## AMENDED SPECIFICATION.

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# N° 2306 A.D. 1914

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*Complete Specification Left, 27th July, 1914—Accepted, 29th July, 1915*

## PROVISIONAL SPECIFICATION.

## Improvements in, and relating to, Hydrogenisation, and Dehydrogenisation.

I, James Yate Johnson, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by the Badische Anilin & Soda Fabrik, of Ludwigshafen-on-Rhine, in the German Empire) to be as follows:—

It is known that many carbon compounds, including the oxides of carbon, can be converted into compounds containing hydrogen, or a greater proportion of hydrogen, by treating them with hydrogen in the presence of a catalytic agent and that the reverse reaction can also be effected. The present invention relates to improvements in the hydrogenisation and dehydrogenisation of carbon compounds, while employing a catalytic agent.

My foreign correspondents have found that they can effect the hydrogenisation and dehydrogenisation of compounds containing carbon, and that the reaction can be carried out rapidly, with certainty and at comparatively low temperatures, by employing, as the catalytic agent, an intimate mixture of either iron, nickel, cobalt, or copper (which I hereinafter refer to as the catalytic metal) with a compound, or compounds, containing oxygen, and characterised by being or containing, or giving rise to, high melting and difficultly reducible oxides, or oxygen compounds of weak basic, or neutral, or acid, character all as hereinafter explained. In particular I mention the oxides and oxygen salts of the earth metals, including the rare earths, (see Zeitschrift für Elektrochemie 17, page 633) and of beryllium, magnesium, manganese, uranium, vanadium, niobium, tantalum, chromium, boron, titanium), and also difficultly soluble salts containing oxygen of the alkaline earths, and of lithium, such as the phosphates, molybdates, tungstates, and selenates. All these compounds containing oxygen, which promote the activity of the catalytic metal, I hereinafter refer to as "promoters."

The said oxygen-containing salts of the alkaline earths and of lithium appear to have the same action as the corresponding salts of aluminium, magnesium, and the like, although lithium oxide and the alkaline earths, namely the oxides of calcium, barium, and strontium, are themselves not suitable for use as promoters.

In order to obtain the advantages of this invention it is necessary to effect an

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intimate mixture of the catalytic metal and a promoter, and it is not sufficient merely to fill the components, for instance, nickel and alumina, side by side, into the reaction space. For instance, good results can be obtained by precipitating the hydroxides, oxides, or carbonates, of the components together from a solution containing salts thereof; or mixtures of the said salts, for instance, the nitrate of the components, can be heated until a molten condition is obtained. Further, the mixture can be obtained, although not always with equal certainty and excellence, by mechanical operations, such as by grinding together as finely as possible, or by kneading in a moist state. If necessary the mixture is subsequently heated and reduced so that in every case the catalytic metal, (iron, nickel, cobalt, or copper,) is obtained in a metallic condition, while the promoter always retains more, or less, oxygen. When the promoter is to consist of an insoluble oxide such, for instance, as aluminium oxide and titanium oxide, it is preferred to start from a soluble compound thereof, and to precipitate, or otherwise form, the insoluble oxide on the catalytic metal, or on the compound from which the catalytic metal is to be prepared. For instance, if aluminium acetate be employed to yield the promoter, namely aluminium oxide, the said acetate can be merely heated in the presence of the catalytic metal, or compound thereof, so that the acetic acid is driven off, and the alumina remains. If insoluble salts, such for instance, as chromates, and borates, be employed as promoters, these are preferably brought into intimate mixture with the compound, which is subsequently to give rise to the metallic catalytic agent, by precipitation from suitable soluble salts, or other compounds. The salts which act as promoters may contain the oxide, to which the promoting action is ascribed, either in the acid, or in the basic, constituent, or in both the acid and the basic constituents. I mention calcium aluminate and aluminium phosphate, as instances of these types. In some cases, as aforesaid, the promoter may consist of a salt of which neither the acid nor the basic, constituent of itself acts as a promoter. As an instance of this type, I mention calcium phosphate.

