

UNITED STATES PATENT OFFICE

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METHOD OF PREPARING CYCLOHEXYL AMINES

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9 Claims. (Cl. 260—563)

The present invention relates to the preparation of cyclohexyl amine and it has particular relation to its preparation by the direct hydrogenation of aniline.

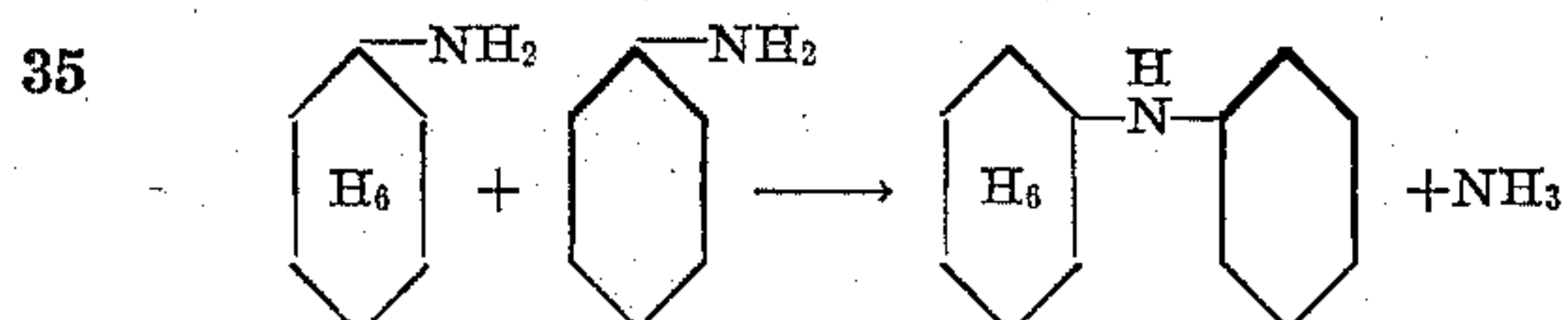
5 The main objects of the invention are:

To provide a process of hydrogenating aniline to form cyclohexyl amine in which the formation of various objectionable high boiling products, such as dicyclohexylaniline, cyclohexylaniline, and the like is substantially eliminated or at least greatly reduced, and

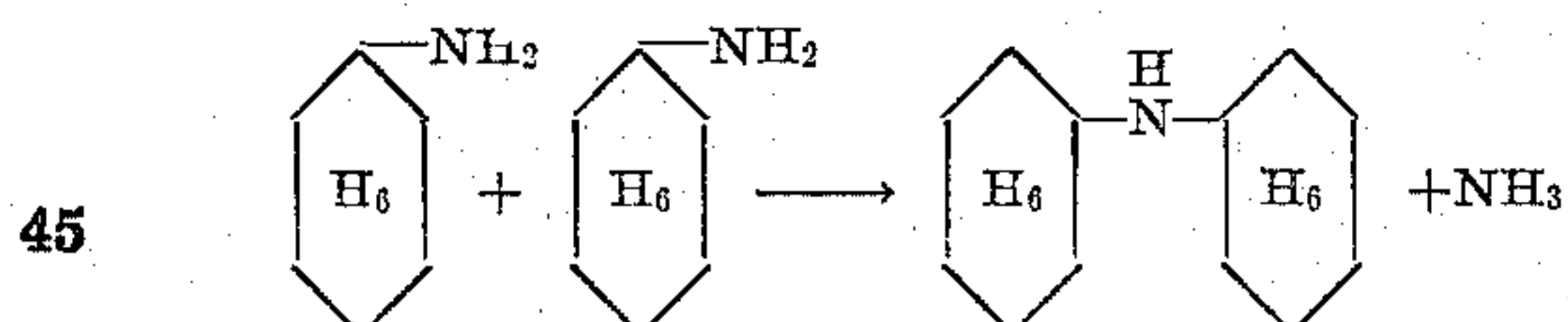
15 To provide a process of the above indicated character which is simple and inexpensive of operation and which results in exceptionally high conversion of aniline into hydrogenated products.

These and other objects will be apparent from consideration of the following specification and the appended claims.

