[Second Edition.]

PATENT SPECIFICATION

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Specification Accepted: April 9, 1940.

PROVISIONAL SPECIFICATION.

No. 22980 A.D. 1938.

Improvements in or relating to the Manufacture of Catalysts.

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh, and JACQUES FRANÇON, a citizen of the French Republic, of 26, Rue Pierre l'Homme, Courbevoie (Seine), France, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of catalysts and has particular reference to the manufacture of nickel catalysts for hydrogenation or dehydrogenation reactions and especially the synthesis of formaldehyde from carbon monoxide and hydrogen.

The preparation of a nickel catalyst for use in formaldehyde synthesis by proceeding through the stages of dissolving nickel in nitric acid, precipitating nickel hydrate by means of caustic soda, and reducing the nickel hydrate by heating in a current of dry hydrogen has been described in our British Patent Specification No. 450,449, and the chief object of the present invention is to provide improvements in that type of manufacturing process.

In the first place as regards the condition of the nickel employed as starting material for dissolving in nitric acid, this is preferably in the form of gauze or a bundle of wires, absolutely free from sulphur and containing not more than 0.04 per cent. of silicon, also not more than 0.04 per cent. of magnesium and about 0.06 per cent. of cobalt. The total impurities must not exceed 1 per cent., and are preferably present by actual addition to otherwise pure nickel. It is advisable that the amounts of zinc and particularly copper if present should be of a very low order.

A roll or bundle of the nickel gauze is half immersed in aqueous nitric acid composed of one part of nitric acid of 36 B strength (free from chlorine) and three parts of water. The roll or bundle is periodically (twice a day) turned end for end the effect of this being to form a solution of ordinary nickel nitrate mixed with basic nickel nitrate. The basic condition of the solution is very important and can be recognised by turning red litmus paper blue. The degree of purity of the nickel is of importance in obtaining the basic condition of the nitrate solution; in particular copper and zinc are detrimental to attaining the basic state, and if desired in the eventual catalyst should be added subsequently. It is desirable to let the basic nitrate bath stand for several days after being formed as this has the effect of making the eventual nickel gel formed from it more voluminous representing an eventual finer state of division of the nickel obtained.

The preparation of the basic nickel nitrate solution as above described must be carried out in the cold and preferably in a glass vessel.

As it is sometimes difficult to obtain nickel in the form of gauze of the required degree of purity the following alternative method of preparing the basic nickel nitrate solution may be employed.

Metallic nickel, free from sulphur and only containing small amounts of cobalt but not necessarily fulfilling all the conditions required for the above described method of preparation is dissolved in nitric acid preferably by heating and when the solution is neutral or basic, impurities, including silica, may be removed by known chemical methods. After precipitation and separation of impurities, nickel hydrate is precipitated either hot or cold by a base such as caustic soda and the suspension is allowed to settle, washed several times with water by decantation, and allowed to drain in a Buchner funnel and dried preferably in an electrically heated oven at about 200° C. It can be dissolved directly in dilute nitric acid in the cold to form the basic nickel nitrate solution.

To form the nickel hydrate gel as above stated, the nickel nitrate solution is first

[*Price* 1/-]

diluted to a degree corresponding to 100 grams of metal in 50 litres of water, and then a 50% excess over the calculated quantity of caustic soda is added as a 10 per cent. solution and the whole is vigorously stirred while maintaining a cold condition. The gel is then allowed to settle and the supernatant liquid is drawn off, and fresh water is added and drawn off. During the entire operation an alkaline condition sufficient to turn red litmus paper blue must be maintained and to assist in this the vessel employed is advantageously a wooden one.

The contents of the wooden vessel are then tipped onto a cloth on which the nickel hydrate gel is retained and this cloth is then rolled up so that the gel is able to dry in free contact with air but sheltered from direct light, as it has been found that the gel formed in the way above described is particularly liable to be blackened by exposure to strong light. After two or more days the paste is removed from the cloth and put onto a Buchner funnel and allowed to drain until its nickel content lies between 8 and 15 per cent. It is then ready to be reduced for use as a catalyst.

Dated this 3rd day of August, 1938.

For THE DISTILLERS COMPANY LIMITED and JACQUES FRANCON:

Stevens, Langner, Parry & Rollinson,
Chartered Patent Agents,
5—9, Quality Court, Chancery Lane,
London, W.C.2, and at
120, East 41st Street, New York City,
New York, U.S.A.