It is particularly advantageous for the purpose of preparing a very active contact mass to prepare, at least the catalytic metal, from carbonaceous salts, or mixtures of salts, thereof, for instance from carbonates, or from formates. The action of the catalytic mixture can further often be increased by adding an alkaline metal compound, for instance, caustic soda, even traces of such compounds have often a favourable action. It is further often useful to add to the mixture, bodies of inorganic, or organic, nature, which act either as carriers, or as binding agents, or which increase the porosity of the contact mass. I instance asbestos; charcoal, and pumice-stone. It is advisable, however, to avoid the introduction of bodies such as chlorine, sulphur, arsenic, and lead, which may, in the elementary form, act as contact poisons, although the new contact mixtures, according to the present invention, are not so sensitive to the action of poisons as are the pure metals. It is consequently possible to employ as a promoter, a salt which contains one of the poisonous elements, but in which the poisonous action is counteracted by the promoting influence of the oxide; for instance, basic aluminium sulphate, possesses a strong promoting action.

The catalytic metal can be employed either in a state of fine division, or in a more compact form, such as wire netting, or " wool ", or in sheet form.

Instead of employing only one of the above mentioned oxides, or other oxygen compounds, a mixture of two, or more, may be added to the catalytic metal.

The proportion of the components employed in the catalytic mixture may be considerably varied, even an addition of one *per cent*. or less, of the said promoters producing favourable action.

In those cases in which reduction has to be resorted to in order to obtain the catalytic metal, such reduction is preferably carried out by means of pure hydrogen, or other suitable agent, at as low a temperature as possible, and, if the catalytic mixture, after having been reduced with hydrogen, has to be exposed to the air, it is generally advisable to previously drive away any excess of hydrogen by passing an indifferent gas, such as carbon dioxide, over the mixture and thus to avoid even superficial oxidation of the metal.

The catalytic mixtures, according to this invention, can be used for the hydrogenisation and dehydrogenisation of compounds containing carbon and are of particular value for the hardening of fats and fatty acids, but they can also be used for other purposes, for instance, for converting phenol into cyclohexanol and for reducing nitrobenzene to aniline, and for the conversion of oxides of carbon into hydrocarbons.

The catalytic reaction according to this invention can be carried out either at ordinary pressure, or under increased pressure, and in most cases proceeds sufficiently rapidly at temperatures considerably below 180° Centigrade.

The process of the present invention is of great importance. It has already been proposed to employ mixtures of metallic nickel, and the like, with sodium hydrate, sodium chloride, barium chloride, sodium nitrate, and sodium sulphate, for the catalytic dehydrogenisation of various compounds; the action of such mixtures is however, relatively small compared with that of the mixtures according to the present invention, and moreover, the employment of strong bases is often detrimental, for instance, in the case of hydrogenisation of fats, since they tend to saponify the fats, and very soon disappear from the contact mass. On the other hand, when employing the promoters according to this invention, that is to say, promoters which have not a strong basic action, contact masses are obtained which are characterised by a strong and more, or less, permanent action. Of course, for different processes of hydrogenisation and dehydrogenisation according to this invention, different mixtures of catalytic metals and promoters may be preferred for particular cases.

The following examples will serve to illustrate further the nature of this invention, which, however, is not confined to these examples. The parts are by weight.

### Example 1.

Dissolve a mixture of fifteen parts of nickel nitrate and one part of beryllium nitrate, precipitate while hot with soda, filter off the precipitate, and wash and dry it. Then at a temperature of from 250° to 300° Centigrade, pass a mixture of gases containing one volume of carbon monoxide and three volumes of hydrogen over the mixture until the reduction of the nickel oxide is complete, and the conversion of the carbon monoxide into methane is taking place. The temperature can then be reduced to about 150° Centigrade, or even less, without the catalytic agent becoming inactive. If desired the entire reduction of the nickel oxide can be carried out with pure hydrogen. The precipitation can, for instance, be carried out by means of alkali hydroxide. Instead of beryllium nitrate, zirconium nitrate, or thorium nitrate, can be employed.

### Example 2.

Pour an aqueous solution of one part aluminium nitrate over five parts of nickel oxalate, evaporate the mixture and dry and reduce it in a current of hydrogen at from 300° to 350° Centigrade.

Then introduce the nickel containing alumina, while excluding air, into a shaking vessel, provided with a stirrer, the said vessel containing fish oil, or other suitable oil, which may have been previously purified. On treatment with hydrogen at, for instance, 100° Centigrade hydrogenisation takes place considerably more rapidly than if pure nickel were employed as the catalytic agent. Instead of aluminium nitrate, cerium nitrate, or cerium ammonium nitrate, can be employed.