20 It has heretofore been proposed to prepare cyclohexyl amine by subjecting the corresponding aromatic amine (aniline) to contact at relatively high temperature and at high pressures with hydrogen gas in the presence of a suitable catalyst, such as finely divided platinum or reduced nickel or cobalt. Although cyclohexyl amine could be formed by application of the process, the method was never commercially satisfactory because large amounts of various high boiling products, such as dicyclohexyl amine and cyclohexylaniline were formed as a result of various secondary reactions. The reaction involved in the formation of cyclohexylaniline may be represented by the equation:



40 while that involved in the formation of dicyclohexyl amine may similarly be represented by the equation:



50 These materials in general are of less value than cyclohexyl amine and, accordingly, it is desirable that their formation in the hydrogenation of aniline be reduced to a minimum. Heretofore, no completely satisfactory method of eliminating their formation was available. In most commercial processes they were formed to the extent of 40 or 50, or even 60%. The typical product, 55 as described by Ellis in his textbook "Hydrogena-

tion of Organic Substances," third edition, published by D. Van Nostrand of New York, page 243, section 2251, has the following composition:

1. A fraction boiling about 80° C. (a little benzene and cyclohexylene).
2. Cyclohexylamine, $\text{C}_6\text{H}_{11}\text{NH}_2$, B.P. 134° 30%.
3. Aniline (182°).
4. 30% dicyclohexylamine (252°): 30% cyclohexylaniline (279°) and some diphenylamine (311°).

The same text in section 2253 describes a further process in which highly purified aniline was hydrogenated with osmium as the catalyst. The product had the following composition:

"4% benzene, 25% cyclohexylamine, 20% dicyclohexylamine, 5% N-cyclohexylaniline and 29% unchanged aniline."

20 The present invention is based upon the discovery that the formation of cyclohexylaniline, dicyclohexyl amine and other by-products in the hydrogenation of aniline may be reduced to a minor amount, if the aniline which is employed in the reaction is first subjected to treatment with lead in a suitable form.

A lead oxide such as litharge, lead dioxide or minium may conveniently be employed in the treatment. The lead is simply added in a suitable amount, for example, 1% more or less, to the aniline and the mixture is subjected to heat treatment at about 180° C. for a few hours (three, more or less). The aniline is then distilled. Aniline formed by any convenient process (e. g. by amination of chlorbenzene or by reduction of nitrobenzene) may be employed.

The aniline, after treatment with lead oxide, is subjected to hydrogenation in an autoclave at a suitable temperature and pressure in the presence of a conventional catalyst. The various conditions involved in such hydrogenation are conventional and well understood by those skilled in the art. The autoclave preferably is provided with some convenient means of agitation, for example a rotary agitator for purposes of thoroughly contacting the aniline with the hydrogen gas. Pressures of 50 to 85 atmospheres and temperatures of about 200 to 235° C. are preferred. However, these ranges need not be strictly adhered to. Any standard catalyst may be employed in the hydrogenation, but excellent results may be obtained by employment of a catalyst obtained by hydrolyzing an alloy of nickel and aluminum or calcium or magnesium. For example, an alloy comprising 33 parts of nickel

and 66 parts of alkaline earth metal treated with hot water or steam, produces good results.

The following results were obtained by hydrogenation of a plurality of batches of aniline of good grade (for example, an aniline from amination of chlorobenzene) 95% of which distills within the range of 183.5 to 184° C. and which is usually substantially free of sulfur compounds and such like catalyst poisons.

Aniline	NiMg catalyst (alloy)	Time hydrogenation	Temperature	Pressure	Hydrogenation	Ratio cyclohexylamine to high boiler
	Percent	Hours	° C.	Atmospheres	Percent	
Plain	0.63	4	225	65-85	7.5	6:1
Do.	1	9	211-220	50-80	19.6	3:1
1% lead oxide, admixed, not distilled	1	9	218	56-66	32.2	5.4:1
Heated 3 hrs. with, and distilled over, 0.8% lead oxide	1	9	215	55-65	45	24:1
Heated 3 hrs. with, and distilled over, 1% of lead oxide	1½	16	230	58	78½	23:1

The data in the first and second horizontal columns were obtained by hydrogenation of plain commercial aniline; while those in the succeeding columns were obtained by corresponding hydrogenation of aniline which had previously been subjected to various treatments with lead oxide. Under the heading "Per cent hydrogenation" is respectively given the total percentages of aniline which were converted into hydrogenated products including cyclohexyl amine and high boiler, and "Ratio cyclohexyl amine to high boiler" means the ratio by weight of cyclohexyl amine to dicyclohexyl amine plus cyclohexyl amine plus diphenylamine in the hydrogenated reaction product.

