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PROCESS FOR PRODUCING UNSYMMETRICAL DIALKYLHYDRAZINES BY CATALYTIC HYDROGENATION OF DIALKYLNITROSAMINES

Paul Besson and Albert Nallet, La Chambre, and Gilbert Luiset, Saint-Etienne-de-Cuines, France, assignors to Société d'Electro-Chimie, d'Electro-Métallurgie et des Aciéries Electriques d'Ugine, Paris, France, a corporation of France

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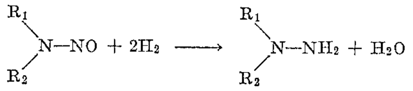
3 Claims. (Cl. 260—583)

This invention relates to catalytic hydrogenation of dialkylnitrosamines to produce unsymmetrical dialkylhydrazines and more particularly to hydrogenation of dialkylnitrosamines in the liquid phase and in the presence of Raney nickel which has been obtained from alloys of Ni-Al subjected to treatment by a caustic solution.

One of the known methods for preparation of unsymmetrical dialkylhydrazines comprises carrying out the hydrogenation of the corresponding dialkylnitrosamines according to the reaction:

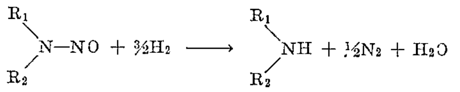


$$\left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle N\!-\!NO + 2H_2 \longrightarrow \left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle N\!-\!NH_2 + H_2O$$

wherein R_1 and R_2 represent hydrocarbonaceous radicals.

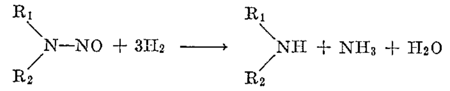
In spite of the extreme simplicity of this reaction, the reduction of unsymmetrical dialkylnitrosamines into dialkylhydrazines is a very delicate operation because the following side reactions may become preponderant under certain conditions:

(a)



$$\left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle N\!-\!NO + \tfrac{3}{2}H_2 \longrightarrow \left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle NH + \tfrac{1}{2}N_2 + H_2O$$

(b)



$$\left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle N\!-\!NO + 3H_2 \longrightarrow \left.\begin{matrix}R_1\\R_2\end{matrix}\right\rangle NH + NH_3 + H_2O$$

For some years, only the reduction processes other than the catalytic hydrogenation enabled one to limit the two above parasite reactions rather successfully.

These processes, while producing satisfactory yields on the whole, nonetheless are subject to some drawbacks which include the cost of the reduction (the raw materials and the carrying out of the operation) and the complex nature of the apparatus. Consequently, these processes are high cost.

Although the first attempts of catalytic hydrogenation of unsymmetrical dialkylnitrosamines have generally resulted in failures due to the parasitic reactions in prevailing number, it has been tried to improve the application of the hydrogenation steps in a strictly catalytic way to overcome these drawbacks.

The investigations which have been performed resulted in the issue of new processes, such as:

Catalytic hydrogenation in liquid phase in the presence of divided precious metals, deposited or not upon supports, such as platinum, palladium, rhodium and iridium (French Patent No. 1,160,629, of November 24, 1956, French Patent No. 1,201,159 of August 6, 1958, and French Patent No. 1,166,266 of February 11, 1957);

Catalytic hydrogenation in liquid phase in the presence of Raney nickel used as a catalyst (French Patent No. 1,160,629 of November 24, 1956, and French Patent No. 1,258,548, of May 18, 1960).

Notwithstanding the progress inherent in these uses of the various catalytic hydrogenation steps of unsymmetrical dialkylnitrosamines, the results obtained are not satisfactory because:

(a) The unsymmetrical dialkylhydrazines yields are sometimes poor, particularly when using Raney nickel as a catalyst;

(b) The duration of activity of these catalysts is never mentioned, but experience shows that same is very short when they are used in the indicated conditions. This has a prime importance since the cost of the catalytic reduction is closely related to the duration of activity of the catalyst.