### Example 3.

Precipitate a hot solution containing nickel nitrate and aluminium nitrate with potassium carbonate, wash the precipitate, dry it, heat it to 300° Centigrade, and reduce it with hydrogen. Then place the catalytic mixture with soy bean oil in an autoclave, while avoiding the presence of air, heat to 80° Centigrade, and allow hydrogen to act at a pressure of twenty atmospheres while suitably mixing the constituents.

The hydrogenisation takes place very rapidly. If desired the pressure can be increased, for instance, up to fifty atmospheres, or higher. In this example, good results can also be obtained if iron nitrate be employed instead of nickel nitrate.

### Example 4.

Mix thirteen parts of nickel hydroxide with two parts of magnesium hydroxide, and warm them gently with concentrated formic acid free from sulphur, until the formates are obtained. Heat the mixture gently, and then treat with hydrogen at 300° Centigrade. On treating olive oil with hydrogen in the presence of this catalytic mixture at say, from 80° to 100° Centigrade more rapid hydrogenisation is brought about than is the case when pure nickel is used. In this example the hydroxides can if desired, be replaced by the corresponding carbonates and carriers, for instance, pieces of clay, can be employed, these being soaked in a melt, or solution, of nickel salts, preferably of the soluble double salts, such as nickel ammonium formate, or ammoniacal nickel carbonate, together with the promoter, and then treated as hereinbefore described.

### Example 5.

Make nickel wire netting into the form of loose spheres, rolls, or the like, and clean these with pure dilute nitric acid, and then wash them and moisten them with a moderately concentrated solution of aluminium nitrate; then dry and treat with hydrogen at from 300° to 350° Centigrade. The contact mass containing alumina can, for instance, be employed for the hydrogenisation of linseed oil which can be allowed to trickle over the catalytic agent while the hydrogen is supplied, and a considerable, or even complete, hardening be effected.

### Example 6.

Dissolve eighty five parts of nickel nitrate and fifteen parts of titanium lactate in a small quantity of hot water and precipitate by means of soda, then filter, wash, dry, and reduce with hydrogen at 300° Centigrade, and add the catalytic mixture containing titanium oxide to cotton seed oil, and then treat with hydrogen at from 100° to 120° Centigrade while keeping the mixture in motion.

If desired the reaction can be carried out under increased pressure, (for instance, 100 atmospheres,) and in this case the hydrogenisation takes place very rapidly and completely even at a temperature of 90° Centigrade or lower. Further, the process can be made continuous by allowing the oil to flow over the catalytic agent in a vessel capable of withstanding pressure while simultaneously passing a current of hydrogen into, or through, the apparatus. The product is drawn off while hot and allowed to solidify.

### Example 7.

Take freshly precipitated nickel carbonate and add from ten, to twenty, *per cent.* of the weight thereof of ammonium borate, or potassium borate, which has previously been dissolved in water. Then form the mass into any desired shape, and dry, and reduce it. The mixture can be employed for hydrogenising oils and fats, either at ordinary pressure, or under increased pressure.

If chromium oxide be used as the promoter, this can be obtained, for instance, from chromium nitrate, or from soluble chromates, by precipitation. Further, when boron oxide is employed as the promoter, the oxide, or carbonate, of the catalytic metal may be mixed with solid, or dissolved, boric acid and then heated and reduced; or the salt of the catalytic metal, for instance, the nitrate, can be mixed with the borate of the same metal, or of a volatile, or non-volatile base, and the mixture then be calcined and reduced.

### Example 8.

Add two parts of dissolved potassium aluminate to a solution containing thirty parts of nickel nitrate and one and a half parts of calcium nitrate and introduce the whole into a boiling solution of sodium carbonate. Then filter, wash well, dry and reduce. Or, add a solution of one and a half parts of magnesium nitrate to five parts of nickel carbonate, and then add a solution of four-fifths of a part of ammonium phosphate and precipitate with soda, filter, wash, dry, and reduce. The nickel catalytic agent containing calcium aluminate, or magnesium phosphate, as the case may be, can be employed for hydrogenisation purposes, for instance, it may be introduced into oil which result from cracking petroleum residues and which is rich in unsaturated compounds, whereupon hydrogen is allowed to react at a temperature of 100° Centigrade and at a pressure of eighty atmospheres. The iodine number is rapidly reduced and at the same time the colour and unpleasant odour diminish.