From the data it will be apparent that by suitable treatment of aniline with lead oxide, the proportion of high boilers formed may be reduced to negligible proportions of the total hydrogenated product. The total amount of hydrogenated product is generally higher than that obtained from untreated aniline but the main feature of the process resides in the unexpected reduction of the formation of high boiler materials.

Explanation of this surprising reduction of high boiler formation by applicant's process is difficult. Assumption that it is because of removal of possible catalyst poisons, such as sulfur compounds, does not seem to be justified because the use of highly purified aniline, according to section 2253 of the previously cited book by Ellis "Hydrogenation of Organic Substances", does not suppress high boiler formation. Moreover, only one phase of the reaction, namely, high boiler formation is substantially affected. It is difficult to explain this selective action upon the basis of removal of a catalyst poison. It seems more logical to assume that lead treatment results in the addition of some material to, or formation of some compound in the aniline that suppresses high boiler formation but not ring hydrogenation. The nature of such compound has not yet been ascertained.

The lead oxide employed in the process may, if desired, be replaced by some other convenient form of lead, such as lead hydroxide, lead carbonate. Basic lead carbonate, powdered lead, etc., may also be used. Other basic compounds, including oxides of other metals such as copper, zinc and calcium may also be admixed with lead oxide, or under some circumstances, they may even be used alone.

What I claim is:

1. A method of preparing cyclohexyl amine by hydrogenation of aniline which comprises heating aniline in the presence of a pretreating agent selected from the group consisting of lead, lead oxides and basic compounds of lead at an elevated temperature below the decomposition point of aniline for a sufficient period to suppress the formation of high-boiling compounds that normally

result during the hydrogenation of aniline, separating the aniline from said agent, and thereafter subjecting the aniline to hydrogenation by contact with hydrogen gas in the presence of a catalyst of hydrogenation.

2. The process as defined in claim 1 and further characterized in that the aniline is separated from the agent by distillation.

3. A method as defined in claim 1 in which the hydrogenation is conducted at a temperature approximately within the range of 200-230° C. and at a pressure of approximately 30 to approximately 100 atmospheres.

4. A method as defined in claim 1 in which the catalyst of hydrogenation consists of a hydrolyzed alloy of nickel and a metal selected from the group consisting of alkaline earth metals, magnesium and aluminum.

5. A process as defined in claim 1 in which the hydrogenation is effected at a temperature of about 215° C., a pressure of about 50 to about 65 atmospheres and in the presence of a catalyst consisting of the product obtained by hydrolysis of an alloy of nickel and magnesium.

6. A method of suppressing the formation of high-boiling compounds normally resulting on hydrogenation of aniline to produce cyclohexyl amine which comprises heating the aniline prior to the hydrogenation with a basic lead compound at a temperature of about 180° C. for a period of approximately three hours.

7. A process as defined in claim 1 in which the agent is litharge.

8. In the method of producing cyclohexyl amine from aniline by hydrogenation in the presence of a nickel catalyst, the preliminary step whereby the proportion of high-boiling products which normally result under the conditions of hydrogenation is reduced, consisting in heating the aniline at an elevated temperature below the decomposition point of aniline with a material selected from the group consisting of lead, lead oxides, and basic compounds of lead, which are subsequently separated therefrom.

9. A method as defined in claim 1 and further characterized in that the agent is an oxide of lead in admixture with an oxide of a metal selected from the group consisting of copper, calcium, and zinc.

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CERTIFICATE OF CORRECTION.

Patent No. 2,184,070.

December 19, 1939.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 4, for the word "about" read above; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 6th day of February, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.