PREPARATION OF 2,2'-BIPYRIDYLS
No Drawing. Filed June 12, 1972, Ser. No. 261,993
Int. Cl. C07D 31/42
U.S. Cl. 260—296 D 7 Claims

ABSTRACT OF THE DISCLOSURE
In the preparation of 2,2'-bipyridyl or alkyl-substituted 2,2'-bipyridyls from pyridine or alkylpyridines in contact with hot Raney nickel catalyst, the optimum yields are obtained when the Raney nickel is prepared from nickel-aluminium alloys consisting essentially of between 52 and 56% of nickel and between 48 and 44% of aluminium.

This invention relates to an improved process for the preparation of 2,2'-bipyridyls and an improved nickel catalyst for use in this process.
2,2'-Bipyridyls may be prepared by contacting hot pyridine or alkylpyridines with nickel catalysts obtained by digesting a 50:50 nickel-aluminium alloy with aqueous alkali.

It has now been found that nickel-aluminium alloys containing a range of higher proportions of nickel are of advantage in that by digestion with aqueous alkali they afford nickel catalysts which give improved yields of bipyridyls from pyridines.

According to the invention there is provided a nickel-aluminium alloy consisting essentially of between 52 and 56% of nickel and between 48 and 44% of aluminium.

According to the invention there is also provided a nickel catalyst obtained by digesting with aqueous alkali a nickel-aluminium alloy consisting essentially of between 52 and 56% of nickel and between 48 and 44% of aluminium.

According to the invention there is further provided an improved process for the preparation of 2,2'-bipyridyls which comprises contacting hot pyridine or an alkylpyridine with catalyst obtained by digesting with alkali a nickel-aluminium alloy consisting essentially of between 52 and 56% of nickel and between 48 and 44% of aluminium.

As alkylpyridines there may be mentioned lower alkylpyridines especially α-, β- and γ-picolines, but ethylpyridine and pyridines containing higher alkyl substituents may be used. Both α-positions of the pyridine should not be substituted.

The pyridine or alkylpyridine may be contacted with the catalyst in any convenient manner at a temperature suitably between 50 and 150° C, and preferably above 80° C, but it is preferred to adopt the procedure of specification No. 897,473 which corresponds to U.S. Pat. 3,053,846 in which liquid pyridine is percolated continuously through the catalyst thus removing the bipyridyl as it is formed. The bipyridyl may then be isolated by any convenient method, for example vacuum distillation or by fractionation and recrystallisation of residues.

The pyridine or alkyl pyridine is preferably desulphurised by passage at an elevated temperature over a Raney nickel catalyst followed by distillation.

The preferred nickel-aluminium alloy consists of 32% of nickel. The nickel-aluminium alloys may be prepared in any conventional manner, for example heating a mixture of nickel and aluminium in the appropriate proportions at a temperature of about 1600° C. for 16 hours under an inert atmosphere such as nitrogen. For preparation of the catalyst the alloy may be broken down to a powder, suitably fine enough to pass a 60 mesh sieve, and digested with alkali and then washed with water in the manner conventional for the preparation of Raney nickel catalyst from the 50:50 nickel-aluminium alloy.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight unless otherwise stated.

PREPARATION OF ALLOY
Nickel shot and aluminium metal in the appropriate proportions are heated in an alumina crucible at 1650° C. under a nitrogen atmosphere for 16 hours and then cooled to room temperature over 7 hours. The alloy is removed from the crucible and broken down by crushing and grinding to a powder passing a 60 mesh sieve.

PREPARATION OF CATALYST
12.5 parts of alloy powder are digested with a solution of 22.5 parts of potassium hydroxide in 72 parts of water at 78° C. for 2 hours. The nickel catalyst obtained is washed by decantation with water until free from alkali.

PREPARATION OF 2,2'-BIPYRIDYL
6.5 parts of catalyst prepared as described above are placed in a fixed bed reactor held at a temperature of 110° C. Pyridine at a rate of 120 parts per hour is percolated for 74 hours through the catalyst bed from above. The treated pyridine is fractionated to give a distillate of pyridine and a residue containing 2,2'-bipyridyl which is purified by crystallisation from light petroleum. The pyridine distillate is reused directly in the process.

The pyridine used above is commercial 2° pyridine which has been desulphurised by several passes through a bed of Raney nickel catalyst at a temperature of 110° C. and distillation. Omission of the desulphurisation process leads to lower yields of bipyridyl. During this desulphurisation process a little bipyridyl is formed but this is not included in the yields given below.

The yields of 2,2'-bipyridyl obtained by the use of catalyst from various nickel-aluminium alloys are listed below.

<table>
<thead>
<tr>
<th>Proportion of nickel</th>
<th>Parts of 2,2'-bipyridyl per 100 parts of nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>424</td>
</tr>
<tr>
<td>50</td>
<td>554</td>
</tr>
<tr>
<td>52</td>
<td>607</td>
</tr>
<tr>
<td>53</td>
<td>735</td>
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<td>54</td>
<td>636</td>
</tr>
<tr>
<td>55</td>
<td>632</td>
</tr>
<tr>
<td>57</td>
<td>466</td>
</tr>
</tbody>
</table>

We claim:
1. A process for the preparation of 2,2'-bipyridyl or a lower alkyl-substituted 2,2'-bipyridyl, provided with both α-positions not substituted, which consists essentially of contacting hot pyridine or an alkylpyridine with a nickel catalyst obtained by digesting with aqueous alkali a nickel-aluminium alloy consisting essentially of between 52 and 56% of nickel and 48 and 44% of aluminium.
2. A process as claimed in Claim 1 wherein the nickel-aluminium alloy consists essentially of 53% of nickel and 47% of aluminium.
3. A process as claimed in Claim 1 in which the pyridine or alkylpyridine is at a temperature between 50 and 150° C.
4. A process as claimed in Claim 1 in which the pyridine or alkylpyridine is at a temperature between 80 and 150° C.
5. A process as claimed in Claim 1 in which the pyridine or alkylpyridine is percolated continually through the catalyst.

6. A process as claimed in Claim 1 in which the pyridine or alkylpyridine is first desulphurised by passage through a bed of Raney nickel catalyst followed by distillation and subsequently contacted with the said digested catalyst.

7. A process as claimed in Claim 1 in which the alkyl substituent is methyl or ethyl.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,822,279                   Dated July 2, 1974

Inventor(s)  JOHN ANTHONY JOY ET AL.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Please add the following to the front page format after the serial number:

--Claims priority, application Great Britain, July 15, 1971, 33310/71--

Signed and sealed this 24th day of June 1975.

(SEAL)
Attest:

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