Our invention covers:

(1) A process for producing unsymmetrical dialkylhydrazines by the reduction of dialkylnitrosamines with hydrogen, in liquid phase, in the presence of Raney nickel obtained by caustic attack of Ni-Al alloys and in a reaction medium which has a hydroxide of an alkaline metal and of an alkaline earth metal and a soluble salt of an alkaline metal, of an alkaline earth metal and of a heavy metal, under conditions which will be described hereinafter.

(2) A process according to (1), wherein the Raney nickel obtained after the chemical attack of Ni-Al alloy is subjected to a dehydrogenation by electrochemical treatments to be identified hereinafter.

(3) A process according to (1), wherein the starting Ni-Al alloys have the following composition:

	Percent
Ni	40 to 55
Al	60 to 38
Co	0 to 1
Fe	0 to 6

The starting reaction medium comprises either pure dialkylnitrosamine or an aqueous solution of dialkylnitrosamine having a weight content which varies over a large range and is usually between 20 and 40%.

The reaction medium is made ionic by addition thereto of a hydroxide of an alkaline metal and of an alkaline earth metal and of a soluble salt of an alkaline metal, of an alkaline earth metal and of a heavy metal. The foregoing compounds are added to the reaction medium in amounts such that the medium contains between substantially about 0.001 to 5 moles per dm.^{3} of same, and preferably substantially about 0.1 mole per dm.^{3} after dissolving.

The reaction medium becomes alkaline by addition of the hydroxide of an alkaline metal such as potassium, sodium or lithium hydroxide and of an alkaline earth metal.

The Raney nickel is obtained by caustic attack of an Ni-Al alloy passing through a No. 26 AFNOR sieve. It is subjected to a first attack with a solution of caustic soda (250 g. per liter) in such quantity that the weight of pure caustic soda dissolved is substantially equal to the weight of the Ni-Al alloy. During this attack, the temperature was maintained at substantially about 100° C.

After decanting, the catalyst is subjected to a second caustic soda attack under identical conditions. Upon completion of this second attack, the caustic soda solution is eliminated and the catalyst is swilled abundantly.

The Raney nickel so obtained is finally subjected to an electrochemical dehydrogenation, according to the French Patent No. 1,303,070, of July 25, 1961, and to the application for a first addition certificate of July 4, 1962: "Process for Activating a Catalyst," wherein the catalyst is disposed close to a corrosion resistant anode in an alkaline electrolyte following which an electric current inferior to 500 milliamperes/cm.^{2} is passed therethrough. The dehydrogenation treatment may also be carried out according to the French Patent No. 1,301,338 of July 4, 1961, and to the application for a first addition certificate of June 20, 1962: "Process for Obtaining Metals Containing an Adjustable Quantity of Hydrogen," consisting in desorbing the contained hydrogen by immersion of the nickel-aluminum alloy in an electrolysis cell in such a manner that electric current lines traverse or pass through the Ni-Al alloy which is not in contact with either of the electrodes.

In another method of preparation of the catalyst, we use the starting Ni-Al alloy of the foregoing composition, and particularly the following composition:

Ni	47.5
Co	0.5
Fe	3
Al	49

This alloy which is passed through a No. 26 AFNOR sieve is subjected to a first attack with a caustic soda solution of 250 g./l., in such quantity that the weight of dissolved sodium hydroxide is substantially equal to the weight of alloy employed. During this attack, the temperature is held at substantially about 100° C.

After decanting, the catalyst is subjected to a second caustic soda solution attack under identical conditions. Upon completion of the attack, the caustic soda solution is eliminated and the catalyst is swilled at least ten times. Then this catalyst is ready for use without further treatment.

If the Raney nickel so obtained is not employed at once, or if after having been employed a while its use is temporarily stopped for any reason whatsoever, it is dipped into an aqueous solution of an alkaline metal hydroxide, whose alkaline hydroxide content is between 50 and 500 g./l., and preferably in the vicinity of 250 g./l.