PROVISIONAL SPECIFICATION.

No. 20214 A.D. 1939.

Improvements in or relating to the Manufacture of Catalysts.

We, The Distillers Company Limited, a British Company, of 12, Torphichen Street, Edinburgh, and Jacques Francon, a citizen of the French Republic, of 26, Rue Pierre l'Homme, Courbevoie (Seine), France, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of catalysts and has particular reference to the manufacture of catalysts containing essentially nickel for use in the synthesis of formaldehyde from carbon monoxide and hydrogen.

In the Specification of our co-pending Application No. 22980/38 there is described a method of manufacturing a nickel catalyst of the kind referred to and the importance of obtaining the nickel from nickel hydrate precipitated from basic nickel hydrate has been indicated; it has also been pointed out that the purity of the nickel is of importance but that small amounts of certain impurities or foreign elements are necessary in that they seem to act as activators.

The present invention is mainly concerned with further improvements in the incorporation of foreign elements or impurities in the nickel catalyst.

It has now been found that the effect of the presence of such impurities or foreign elements as are necessary or advantageous especially small amounts of copper, silver, zinc, lead, manganese, cobalt, silicon, iron and magnesium is dependent on the manner in which they are incorporated. In the co-pending application referred to we have indicated that the nickel should be prepared from nickel hydrate precipitated from basic nickel nitrate and that the latter should be prepared in the cold. It has now been found that the preparation of the nickel nitrate in the basic state and without unduly raising the temperature has an influence on the nature of the incorporation of impurities with it. It is believed that the most satisfactory form of the incorporation is a form in which the impurities assume a coupled state with one another or with the predominant nickel in the eventual catalyst. One way of ensuring this particular state of the impurities when preparing the complexes in the presence of nickel is to include a small amount of magnesium probably because it ensures a basic condition of the nickel nitrate. It is believed that the magnesium also has the effect of forming momentarily a coupled state with the other metal impurities present and that these metal impurities then form a stable coupled relation with respect to one another or to the nickel. In particular nickel and iron are able to assume this coupled state and exert a favourable influence on the catalytic properties of the eventual catalyst.

In so far as our research has indicated up to the present, silicon has a similar effect to that of magnesium.

The amount of impurities added may be as much as 5 per cent. of the total weight.

The incorporation of the metallic impurities in the state above indicated may be ensured by adding them to the nickel or alloying them with it, then forming the basic nitrate solution in the cold, and precipitating the hydrate and drying and reducing the same. As regards the physical condition of the nitrate-forming bath, the temperature should be kept low, but a small rise up to about 40° C. is not harmful and has even been found to be beneficial.

Another method of incorporating the impurities is to make them separately, e.g. as a fairly cold basic solution, and therefrom obtain the hydrates or the metal complexes themselves and add these to separately prepared nickel hydrate.

The following are some details of how to make some of the complexes above indicated :—

Fe-Ni Complex.

(1) Add to a hot basic solution of nickel chloride ($NiCl_2$) some crystals of iron chloride ($FeCl_3$). Allow the yellowish hydrate precipitate to settle and separate it from the solution.

(2) Prepare iron acetate solution (by the action of acetic acid on finely divided iron) and mix it with half its weight of magnesium acetate solution (prepared by the action of acetic acid on magnesium ribbon) and with its own weight or more of nickel acetate solution. Then treat this mixture with hot slightly washed nickel hydrate gel. Then treat this bath with hydrogen peroxide and thereby obtain a greenish-yellow complex precipitate. Separate the precipitate and if desired dissolve it in dilute nitric acid and re-precipitate (again in the form of a complex) in the form of hydrate or carbonate. The initial bath can be replenished by the addition of more iron acetate and nickel hydrate gel.

Mn-Ni Complex.

Make a mixture of manganese acetate solution and nickel acetate solution in equal parts. Neutralise accurately by adding sodium hydroxide and then precipitate the complex hydrate by means of more sodium hydroxide.

Ni-Mg Complex.

Add magnesium cleaned by hydrochloric acid to 5 ccs. of a solution of ammonium chloride containing 0.2% of nickel chloride. The nickel is deposited on the magnesium as a very thin layer. Dissolve the metal complex slowly in cold nitric acid. Then precipitate the complex hydrate by means of sodium hydrate.

