# PATENT SPECIFICATION

# 662,907

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*Date of filing Complete Specification: July 28, 1950.*

*Application Date: Aug. 19, 1949. No. 21595/49.*

*Complete Specification Published: Dec. 12, 1951.*

Index at Acceptance:—**Classes 1(i), F3b1; and 2(iii),** B2, C2a(2:13).

## COMPLETE SPECIFICATION.

## Preparation of Hydrogenation Catalysts by Reduction.

We, The Distillers Company Limited, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, Thomas Bewley, a British Subject, of the Company's Research and Development Department, Great Burgh, Epsom, Surrey, and Peter Lionel Bramwyche, a British Subject, of Hayes Road, Sully, Penarth, Glamorganshire, Wales, formerly of the Company's Research and Development Department, Great Burgh, Epsom, Surrey, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to the preparation of active hydrogenation catalyst by the reduction of kieselguhr-supported or nickel compounds suspended in a fluid medium.

It has been found that, if a liquid or semi-liquid organic polysiloxane is present during the reduction of the supported metal compound, the production of an active hydrogenation catalyst is greatly facilitated. The invention comprises the novel processes and steps of processes, specific embodiments of which are described hereinafter by way of example and in accordance with which we now prefer to practise the invention.

The present invention comprises a process for the preparation of active hydrogenation catalysts which comprises reduction to the active condition by the treatment with hydrogen of a kieselguhr-supported copper or nickel compound which is reducible to the metal, suspended in a liquid medium comprising an organic polysiloxane. This reduction may be effected as a preliminary step before the material to be hydrogenated is added to the catalyst, or the latter may be present from the commencement, the effective hydrogenation naturally not taking place before substantial reduction of the catalyst has been effected. The copper and nickel compounds which may be used are suitably those compounds such as oxide, hydroxide or carbonate, which are susceptible to reduction by hydrogen to the active state.

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The organic polysiloxane employed is preferably polydimethyl siloxane; also it is to be noted that other organic polysiloxanes are also suitable. The liquid medium which is used may consist of a substantially liquid polysiloxane or, alternatively, it may consist of an organic polysiloxane, whether liquid or not, in solution in an organic solvent. Suitable organic solvents include alcohols such as 2-ethylhexanol and 2-methyl-2:4-pentane diol, and others such as 2:-dibutoxydiethyl ether.

The following examples, in which the parts referred to are by weight, illustrate the process of the present invention and show, at the same time, some applications of the catalysts produced.

### Example 1.

30 parts of a basic copper carbonate-kieselguhr catalyst (prepared by precipitating from a copper salt solution in the presence of kieselguhr by means of potassium carbonate solution, washing until neutral and drying at 60° C.) were dispersed in a medium consisting of 250 parts of 2-ethyl hexanol and 10 parts of liquid polydimethylsiloxane and heated to 145° C. Hydrogen was passed through the stirred suspension for 6 hours during which time the temperature was raised slowly to 165° C., the loss of the 2-ethyl hexanol being avoided by means of a reflux condenser. Four 100 part batches of alphamethylstyrene in isopropyl benzene (50:50 mixture) were then hydrogenated to isopropyl benzene at 160° C., using this catalyst suspension, without appreciable loss of catalytic activity, the average time required for complete reduction per batch being 2—3 hours. The hydrogenation products were distilled from the reaction medium in each case through a short fractionating column and the alphamethylstyrene content of the products was less than 0.5%.

Precisely similar results were obtained in two subsequent catalyst preparations using a medium consisting of 5 parts and 2.5 parts respectively of the polydimethylsiloxane and 255 parts and 257.5 parts respectively of 2-ethyl hexanol, the temperature employed for the reduction in the latter case being 160 to 170° C., all the other conditions being the same. Attempts to hydrogenate alphamethylstyrene in this way with catalysts prepared in the absence of the polysiloxane were unsuccessful.

### EXAMPLE 2.

A mixture of 150 parts of 2,2'-dibutoxydiethyl ether, 5 parts of polydimethylsiloxane grease and 30 parts of the basic copper carbonate-kieselguhr catalyst decribed in Example 1 was treated with hydrogen at 150° C. for 13 hours. The resulting catalyst suspension was very active for the hydrogenation of alphamethylstyrene at 150° C.