The catalyst is used in such proportions that the ratio by weight

$$\frac{\text{catalyst}}{\text{reaction medium}}$$

is between 0.001 and 0.50, and preferably between 0.05 and 0.10. The ratio by weight of

$$\frac{\text{catalyst}}{\text{dialkylinitrosamine}}$$

is between 0.001 and 1.0, and preferably between 0.15 and 0.5.

The hydrogen pressure is between 5 atmospheres and below 50 atmospheres and usually amounts to 30 atmospheres.

The hydrogenation is carried out at a temperature between −20° C. and +50° C., and advantageously at about +10° C.

Stirring of the reaction medium is effected to obtain a good contact among the three phases: liquid, solid and gaseous phases.

By our invention it is possible to obtain a high yield of catalytic reduction of unsymmetrical dialkylnitrosamines in liquid phase under excellent economical conditions as to the materials employed as well as the duration activity of the catalyst, and with simplified apparatus.

The following non-limitative examples show various embodiments of our process and of the use of the catalyst according to our invention, and set forth advantages achieved in comparison with previous methods.

EXAMPLE 1

Into a stainless steel, horizontal autoclave having a capacity of 5 dm.^{3}, we introduced:

	G.
Dimethylnitrosamine	538
Water	1762
Sodium hydroxide	11
Raney catalyst (prepared as indicated above and dehydrogenated according to the French Patent No. 1,303,070)	100

The dimethylnitrosamine concentration by weight in the reaction mixture, excluding the catalyst, amounted to 23.3%. The catalyst concentration by weight in the reaction mixture, excluding the catalyst, amount to 4.3%. The sodium hydroxide concentration in the reaction mixture, excluding the catalyst, amounted to 0.1 mole/dm.^{3}.

The autoclave was equipped with a stirring system having a to-and-fro motion perpendicularly to its axis and obtained 220 stirrings a minute.

The temperature was raised to +10° C. and the pressure to 40 atmospheres by hydrogen injection. This operation was carried out at a temperature equal to +10° C. and the pressure varied between 30 and 40 atmospheres.

Under these conditions, the time of the catalytic reduction was about 20 hours. Upon completion of the reaction, the obtained mixture was distilled for recovery of the unsymmetrical dimethylhydrazine. The unsymmetrical dimethylhydrazine yield amounted to 87.4% relative to the dimethylnitrosamine employed.

With the same catalyst which showed no lessening in activity, it was possible to carry out more than 15 operations which achieved the following results, under identical conditions:

Average time of the catalytic reduction operation ……hours	20
Unsymmetrical dimethylhydrazine average yield relative to the dimethynitrosamine employed ……percent	84.4

The addition of sodium hydroxide proved important because tests carried out under absolutely identical conditions, but without sodium hydroxide, led to the following results, showing that the catalyst activity decreases very rapidly as does the unsymmetrical dimethylhydrazine yields:

No. of the Catalytic Reduction Step	Time of the Operation (hours)	Unsymmetrical Dimethylhydrazine Yield Relative to the Dimethylnitrosamine Employed (percent)
1	19.0	85.2
2	21.5	81.5
3	30.0	75.3

EXAMPLE 2

Into the autoclave described in Example 1, we introduced:

	G.
Dimethylnitrosamine	538
Water	1762
Sodium hydroxide	11
Raney catalyst (identical to the one of Example 1)	100

The dimethylnitrosamine concentration by weight in the reaction mixture, excluding the catalyst, amounted to 23.3%. The catalyst concentration by weight in the reaction mixture, excluding the catalyst, amounted to 4.3%. The sodium hydroxide concentration in the reaction mixture, excluding the catalyst, amounted to 0.1 mole/dm.^{3}.

The temperature was raised to +20° C. and the pressure to 40 atmospheres by hydrogen injection. This operation was carried out at a temperature equal to +20° C. and the pressure varied between 30 and 40 atmospheres.

Under these conditions, the time of the catalytic reduction was about 12 hours. The unsymmetrical dimethylhydrazine yield amounted to 82.1% relative to the dimethylnitrosamine employed.

At the end of the catalytic reduction reaction, the catalyst kept its entire catalytic activity and it was possible to carry out other tests, the results of which were identical.