Mn-Co Complex.

(a) Heat up together 1 part of manganese nitrate 1 part of cobalt nitrate and some sodium acetate. Then add a little dilute sodium hydrate. A bright blue-green body is obtained which is then washed with hydrogen peroxide.

(b) Make a mixture of equal parts of cobalt acetate and manganese acetate, and neutralise exactly by slow careful addition of sodium hydrate. Then precipitate the complex hydrate by further addition of the sodium hydrate. The operation is best carried out in the hot state.

We have found that when making nickel hydrate by precipitation from the corresponding nitrate, a considerable number of washings of the precipitate is necessary to separate the nitrate from the gel or precipitate of hydrate. To obviate the repeated washings the following procedure has been found very satisfactory. Within a glass tank are placed two concentric porous pots one inside the other. An electrode of nickel or preferably of a non-oxidisable metal to act as cathode is placed inside the inner porous pot, and another electrode of nickel or non-oxidisable metal is placed in the tank outside the outer porous pot to act as anode. The space inside the inner porous pot and the annular space between the outer porous pot and the glass tank wall are charged with sodium hydroxide electrolyte of a strength ranging from about 0.05 Normal to 0.5 Normal containing about 5 to 10 ccs. of ethyl alcohol per litre. The annular space between the two porous pots is charged with the liquid containing the gel of nickel hydrate which should be and usually is somewhat alkaline.. A current of from about 0.004 to 0.01 amperes per square centimetre of electrode surface at a pressure of from 4 to 8 volts is then passed between the electrodes. After some hours the NO_3 ions of the nitrate will have passed into the annular space containing the anode and the sodium becomes concentrated in the inner porous pot containing the cathode. The alkalinity of the hydrate gel can be regulated by a similar electrolytic procedure. For this purpose after having eliminated the nitrate from the nickel hydrate gel, the anode is placed into the annular space containing the nickel hydrate gel and the current is continued until the alkalinity of the nickel hydrate gel has fallen to a predesired value, the strength of the sodium hydrate solution around the cathode being correspondingly increased.

The above described method of removing nickel nitrate from nickel hydrate is also applicable to the removal of the nitrates from the hydrates of the metal complex hydrates hereinbefore described.

Dated this 11th day of July, 1939.

For THE DISTILLERS COMPANY LIMITED and JACQUES FRANCON:
Stevens, Langner, Parry & Rollinson.
Chartered Patent Agents.
5—9, Quality Court, Chancery Lane.
London, W.C.2, and at
120, East 41st Street, New York City,
New York, U.S.A.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Catalysts.

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh, and JACQUES FRANCON, a citizen of the French Republic, of 26, Rue Pierre l'Homme, Courbevoie (Seine), France, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention is for improvements in or relating to the manufacture of catalysts and has particular reference to the manufacture of nickel catalysts for hydrogenation and de-hydrogenation reactions and especially for the synthesis of formaldehyde from carbon monoxide and hydrogen.

The preparation of a nickel catalyst by proceeding through the stages of dissolving nickel in nitric acid, precipitating nickel hydrate by means of caustic soda, and reducing the nickel hydrate by heating in a current of dry hydrogen is known and in British Patent Specification No. 450,449 of one of us relating to formaldehyde synthesis, small amounts of one or more promoters (activators) are added.

The present invention comprises a method of manufacturing catalytic nickel-containing materials for hydrogenating and dehydrogenating reactions especially the synthesis of formaldehyde from carbon monoxide and hydrogen consisting in subjecting pure nickel or pure nickel hydrate to the action of nitric acid at a temperature below about 40° C. whereby basic nickel nitrate is produced, converting said nitrate to nickel hydrate, reducing the nickel hydrate to nickel and incorporating in said catalyst one or more of the following activators, cobalt, copper, silver, zinc, lead, manganese, magnesium, iron or silicon. The preparation of the nickel nitrate in the basic state is an essential feature of the present invention.

Although a high temperature must be avoided during the preparation of the nickel nitrate, a temperature up to about 40° C. is permissible and has even been found beneficial. It is desirable to use a glass vessel for this preparation.