### EXAMPLE 3.

60 parts of the basic copper carbonate-kieselguhr catalyst described in Example 1 were dispersed in 500 parts of polydimethylsiloxane fluid and the catalyst was reduced with hydrogen for 2 hours at 150° C. followed by 2 hours at 175° C. when hydrogen absorption was complete. 400 parts of nitrobenzene were added to the catalyst suspension during 9 hours at a temperature of 240 to 250° C., the hydrogen feed being approximately 3 parts per hour. The percentage conversion to aniline was 97.4.

### EXAMPLE 4.

616 parts of nickel nitrate crystals were dissolved in 1,000 parts of water, and 125 parts of kieselguhr were stirred in. Aqueous potassium carbonate was then added to the well-stirred mixture until the product was alkaline to phenolphthalein and the precipitate-kieselguhr mixture was filtered off and washed until neutral to phenolphthalein, giving 302 parts of catalyst after drying at 100° C. 30 parts of this catalyst were then dispersed in 250 parts of polydimethylsiloxane fluid, heated to 200° C. and treated with hydrogen until absorption was complete, taking 6 hours. Nitrobenzene was then fed into the suspension at 200 to 220° C. during 14 hours with somewhat more than the theoretical amount of hydrogen, the total feed being 600 parts of nitrobenzene. The conversion to aniline was 65.5%.

For the purposes of comparison, attempts were made to reduce the above-described nickel-kieselguhr catalyst to the active state dispersed in corresponding amounts of aniline, liquid polymeric alphamethylstyrene and nitrobenzene at 170 to 210° C. These attempts proved unsuccessful, and the catalyst, after treating with hydrogen as described above, would not promote the hydrogenation of nitrobenzene or alphamethylstyrene at 200 to 220° C.

The process of the foregoing examples may be repeated using other copper or nickel compounds reducible by hydrogen to the active state, such as the oxides and hydroxides.

The hydrogenation catalysts prepared in accordance with the present invention catalyse the hydrogenation of unsaturated and reducible compounds such as acrolein, crotonaldehyde, propionaldehyde, alkoxyaldehydes or unsaturated hydrocarbons.

For comparative purposes the following experiments were carried out.

*Experiment* 1.

A copper oxide-kieselguhr catalyst was prepared by the precipitation from a hot solution of copper sulphate in the presence of kieselguhr by means of sodium hydroxide. This catalyst, after drying at 60° C. was suspended in 2-methyl-2 : 4-pentane diol and reduced by treatment with hydrogen for 12 hours at a temperature of between 160° to 170° C. The catalyst obtained exhibited such a powerful dehydrogenation activity that the 2-methyl-2 : 4-pentane diol was rapidly split to acetone.

*Experiment* 2.

A copper oxide kieselguhr catalyst prepared as described in experiment 1 was suspended in 2 : 2-di-butoxydiethyl ether and reduced by treatment with hydrogen at 170° C. The catalyst obtained was khaki-coloured and proved inactive for the hydrogenation of di-acetone alcohol at 75° C. under 300 lbs./sq. in. pressure.

*Experiment* 3.

A copper oxide kieselguhr catalyst prepared as described in Experiment 1 was suspended in dibutyl phthalate and reduced by treatment with hydrogen at 160—170° C. for 12 hours. When the catalyst obtained was used for the hydrogenation of di-acetone alcohol, no hydrogen absorption was observed and the di-acetone alcohol was quantitatively split to acetone.

*Experiment* 4.

A copper oxide kieselguhr catalyst prepared as described in Experiment 1 was suspended in dibutylphthalate and reduced by treatment with hydrogen at 160—170° C. for 12 hours. A mixture of crotonaldehyde and hydrogen were passed into this catalyst suspension at 170° C. and it was found that the catalyst remained active for only about 12 hours.

These comparative experiments detailed above show clearly the advantages attendant upon the process of the present invention and the necessity of effecting reduction of kieselguhr-supported copper or nickel compounds in the presence of an organic polysiloxane if an active hydrogenation catalyst is to be obtained.

What we claim is:—

1. A process for the preparation of active hydrogenation catalysts which comprises the reduction by treatment with hydrogen of a material consisting of a metal compound selected from the group consisting of copper and nickel compounds reducible to the metal disposed on a kieselguhr support, which is suspended in a liquid medium comprising an organic polysiloxane.