EXAMPLE 3

Into a stainless steel, horizontal autoclave having a capacity of 5 dm.^{3}, we introduced:

	G.
Dimethylnitrosamine	538
Water	1762
Sodium hydroxide	11
Raney catalyst (prepared according to the second form of proceeding described above and used without any electrochemical treatment)	200

The dimethylnitrosamine concentration by weight in the reaction mixture, excluding the catalyst, amounted to 23.30%. The catalyst concentration by weight in the reaction mixture, excluding the catalyst, amounted to 8.6%. The catalyst concentration by weight in the pure dimethylnitrosamine employed amounted to 37.2%. The sodium hydroxide concentration in the reaction mixture, excluding the catalyst, amounted to 0.1 mole/dm.^{3}.

The autoclave was equipped with a stirring system having a to-and-fro motion perpendicularly to its axis and obtained 220 stirrings per minute.

The temperature was raised to +10° C. and the pressure to 40 atmospheres by hydrogen injection. This operation was carried out at a temperature equal to +10° C. and the hydrogen pressure varied between 30 and 40 atmospheres.

Under these conditions, the time of the catalytic reduction was about 6 hours. The obtained unsymmetrical dimethylhydrazine was recovered by distillation. The unsymmetrical dimethylhydrazine yield compared to the dimethylnitrosamine employed amounted to 85.5%.

Fifteen identical operations were carried out with this catalyst under the same conditions:

The average time of the catalytic operation amounted to ____hours__	7
The unsymmetrical dimethylhydrazine average yield compared to the dimethylnitrosamine employed amounted to ___percent__	83.5

At the end of these fifteen operations, the catalyst retained its entire activity.

EXAMPLE 4

Into the autoclave described in Example 3, we introduced:

	G.
Dimethylnitrosamine	538
Water	1762
Sodium hydroxide	11
Raney catalyst (prepared according to the second method for preparation of the catalyst described above and used without any electrochemical treatment)	100

The dimethylnitrosamine concentration by weight in the reaction mixture, excluding the catalyst, amounted to 23.30%. The catalyst concentration by weight in the reaction mixture, excluding the catalyst, amounted to 43.30%. The catalyst concentration by weight in the pure dimethylnitrosamine employed amounted to 18.6%. The sodium hydroxide concentration in the reaction mixture, excluding the catalyst, amounted to 0.1 mole/dm.^{3}.

The temperature was raised to +10° C. and the pressure to 40 atmospheres by hydrogen injection.

This operation was carried out at a temperature equal to +10° C. and the hydrogen pressure varied between 30 and 40 atmospheres.

Under these conditions, the time of the catalytic reduction was in the vicinity of 14.5 hours. The unsymmetrical dimethylhydrazine obtained was recovered by distillation. The unsymmetrical dimethylhydrazine yield compared to the dimethylnitrosamine employed amounted to 80.3%.

Eleven identical operations were carried out with this catalyst under analogous conditions:

The average time of the catalytic operation amounted to ____hours__	18.75
The unsymmetrical dimethylhydrazine average yield compared to the dimethylnitrosamine employed amounted to ____percent__	76.20

At the end of these eleven operations, the catalyst retained its entire activity.

EXAMPLE 5

Into a stainless steel, horizontal autoclave having a capacity of 5 dm.^{3}, we introduced:

	G.
Dimethylnitrosamine	538
Water	1762
Potassium chloride	17
Raney nickel	100

The dimethylnitrosamine concentration by weight in the reaction mixture, excluding the catalyst, amounted to 23.30%. The catalyst concentration by weight in the reaction mixture, excluding the catalyst, amounted to 4.30%. The catalyst concentration by weight in the pure dimethylnitrosamine employed amounted to 18.60%. The potassium chloride concentration in the reaction mixture, excluding the catalyst, amounted to 0.1 mole/dm.^{3}.

The temperature was raised to +20° C. and the pressure to 40 atmospheres by hydrogen injection. This operation was carried out at +20° C. and the pressure varied between 30 and 40 atmospheres.