The nickel nitrate may be obtained in the basic condition by treatment with nitric acid at a temperature below about 40° C. in any convenient way. For example a roll or bundle of pure nickel gauze may be half immersed endwise in aqueous nitric acid composed of one part of nitric acid of 36 B. strength (free from chlorine) and three parts of water. The roll or bundle is periodically (twice a day) turned end for end the effect of this being to form a solution of ordinary nickel nitrate mixed with basic nickel nitrate. The basic condition of the solution can be recognised by turning red litmus paper blue. It is desirable to let the basic nitrate bath stand for several days after being formed as this has the effect of making the eventual nickel gel formed from it more voluminous, representing an eventual finer state of division of the nickel obtained.

As it is sometimes difficult to obtain pure nickel in the form of gauze, the following alternative method of preparing the basic nickel nitrate solution and thereafter nickel hydrate may be employed:—Metallic nickel, free from sulphur and copper and containing only small amounts of cobalt but not necessarily free from other impurities is dissolved in nitric acid preferably by heating and when the solution is neutral or basic, impurities are removed by known chemical methods. After precipitation and separation of such impurities, nickel hydrate is precipitated either hot or cold by a base such as caustic soda, and the suspension is allowed to settle, washed several times with water by decantation, and allowed to drain in a Buchner funnel and dried preferably in an electrically heated oven at about 200° C. It is then dissolved directly in dilute nitric acid in the cold to form the basic nickel nitrate solution.

To form the nickel hydrate gel as above stated, the nickel nitrate solution is first diluted to a degree corresponding to 100 grams of metal in 50 litres of water, and then caustic soda is added as a 10 per cent. solution and the whole is vigorously stirred while maintaining a cold condition. The gel is then allowed to settle and the supernatant liquid is drawn off, and fresh water is added and drawn off. During the entire operation an alkaline condition sufficient to turn red litmus paper blue must be maintained, and to assist in this the vessel employed is advantageously a wooden one and provided with a cover to exclude light which tends to convert the basic condition of the gel to an acidic condition.

The contents of the wooden vessel are then tipped on to a cloth on which the nickel hydrate gel is retained and this cloth is then rolled up so that the gel is able to dry in free contact with air but sheltered from direct light, as it has been found that the gel formed in the way above described is particularly liable to be blackened by exposure to strong light. After two or more days the paste is removed from the cloth and put into a bag and allowed to drain until its nickel content lies between 8 and 15 per cent. It is then heated in an electric furnace at a moderate temperature (not exceeding 50° C.) to bring it to the right condition for reduction for use as a catalyst.

As regards the incorporation of the impurities or foreign elements serving as nickel activators, one method of incorporation is by adding them to the nickel or alloying them with it, then forming the basic nitrate solution in the cold, and precipitating the hydrate and drying and reducing the same. In the case of copper and zinc this procedure should not be followed and those metals should be incorporated at a later stage in the preparation of the catalyst.

Another method of incorporating the metallic impurities is to produce a cold basic nitrate solution thereof and obtain therefrom the hydrates and add these to separately prepared nickel hydrate.

It has been found particularly advantageous to incorporate the activators in a state of intimate admixture with one another and/or with the predominant nickel. In particular such mixtures containing nickel or iron exert a favourable influence on the catalytic properties of the eventual catalyst. The employment of magnesium or silicon has not only the effect of making the nickel nitrate basic as above mentioned but also has the effect of producing the above mentioned coupled state, and such employment is therefore one way of ensuring the aforesaid state.

The amount of impurities added may be as much as 5 per cent. of the total weight.

The following are some details of how to make some of the complexes above indicated :—

Fe-Ni Complex.

(1) Add to a hot basic solution of nickel chloride ($NiCl_2$) some crystals of iron chloride ($FeCl_2$). Allow the yellowish hydrate precipitate to settle and separate it from the solution.

(2) Prepare iron acetate solution (by the action of acetic acid on finely divided iron) and mix it with half its weight of magnesium acetate solution (5—10% solution) (prepared by the action of acetic acid on magnesium ribbon) and with its own weight or more of nickel acetate solution, the quantities being used in their chemical equivalents. Then treat this mixture with high slightly washed nickel hydrate gel (the amount is not critical and success is obtained with amounts varying from the same weight to double the weight of the mixed nitrates). Then treat this bath with hydrogen peroxide and thereby obtain a greenish-yellow complex precipitate. Separate the precipitate and if desired dissolve it in dilute nitric acid and re-precipitate (again in the form of a complex) in the form of hydrate or carbonate. The initial bath can be replenished by the addition of more iron acetate and nickel hydrate gel.