In a similar manner other contact mixtures can be employed, which contain as a promoter, for instance, calcium vanadate, barium chromate, aluminium borate, barium tungstate, or lithium phosphate, or the compounds which result on the reduction of these bodies.

Dated this 28th day of January, 1914.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C.,
Agents.

## COMPLETE SPECIFICATION (AMENDED).

# Improvements in, and relating to, Hydrogenisation and Dehydrogenisation.

I, James Yate Johnson, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by the Badische Anilin & Soda Fabrik, of Ludwigshafen-on-Rhine, in the German Empire) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is known that many carbon compounds, including the oxides of carbon, can be converted into compounds containing hydrogen, or a greater proportion of hydrogen, by treating them with hydrogen in the presence of a catalytic agent and that the reverse reaction can also be effected. The present invention relates to improvements in the hydrogenisation and dehydrogenisation of carbon compounds, while employing a catalytic agent.

My foreign correspondents have found that they can effect the hydrogenisation and dehydrogenisation of compounds containing carbon, and that the reaction can be carried out rapidly, with certainty and at comparatively low temperatures, by employing, as the catalytic agent, an intimate mixture of either iron, nickel, cobalt, or copper, (which I hereinafter refer to as the catalytic metal) with a compound, or compounds, containing oxygen, and characterised by being, or containing, or giving rise to, high melting and difficulty reducible oxides, or oxygen compounds of weak basic, or neutral, or acid, character, all as hereinafter explained. In particular, I mention the oxides and oxygen salts of the earth metals, (see Ostwald, "Principles of Inorganic Chemistry" (English translation 1908 page 558) including the rare earths, (see Zeitschrift für Elektrochemie 17, page 633) and of beryllium, magnesium, manganese, uranium, vanadium, niobium, tantalum, chromium, boron, titanium, and also difficultly soluble phosphates, molybdates, tungstates and selenates of the alkaline earths, and of lithium, or the reduction products, containing oxygen of these phosphates, molybdates, tungstates, or selenates, for instance, the corresponding selenites. All of these compounds containing oxygen, which promote the activity of the catalytic metal, I hereinafter refer to as "promoters".

The said oxygen-containing salts of the alkaline earths and of lithium appear to have the same action as the corresponding salts of aluminium, magnesium, and the like, although lithium oxide and the alkaline earths, namely the oxides of calcium, barium, and strontium, are themselves not suitable for use as promoters.

In order to obtain the advantages of this invention it is necessary to effect an intimate mixture of the catalytic metal and a promoter, and it is not sufficient merely to fill the components, for instance, nickel and alumina, side by side, into the reaction space and it is insufficient to absorb a solution of a salt of the catalytic metal into a porous mass, such as magnesia and then decompose the salt of the catalytic metal. Good results for instance can be obtained by precipitating the hydroxides, oxides or carbonates, of the components together from a solution containing salts thereof; or mixtures of the said salts, for instance, the nitrates of the components, can be heated until a molten condition is obtained. Further the mixture can be obtained, although not always with equal certainty and excellence, by mechanical operations, such as by grinding together as finely as possible, or by kneading in a moist state. If necessary the mixture is subsequently heated and reduced so that in every case the catalytic metal, (iron, nickel, cobalt, or copper,) is obtained in a metallic condition, while the promoter always retains more, or less, oxygen. When the promoter is to consist of an insoluble oxide such, for instance, as aluminium oxide and titanium oxide, it is preferred to start from a soluble compound thereof and to precipitate, or otherwise form, the insoluble oxide on the catalytic metal, or on the compound from which the catalytic metal is to be prepared. For instance, if aluminium acetate be employed to yield the promoter, namely aluminium oxide, the said acetate can be merely heated in the presence of the catalytic metal, or compound thereof, so that the acetic acid is driven off, and the alumina remains. If insoluble salts, such for instance, as chromates, and borates, be employed as promoters, these are preferably brought into intimate mixture with the compound, which is subsequently to give rise to the metallic catalytic agent, by precipitation from suitable soluble salts, or other compounds. The salts which act as promoters may contain the oxide, to which the promoting action is ascribed, either in the acid constituent, or in the basic constituent, or in both the acid and the basic constituents. I mention calcium aluminate, and aluminium phosphate, as instances. In some cases, as aforesaid, the promoter may consist of a salt, of which neither the acid constituent, nor the basic constituent of itself acts as a promoter. As an instance of this type, I mention calcium phosphate.