Under these conditions, the time of the catalytic reduction was in the vicinity of 14 hours.

Finally, the unsymmetrical dimethylhydrazine was recovered by a careful distillation. The unsymmetrical dimethylhydrazine yield relative to the dimethylnitrosamine employed amounted to 76.8%.

With this already used catalyst, we carried out ten operations in succession under identical conditions except that the temperature was either +10° C. or +20° C., and obtained the following results:

Average time of the catalytic hydrogenation hours__	23.4
Unsymmetrical dimethylhydrazine average yield relative to the dimethylnitrosamine employed percent__	73.1

After these ten operations, the catalyst retained its entire activity.

EXAMPLE 6

Into a stainless steel, horizontal autoclave having a capacity of 1 dm.^{3}, we introduced:

	G.
Dimethylnitrosamine	81.9
Water	268.1
Barium chloride $BaCl_2 2H_2O$	9.2
Raney nickel	12.5

The dimethylnitrosamine concentration by weight in the reaction mixture, excluding the catalyst, amounted to 22.8%. The catalyst concentration by weight in the reaction mixture, excluding the catalyst, amounted to 3.48%. The catalyst concentration by weight in the pure dimethylnitrosamine employed amounted to 15.3%. The barium chloride concentration in the reaction mixture, excluding the catalyst, amounted to 0.1 mole/dm.^{3}.

The autoclave was equipped with a stirring system having a to-and-fro motion perpendicularly to its axis and obtained 280 stirrings a minute.

The temperature was raised to +10° C. and the pressure to 40 atmospheres by hydrogen injection. This operation was carried out at +10° C. and the pressure varied between 30 and 40 atmospheres.

Under these conditions, the time of the catalytic reduction was in the vicinity of 13.5 hours.

Finally, the unsymmertical dimethylhydrazine was recovered by a careful distillation. The unsymmertical dimethylhydrazine yield relative to the dimethylnitrosamine employed amounted to 74.7%.

With this same catalyst, used under identical conditions, another reduction operation was carried out and consumed 19.75 hours. The unsymmetrical dimethylhydrazine yield relative to the dimethylnitrosamine employed amounted to 75.4%.

After these two operations, the catalyst retained its entire activity.

EXAMPLE 7

Into the autoclave described above in Example 6, we introduced:

	G.
Dimethylnitrosamine	81.9
Water	268.1
Potassium nitrate	3.8
Raney nickel	12.5

The dimethylnitrosamine concentration by weight in the reaction mixture, excluding the catalyst, amounted to 23.2%. The catalyst concentration by weight in the reaction mixture, excluding the catalyst, amounted to 3.54%. The catalyst concentration by weight in the pure dimethylnitrosamine employed amounted to 15.30%. The potassium nitrate concentration in the reaction mixture, excluding the catalyst, amounted to 0.1 mole/dm.^{3}.

The temperature was raised to +10° C. and the pressure to 40 atmospheres by hydrogen injection. This operation was carried out at +10° C. and the pressure varied between 30 and 40 atmospheres.

Under these conditions, the time of the catalytic reduction was in the vicinity of 18.75 hours. Then the unsymmetrical dimethylhydrazine was recovered by a careful distillation. The following results were obtained:

The unsymmetrical dimethylhydrazine yield relative to the dimethylnitrosamine employed amounted to 81.6%.

With this same catalyst used under identical conditions, another reduction operation was carried out during 14.15 hours. The unsymmetrical dimethylhydrazine yield relative to the dimethylnitrosamine employed amounted to 79.4%.

After these two operations, the catalyst retained its entire activity.

In order to set off the advantages of our process, the following tests were carried out, but some characteristic elements of the invention process have been deliberately neglected.

Test No. 1

A pulverulent alloy nickel-aluminum having the following composition:

	Percent
Nickel	49.2
Aluminum	50.6
Iron	0.2

was subjected to two caustic soda attacks under the hereinabove-described conditions. The Raney nickel obtained was used as a catalyst without any subsequent electrolytic dehydrogenation and under identical conditions to the ones set forth in Example 4, except that sodium hydroxide was not added to the reaction medium.