2. A process as claimed in Claim 1, wherein the liquid medium also contains an organic solvent for the organic polysiloxane.

3. A process as claimed in Claim 1 or 2, wherein the metal compound is an oxide.

4. A process as claimed in Claim 1 or 2, wherein the metal compound is a hydroxide.

5. A process as claimed in Claim 1 or 2, wherein the metal compound is a carbonate.

6. A process as claimed in any of the preceding claims, wherein the organic polysiloxane is a polydimethyl siloxane.

7. A process as claimed in any of the preceding Claims 2 to 6, wherein the organic solvent employed is 2 : ethyl hexanol.

8. A process as claimed in any of the preceding Claims 2 to 6, wherein the organic solvent employed is 2 : -dibutoxy di-ethyl ether.

9. Processes for the production of active hydrogenation catalysts substantially as described in any of the examples 1 to 4.

10. Active hydrogenation catalysts prepared according to the processes claimed in any of the preceding claims.

11. A process for the hydrogenation of reducible organic compounds, which comprises treating said compounds with hydrogen in the presence of a catalyst as claimed in Claim 10.

N. F. BAKER,
Agent for the Applicants.

## PROVISIONAL SPECIFICATION.

## Preparation of Hydrogenation Catalysts by Reduction.

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, THOMAS BEWLEY and PETER LIONEL BRAMWYCHE, both British Subjects and both of the Company's Research and Development Department, Great Burgh, Epsom, Surrey, do hereby declare the nature of this invention to be as follows:—

The present invention relates to the preparation of active hydrogenation catalysts by the reduction of kieselguhr-supported copper or nickel compounds suspended in a fluid medium.

It has been found that, if a liquid or semi-liquid organic polysiloxane is present during the reduction of the supported metal compound, the production of an active hydrogenation catalyst is greatly facilitated, and accordingly the present invention comprises the reduction of kieselguhr supported copper or nickel compounds as hereinafter defined to the active condition by their hydrogenation in the presence of a fluid medium comprising an organic polysiloxane. This reduction may be effected as a preliminary step before the material to be hydrogenated is added, or the latter may be present from the commencement, the effective hydrogenation thereof naturally not taking place until substantial reduction of the catalyst has been effected. By "copper or nickel compounds" is meant those compounds, such as the oxide, hydroxide or carbonate, susceptible to reduction by hydrogen to the active metal or metal oxide.

The following examples, in which the parts referred to are by weight, illustrate the process of the present invention and show, at the same time, some applications of the catalysts produced.

### EXAMPLE 1.

30 parts of a basic copper carbonate-kieselguhr catalyst (prepared by precipitating from a copper salt solution in the presence of kieselguhr by means of potassium carbonate solution, washing until neutral and drying at 60° C.) were dispersed in a medium consisting of 250 parts of 2-ethyl hexanol and 10 parts of liquid polydimethylsiloxane and heated to 145° C. Hydrogen was passed through the stirred suspension for 6 hours during which time the temperature was raised slowly to 165° C., the loss of the 2-ethyl hexanol being avoided by means of a reflux condenser. Four 100 part batches of alphamethylstyrene in isopropyl benzene (50 : 50 mixture) were then hydrogenated at 160° C., using this catalyst suspension, without appreciable loss of catalytic activity, the average time required for complete reduction per batch being 2—3 hours. The hydrogenation products were distilled from the reaction medium in each case through a short fractionating column and the alphamethylstyrene content of the products was less than 0.5%.

Precisely similar results were obtained in two subsequent catalyst preparations using only 5 parts and 2.5 parts respectively of the polydimethylsiloxane in the 200 parts of medium, the temperature employed for the reduction in the latter case being 160 to 170° C., all the other conditions being the same. Attempts to hydrogenate alpha-methylstyrene in this way with catalysts prepared in the absence of the polysiloxane were unsuccessful.

### EXAMPLE 2.

A mixture of 150 parts of 2,2¹-dibutoxydiethyl ether, 5 parts of polydimethylsiloxane grease and 30 parts of the basic copper carbonate-kieselguhr catalyst described in Example 1 was treated with hydrogen at 150° C. for 13 hours. The resulting catalyst suspension was very active for the hydrogenation of alpha-methylstyrene at 150° C.