It is particularly advantageous for the purpose of preparing a very active contact mass to prepare, at least the catalytic metal, from carbonaceous salts, or mixtures of salts, thereof, for instance from carbonates, or from formates. The action of the catalytic mixture can further often be increased by adding an alkaline metal compound, for instance, caustic soda, even traces of such compounds have often a favourable action. It is further often useful to add to the mixture, bodies of inorganic, or organic, nature, which act either as carriers, or as binding agents, or which increase the porosity of the contact mass. I instance asbestos, charcoal, and pumice-stone. It is advisable, however, to avoid the introduction of bodies such as chlorine, sulphur, arsenic, and lead, which may, in the elementary form, act as contact poisons, although the new contact mixtures, according to the present invention, are not so sensitive to the action of poisons as are the pure metals. It is consequently possible to employ as a promoter, an oxygen salt which contains one of the poisonous elements, but in which the poisonous action is counteracted by the promoting influence of the oxide; for instance, basic aluminium sulphate possesses a strong promoting action.

The catalytic metal can be employed either in a state of fine division, or in a more compact form, such as wire netting, or "wool", or in sheet form.

Instead of employing only one of the above mentioned oxides, or other oxygen compounds, a mixture of two, or more, may be added to the catalytic metal.

The proportion of the components employed in the catalytic mixture may be varied considerably, even an addition of one *per cent.* or less, of the said promoters producing, in most cases, favourable action.

In those cases in which reduction has to be resorted to in order to obtain the catalytic metal, such reduction is preferably carried out by means of pure hydrogen, or other suitable agent, at as low a temperature as possible, and, if the catalytic mixture, after having been reduced with hydrogen, has to be exposed to the air, it is generally advisable to previously drive away any excess of hydrogen by passing an indifferent gas, such as carbon dioxide, over the mixture and thus to avoid even superficial oxidation of the metal.

The catalytic mixtures, according to this invention, can be used for the hydrogenisation and dehydrogenisation of compounds containing carbon, and are of particular value for the hardening of fats and fatty acids, but they can also be used for other purposes, for instance, for converting phenol into cyclohexanol and for reducing nitrobenzene to aniline. and for the conversion of oxides of carbon into hydrocarbons.

The catalytic reaction according to this invention can be carried out either at ordinary pressure, or under increased pressure, and in most cases proceeds sufficiently rapidly at temperatures considerably below 180° Centigrade.

The process of the present invention is of great importance. The Specification of Letters Patent No. 7315 A.D. 1909 proposes to employ, for the hydrogenation, or dehydrogenation, of organic compounds, a catalyst consisting of a mixture of a suitable metal, or metals, with a small quantity of metal salts which are not transformed into the metallic state by heat, or reduction but the only instances given are with regard to the conversion of borneol into camphor, using a mixture of nickel with sodium nitrate, sodium sulphate, or sodium chloride. The action of such mixtures in the hydrogenation of fats is however, relatively small, compared with that of the mixtures according to the present invention, and moreover, the employment of strong bases is, in such cases, detrimental, since they tend to saponify, and very soon disappear from the contact mass. On the other hand, when employing the promoters according to this invention, that is to say, promoters which have not a strong basic action, contact masses are obtained which are characterized by a strong, and more, or less, permanent action. Of course, for different processes of hydrogenisation and dehydrogenisation according to this invention, different mixtures of catalytic metals and promoters may be preferred for particular cases.

The following are examples of how catalysts can be prepared for the purposes of this invention and how this invention can be carried into practical effect, but the invention is not limited to these examples. The parts are by weight.

### EXAMPLE 1.

Dissolve a mixture of fifteen parts of nickel nitrate and one part of beryllium nitrate, precipitate while hot with caustic soda, filter off the precipitate, and wash and dry it. Then at a temperature of from 250°, to 300°, Centigrade, pass a mixture of gases containing one volume of carbon monoxide and three volumes of hydrogen over the mixture until the reduction of the nickel oxide is complete, and the conversion of the carbon monoxide into methane is taking place. The temperature can then be reduced to about 150° Centigrade, or even less, without the catalytic agent becoming inactive. If desired the entire reduction of the nickel oxide can be carried out with pure hydrogen. The precipitation can, for instance, be carried out by means of alkali carbonate. Instead of beryllium nitrate, zirconium nitrate, or thorium nitrate, can be employed.

