, such as for instance methylamine, ethylamine or butylamine, in gaseous state over a metal which is known to be a hydrogenating catalyst, the metal being in a finely subdivided form, advantageously carried on a porous material and heated, according to the character of the metal, to a temperature of between 150° C. and 280° C. From the product secondary and tertiary aliphatic amines are obtained besides ammonia; whether the secondary amines or the tertiary amines are produced in the larger or predominating proportion depends mainly on the velocity of the gaseous current.

The following examples serve to illustrate our invention, but they are not intended to limit it thereto:—

1. A continuous current of ethylamine is passed at a temperature between 260° C. and 270° C., over a contact containing about 6 per cent. of copper which is prepared by subjecting copper carbonate carried on pumice stone to careful reduction in a current of hydrogen. The velocity of the vapor of ethylamine is regulated in such a manner that every hour 140–150 grams of the amine pass the tube filled with two liters of a catalyst of copper. The products leaving the contact are cooled in stages, the first refrigerator being kept at a temperature between 30° C. and 40° C. and the last at −10° C. In the first refrigerator the diethylamine and triethylamine formed are condensed, whilst the unchanged ethylamine is liquefied in the low-temperature refrigerator and thereby separated from the ammonia which has been formed. The unchanged ethylamine, which amounts to about 25–30 per cent. of the ethylamine used during one passage over the contact, is reconducted into the contact chamber.

The crude product condensed at the higher temperature consists of 70 per cent. of diethylamine and 28 per cent. of triethylamine, the rest being condensation products of higher boiling point.

2. Vapor of ethylamine is passed at a temperature between 220° C. and 230° C. over a contact made by subjecting cobalt carbonate carried on pumice stone to reduction by a current of hydrogen, the velocity being such that 65 per cent. of the vapor is converted. By working up the product as described above, a condensate is obtained which contains 78 per cent. of diethylamine and 20 per cent. of triethylamine. By fractionating the condensate diethylamine of 90 per cent. strength can easily be obtained.

3. Vapor of normal butylamine is passed over the contact described in Example 1 so that about 70 per cent. of the butylamine is converted. The condensate obtained as described in Example 1 consists of 76 per cent. of dibutylamine, the rest being tributylamine

and small quantities of condensation products.

We claim:

1. Process of preparing secondary and tertiary aliphatic amines from primary aliphatic amines, which comprises passing the vapor of a primary aliphatic amine at a temperature below 300° C. over a metal which is known to be a hydrogenating catalyst.

2. Process of preparing diethylamine and triethylamine from ethylamine, which comprises passing the vapor of ethylamine at a temperature below 300° C. over a metal which is known to be a hydrogenating catalyst.

3. Process of preparing diethylamine and triethylamine from ethylamine, which comprises passing the vapor of ethylamine at 260° C. to 280° C. over a catalyst of copper.

In testimony whereof, we affix our signatures.

OTTO NICODEMUS.
WALTER SCHMIDT.