### EXAMPLE 3.

60 parts of the basic copper carbonate-kieselguhr catalyst described in Example 1 were dispersed in 500 parts of polydimethylsiloxane fluid and the catalyst was reduced with hydrogen for 2 hours at 150° C. followed by 2 hours at 175° C. when hydrogen absorption was complete. 400 parts of nitro-benzene were added to the catalyst suspension during 9 hours at a temperature of 240 to 250° C., the hydrogen feed being approximately 3 parts per hour. The percentage conversion to aniline was 97.4.

### EXAMPLE 4.

616 parts of nickel nitrate crystals were dissolved in 1,000 parts of water, and 125 parts of kieselguhr were stirred in. Aqueous potassium carbonate was then added to the well stirred mixture until the product was alkaline to phenolphthalein and the precipitate-kieselguhr mixture was filtered off and washed until neutral to phenolphthalein, given 302 parts of catalyst after drying at 100° C. 30 parts of this catalyst were then dispersed in 250 parts of polydimethylsiloxane fluid, heated to 200° C. and treated with hydrogen until absorption was complete, taking 6 hours. Nitro-benzene was then fed into the suspension at 200 to 220° C. during 14 hours with somewhat more than the theoretical amount of hydrogen, the total feed being 600 parts of nitrobenzene. The conversion to aniline was 65.5%.

Attempts to reduce the above described nickel-kieselguhr catalyst to the active state in corresponding amounts of aniline, liquid polymeric alpha-methylstyrene and nitrobenzene at 170 to 210° C. proved unsuccessful, and the catalyst, after treating with hydrogen in this way, would not promote the hydrogenation of nitro-benzene or alpha-methylstyrene at 200 to 220° C.

Dated this 18th day of August, 1949.

N. F. BAKER,
Agents for the Applicants.

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Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1951.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies, price 2s. per copy; by post 2s. 1d. may be obtained.

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## COMPLETE SPECIFICATION.

SPECIFICATION NO. 662907

INVENTORS:- THOMAS BEWLEY AND
PETER LIONEL BRAMWYCHE

By a direction given under Section 17(1) of the Patents Act 1949 this applica' proceeded in the name of The Distillers Company Limited, a British Company, of 12, Torphichen Street, Edinburgh, 3.

THE PATENT OFFICE,
*12th February, 1952*

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which it is to be performed, to be particularly described in and by the following statement:

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It has been found that, if a liquid or semi-liquid organic polysiloxane is present during the reduction of the supported metal compound, the production of an active hydrogenation catalyst is greatly facilitated. The invention comprises the novel processes and steps of processes, specific embodiments of which are described hereinafter by way of example and in accordance with which we now prefer to practise the invention.

The present invention comprises a process for the preparation of active hydrogenation catalysts which comprises reduction to the active condition by the treatment with hydrogen of a kieselguhr-supported copper or nickel compound which is reducible to the metal, suspended in a liquid medium comprising an organic polysiloxane. This reduction may be effected as a preliminary step before the material to be hydrogenated is added to the catalyst, or the latter may be present from the commencement, the effective hydrogenation naturally not taking place before substantial reduction of the catalyst has been effected. The copper and nickel compounds which may be used are suitably those compounds such as oxide, hydroxide

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as 2 : -dibutoxydiethyl ether.

The following examples, in which the parts referred to are by weight, illustrate the process of the present invention and show, at the same time, some applications of the catalysts produced.

### EXAMPLE 1.

30 parts of a basic copper carbonate-kieselguhr catalyst (prepared by precipitating from a copper salt solution in the presence of kieselguhr by means of potassium carbonate solution, washing until neutral and drying at 60° C.) were dispersed in a medium consisting of 250 parts of 2-ethyl hexanol and 10 parts of liquid polydimethylsiloxane and heated to 145° C. Hydrogen was passed through the stirred suspension for 6 hours during which time the temperature was raised slowly to 165° C., the loss of the 2-ethyl hexanol being avoided by means of a reflux condenser. Four 100 part batches of alphamethylstyrene in isopropyl benzene (50 : 50 mixture) were then hydrogenated to isopropyl benzene at 160° C., using this catalyst suspension, without appreciable loss of catalytic activity, the average time required for complete reduction per batch being 2—3 hours. The hydrogenation products were distilled from the reaction medium in each case through a short fractionating column and the alphamethylstyrene content of the products was less than 0.5%.