### Example 2.

Pour an aqueous solution of one part aluminium nitrate over five parts of nickel oxalate, evaporate the mixture and dry it and reduce it in a current of hydrogen at from 300° to 350°, Centigrade. Then introduce the nickel containing alumina, while excluding air, into a shaking vessel, provided with a stirrer, the said vessel containing fish oil, or other suitable oil, which may have been previously purified. On treatment with hydrogen at, for instance, 100° Centigrade, hydrogenisation takes place considerably more rapidly than if pure nickel were employed as the catalytic agent. Instead of aluminium nitrate, cerium nitrate, or cerium ammonium nitrate, can be employed.

### Example 3.

Precipitate a hot solution containing nickel nitrate and aluminium nitrate with potassium carbonate, wash the precipitate, dry it, heat it to 300° Centigrade, and reduce it with hydrogen. Then place the catalytic mixture with soya bean oil in an autoclave, while avoiding the presence of air, heat to 80° Centigrade, and allow hydrogen to act at a pressure of twenty atmospheres while suitably mixing the constituents. The hydrogenisation takes place very rapidly. If desired the pressure can be increased, for instance, up to fifty atmospheres, or higher. In this example, good results can also be obtained if iron nitrate be employed instead of nickel nitrate.

### Example 4.

Mix thirteen parts of nickel hydroxide with two parts of magnesium hydroxide, and warm them gently with concentrated formic acid free from sulphur, until the formates are obtained. Heat the mixture gently till dry, and then treat with hydrogen at 300° Centigrade. On treating olive oil with hydrogen in the presence of this catalytic mixture at say, from 80° to 100°, Centigrade hydrogenisation is effected more rapidly than is the case when pure nickel is used. In this example the hydroxides can, if desired, be replaced by the corresponding carbonates and carriers, for instance, pieces of clay can be employed, these being soaked in a melt, or solution, of nickel salts, preferably of the soluble double salts, such as nickel ammonium formate, or ammonical nickel carbonate, together with similar salts of the promoter, and then treated as hereinbefore described.

### Example 5.

Make nickel wire netting into the form of loose spheres, rolls, or the like, and clean these with pure dilute nitric acid, and then wash them and moisten them with a moderately concentrated solution of aluminium nitrate; then dry them and treat them with hydrogen at from 300°, to 350°, Centigrade. The contact mass containing alumina can, for instance, be employed for the hydrogenisation of linseed oil which can be allowed to trickle over the catalytic agent while the hydrogen is supplied, and a considerable, or even complete, hardening be effected.

### Example 6.

Dissolve eighty-five parts of nickel nitrate and fifteen parts of titanium lactate in a small quantity of hot water and precipitate by means of caustic soda, or sodium carbonate, then filter, wash, dry, and reduce with hydrogen at 300°, Centigrade, and add the catalytic mixture containing titanium oxide to cotton seed oil, and then treat with hydrogen at from 100°, to 120°, Centigrade while keeping the mixture in motion. If desired the reaction can be carried out under increased pressure, (for instance, 100 atmospheres,) and in this case the hydrogenisation takes place very rapidly and completely even at a temperature of 90°, Centigrade, or lower. Further, the process can be made continuous by allowing the oil to flow over the catalytic agent in a vessel capable of withstanding pressure while simultaneously passing a current of hydrogen into, or through, the apparatus. The product is drawn off while hot and allowed to solidify.

### EXAMPLE 7.

Take freshly precipitated nickel carbonate and add from ten, to twenty *per cent.* of the weight thereof of ammonium borate, or potassium borate, which has previously been dissolved in water. Then form the mass into any desired shape, and dry, and reduce it. The mixture can be employed for hydrogenising oils and fats, either at ordinary pressure, or under increased pressure. If chromium oxide be used as the promoter, this can be obtained, for instance, from chromium nitrate, or from soluble chromates, by precipitation. Further, when boron oxide is employed as the promoter, the oxide, or carbonate, of the catalytic metal may be mixed with solid, or dissolved, boric acid and then be heated and reduced; or the salt of the catalytic metal, for instance, the nitrate, can be mixed with the borate of the same metal, or of a volatile, or non-volatile base, and the mixture then be calcined and reduced.