The following results were obtained:

Test No.	Time of the Reduction Operation (hours)	Unsymmetrical Dimethylhydrazine Yield Compared to the Dimethylnitrosamine Employed (percent)
1	23.33	44.5
2	39.00	65.9

The catalyst was used again under the hereinabove conditions, but at a temperature equal to +30° C.

The following results were obtained:

Test No.	Time of the Reduction Operation (hours)	Unsymmetrical Dimethylhydrazine Yield Relative to the Dimethylnitrosamine Employed (percent)
3	16.33	59.4
4	16.00	47.9

Test No. 2

Tests were carried out with the Raney nickel of Example 4 and under identical conditions, except that the temperature was higher and no alkaline hydroxide was added to the reaction medium.

These tests enabled one to observe the following results:

Test No.	Temperature, ° C.	Time of the Reduction Operation (hours)	Unsymmetrical Dimethylhydrazine Yield Relative to the Dimethylnitrosamine Employed (Percent)
1	90	0.42	0.00
2	55	0.92	0.00
3	32	1.33	24.00

Test No. 3

Tests were carried out under conditions rigorously similar to the ones of Example 4, except that no alkaline hydroxide was added into the reaction medium.

The following results were obtained, a similar weight of catalyst having been used for carrying out these tests:

Test No.	Time of the Reduction Operation (hours)	Unsymmetrical Dimethylhydrazine Yield Relative to the Dimethylnitrosamine Employed (Percent)
1	9.25	71.7
2	16.00	68.6
3	19.00	72.4
4	21.00	72.0

Test No. 4

Into the autoclave described in Example 5, the same quantities of reagents and of Raney nickel as the ones employed in the example were introduced, except that no metallic salt was added.

Hydrogenation has been carried out under the conditions of Example 5.

The following results were obtained:

Test No.	Time of Hydrogenation (Hours)	Unsymmetrical Dimethylhydrazine Yield Relative to the Dimethylnitrosamine Employed (Percent)
1	23.33	44.5
2	39.00	65.9

While we have shown and described preferred embodiments of our invention, it may be otherwise embodied within the scope of the appended claims.

We claim:

1. A process for production of unsymmetrical dimethylhydrazine comprising hydrogenating dimethylnitrosamine in the liquid phase in the presence of a Raney nickel catalyst whose composition is nickel—40–55%, aluminum—38–60%, cobalt—0–1% and iron—0–6% by weight, said catalyst being subjected to a first treatment with a solution of caustic soda in an amount such that the weight of caustic soda dissolved is substantially that of the weight of the catalyst; after decanting, said catalyst being subjected to a second treatment identical to said first treatment followed by elimination of said caustic soda solution; in carrying out said hydrogenating forming a reaction medium comprising a dimethylnitrosamine and a member selected from the group consisting of a hydroxide of an alkaline metal, of an alkaline earth metal, a salt of an alkaline metal and of an alkaline earth metal, said dimethylnitrosamine being at least 20% by weight of said reaction medium, said member being about 0.001 to 5 moles per dm.^{3} of said reaction medium, said catalyst being present in said reaction medium in a ratio by weight of

$$\frac{\text{catalyst}}{\text{dimethylnitrosamine}}$$

of about 0.001–1.0, said hydrogenating being carried out at a pressure between about 5 and less than 50 atmospheres, and at a temperature between substantially −20° C. and +50° C.

2. The process of claim **1** characterized by subjecting said catalyst to electrochemical dehydrogenation prior to its use in said hydrogenating said dimethylnitrosamine.

3. The process of claim **1** characterized by said member being substantially about 0.1 mole per dm.^{3} of said reaction medium, by said ratio being substantially about 0.15–0.5, by said pressure being substantially between about 30 and 40 atmospheres, and by said temperature being substantially about +10° C.

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CHARLES B. PARKER, *Primary Examiner.*

R. L. RAYMOND, *Assistant Examiner.*