Mn-Ni Complex.

Make a mixture of manganese acetate solution and nickel acetate solution in chemically equivalent parts and of 5—10% strength. Neutralise accurately by adding sodium hydroxide and then precipitate the complex hydrate by means of more sodium hydroxide.

Ni-Mg Complex.

Add magnesium cleaned by hydrochloric acid to 5 ccs. of a 5—10% solution of ammonium chloride containing 0.2% of nickel chloride, the quantity of magnesium is not critical as any excess is converted into magnesium nitrate. The nickel is deposited on the magnesium as a very thin layer. Dissolve the metal complex slowly in cold nitric acid. Then precipitate the complex hydrate by means of sodium hydrate.

Mn-Co Complex.

(a) Heat up together 1 part of manganese nitrate 1 part of cobalt nitrate and about 5—10% by weight of sodium acetate. Then add a little dilute sodium hydrate. A bright blue-green body is obtained which is then washed with hydrogen peroxide.

(b) Make a mixture of equal parts of cobalt acetate and manganese acetate, and neutralise exactly by slow careful addition of sodium hydrate. Then precipitate the complex hydrate by further addition of the sodium hydrate. The operation is best carried out in the hot state.

We have found that when making nickel hydrate by precipitation from the corresponding nitrate, a considerable number of washings of the precipitate is necessary to separate the nitrate from the gel or precipitate of hydrate. To obviate the repeated washings the following procedure has been found very satisfactory. Within a glass tank are placed two concentric porous pots one inside the other. An electrode of nickel or preferably of a non-oxidisable metal to act as cathode is placed inside the inner porous pot and another electrode of nickel or non-oxidisable metal is placed in the tank outside the outer porous pot to act as anode. The space inside the inner porous pot and the annular space between the outer porous pot and the glass tank wall are charged with sodium hydroxide electrolyte of a strength ranging from about 0.05 Normal to 0.5 Normal containing about 5 to 10 ccs. of ethyl alcohol per litre. The annular space between the two porous pots is charged with the liquid containing the gel of nickel hydrate which should be and usually is somewhat alkaline. A current of from about 0.004 to 0.01 amperes per square centimetre of electrode surface at a pressure of from 4 to 8 volts is then passed between the electrodes. After some hours the NO_3 ions of the nitrate will have passed into the annular space containing the anode and the sodium becomes concentrated in the inner porous pot containing the cathode.

The alkalinity of the hydrate gel can be regulated by a similar electrolytic procedure. For this purpose after having eliminated the nitrate from the nickel hydrate gel, the anode is placed into the annular space containing the nickel hydrate gel and the current is continued until the alkalinity of the nickel hydrate gel has fallen to a pre-desired value, the strength of the sodium hydrate solution around the cathode being correspondingly increased.

The above described method of removing nickel nitrate from nickel hydrate is also applicable to the removal of the nitrates from the hydrates of the metal complex hydrates hereinbefore described.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is :—

1. A method of manufacturing catalytic nickel-containing materials for hydrogenation and dehydrogenating reactions especially the synthesis of formaldehyde from carbon monoxide and hydrogen consisting in subjecting pure nickel or pure nickel hydrate to the action of nitric acid at a temperature below about 40° C. whereby basic nickel nitrate is produced, converting said nitrate to nickel hydrate, reducing the nickel hydrate to nickel and incorporating in said catalyst one or more of the following activators, cobalt, copper, silver, zinc, lead, manganese, magnesium, iron or silicon.

2. A method according to claim 1 wherein the activator other than copper or zinc is added to the initial pure nickel or wherein the hydrate of said activator is added to the nickel hydrate.

3. A method according to either of the preceding claims wherein the basic nickel nitrate is allowed to stand for several days before being converted into the hydrate.

4. A method according to any of the preceding claims wherein light is excluded from the nickel hydrate during and after its formation to preserve the basic condition thereof.

5. A method according to any of the preceding claims wherein any residual nitrate ions are removed from the precipitated hydrate by electrodialysis.

6. A method of manufacturing catalytic nickel-containing materials for hydrogenation and dehydrogenating reactions substantially as described.

7. Catalytic nickel-containing materials when prepared or produced by the method hereinbefore particularly described and ascertained.

Dated this 13th day of July, 1939.
For THE DISTILLERS COMPANY LIMITED and JACQUES FRANCON:
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