### EXAMPLE 8.

Add two parts of dissolved potassium aluminate to a solution containing thirty parts of nickel nitrate and one and a half parts of calcium nitrate and introduce the whole into a boiling solution of sodium carbonate. Then filter, wash well, dry and reduce. Or, add a solution of one and a half parts of magnesium nitrate to five parts of nickel carbonate, and then add a solution of four-fifths of a part of ammonium phosphate and precipitate with caustic soda, or sodium carbonate, filter, wash, dry and reduce. The nickel catalytic agent containing calcium aluminate, or magnesium phosphate, as the case may be, can be employed for hydrogenisation purposes, for instance, it may be introduced into oil which results from cracking petroleum residues and which is rich in unsaturated compounds, whereupon hydrogen is allowed to react at a temperature of 100° Centigrade and at a pressure of eighty atmospheres. The iodine number is rapidly reduced and at the same time the colour and unpleasant odour diminish.

In a similar manner other contact mixtures can be employed, which contain as a promoter, for instance, calcium vanadate, barium chromate, aluminium borate, barium tungstate, or lithium phosphate, or the compounds which result on the reduction of these bodies.

### EXAMPLE 9.

Take a hot aqueous solution of thirty parts of anhydrous sodium carbonate and add, while shaking, a hot solution containing seventy-five parts of nickel nitrate and six parts of manganese nitrate. Then filter off the precipitate, wash it well and dry it and reduce it with hydrogen at 300° Centigrade. The product can be employed in the hydrogenising of pig nut oil and even when employing temperatures of 100°, to 120°, Centigrade, the hydrogenising proceeds very rapidly.

### EXAMPLE 10.

To a hot solution of thirteen parts of nickel nitrate and two parts of chromium nitrate, add a hot solution containing six parts of anhydrous sodium carbonate. Then filter off the precipitate, wash it until the filtrate is free from alkali, then dry and reduce it. With the help of this catalytic agent, soy bean oil can be hydrogenised rapidly at a low temperature.

### Example 11.

Suspend forty parts of nickel carbonate in a solution containing one part of ammonium tungstate and then add a solution of one part of barium nitrate. Filter off the product, wash it well, dry and reduce it at 300° Centigrade. The product can be employed for example for hydrogenising sesame oil at 120° Centigrade.

### Example 12.

Mix to a paste fifty parts of nickel carbonate and a solution of thirteen parts of calcium nitrate and then stir in a solution of seven parts of ammonium phosphate. Filter off the product, wash well, dry and reduce at from 300°, to 350°, Centigrade. The product can be employed for example for hydrogenising fish oil.

### Example 13.

Stir eighty parts of nickel carbonate into a solution of 2.6 parts of strontium nitrate, and add a solution of two parts of ammonium selenite. Filter off the product, wash well, dry and reduce. The product can be used for example for hydrogenising cotton seed oil.

I am aware that the Specification of Letters Patent No. 7670 A.D. 1914 lays claim to use, in the production of saturated compounds from unsaturated fatty acids and their glycerides, nickel borate, and also to produce and employ a product obtained by carefully heating nickel borate in dry hydrogen and I make no claim, under my present application, to such production and use.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that I do not claim the use of oxides in conjunction with silica as described in the Specification of Letters Patent No. 13,382, A.D. 1913, nor do I claim the use of silicates, but what I claim is:—

1. In the hydrogenisation, or dehydrogenisation, of compounds containing carbon, the employment as a catalytic agent, of an intimate mixture as hereinbefore explained, of either iron, nickel, cobalt, or copper, with a promoter consisting of an oxide, or oxygen-salt, of an earth metal including the rare earths, or of beryllium, magnesium, manganese, uranium, vanadium, niobium, tantalum, chromium, boron, or titanium.

2. In the hydrogenisation, or dehydrogenisation, of compounds containing carbon, the employment as a catalytic agent of an intimate mixture of either iron, nickel, cobalt, or copper, with a promoter consisting of a difficultly soluble phosphate, molybdate, tungstate, or selenate, of an alkaline earth metal, or of lithium, or a reduction product, containing oxygen, of any of these compounds.

3. In the hydrogenisation, or dehydrogenisation, of compounds containing carbon, the employment of catalytic agents which have been produced as described in any one of the foregoing examples.

Dated this 27th day of July, 1914.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C.,
Agents.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1916.