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HYDROGENIZATION AND DEHYDROGENIZATION OF CARBON COMPOUNDS.

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Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that we, CARL BOSCH, ALWIN MITTASCH, and CARL KRAUCH, citizens of the German Empire, residing at Ludwigshafen-on-the-Rhine, Germany, have invented new and useful Improvements in the Hydrogenization and Dehydrogenization of Carbon Compounds, of which the following is a specification.

10 Our invention relates to the hydrogenization and dehydrogenization in the presence of a catalytic agent of compounds containing carbon, and to catalytic mixtures by means of which the said hydrogenization
15 and dehydrogenization can be carried out rapidly, with certainty and at comparatively low temperatures. We have discovered that these advantages can be obtained by employing as the catalytic agent an intimate mixture of a common metal, in particular iron, nickel, cobalt and copper (which we hereinafter refer to as the catalytic metal), with a precipitated difficultly
20 reducible oxygen-containing compound of a metal which is capable of forming only a weak basic oxid. In particular we mention the oxids and oxygen-containing salts of the earth metals, including the rare earths, (see *Zeitschrift für Elektrochemie*,
25 vol. 17, p. 633), and of beryllium, magnesium, manganese, uranium, vanadium, columbium, tantalum, chromium and titanium. All of these oxygen-containing compounds which promote the activity of the catalytic
30 metal, we refer to hereinafter as "promoters."

In order to obtain the advantages of this invention it is necessary to effect an intimate mixture of the catalytic metal and the
40 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 hydroxids,
45 oxids 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 grinding together as finely as
50 possible, or by kneading in a moist state.

If necessary, the mixture is subsequently
55 heated and reduced so that in every case the catalytic metal, that is to say iron, nickel, cobalt or copper, is obtained in a metallic condition, while the promoter always retains more or less oxygen. When the promoter
60 is to consist of an insoluble oxid such, for instance, as aluminium oxid and titanium oxid, it is preferred to start from a soluble compound thereof, and to precipitate the insoluble oxid on the catalytic metal, or on
65 the compound from which the catalytic metal is to be prepared. For instance, if aluminium acetate be employed to yield the promoter, namely aluminium oxid, the said acetate can be merely heated in the presence
70 of the catalytic metal or compound thereof, so that the acetic acid is driven off, or decomposed, and the alumina remains. If insoluble salts, such for instance, as chromates 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 solutions of suitable soluble salts or other compounds. The salts which act as
80 promoters may contain the oxid to which the promoting action is ascribed either in the acid, or in the basic constituent, or in both the acid and the basic constituent. We mention, calcium aluminate, aluminium
85 phosphate and magnesium aluminate as instances of these three types.

It is particularly advantageous for the purpose of preparing a very active contact mass to prepare, at least the catalytic metal,
90 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 alkali metal compound, for instance, caustic soda; even traces of such compounds have often a favorable 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
100 agents, or which increase the porosity of the contact mass. We mention, for instance, asbestos charcoal and pumice. It is advisable however, to avoid the introduction of bodies such as chlorin, sulfur, arsenic and lead,
105 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 oxid; for instance, basic aluminium sulfate, 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 oxids, 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 often producing favorable action. It is generally preferred, however, to add larger quantities of the promoter, say from ten to twenty per cent. or even more.

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 previously to drive away any excess of hydrogen by passing an indifferent gas such as carbon dioxide over the mixture and thus avoid even superficial oxidation of the metal.

The catalytic mixtures according to this invention can be used for the hydrogenization and dehydrogenization of compounds containing carbon and 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 anilin, and for the conversion of oxids of carbon into hydrocarbons.

The catalytic reaction according to this invention can be carried out either at ordinary pressure or under increased pressure, for instance, above 50 atmospheres, and in most cases proceeds sufficiently rapidly at temperatures considerably below 180° C.

The process of the present invention is of great importance. It has indeed been proposed to employ mixtures of metallic nickel and the like with sodium hydrate, sodium chlorid, barium chlorid, sodium nitrate and sodium sulfate, for the catalytic dehydrogenization 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 hydrogenization of fats, since they

tend to saponify the fats, and very soon disappear from the contact mass. On the other hand, when employing promoters according to our 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 hydrogenization and dehydrogenization according to this invention, different mixture of catalytic metals and promoters may be preferred in 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 15 parts of nickel nitrate and 1 part of beryllium nitrate, precipitate while hot with soda, filter off the precipitate, and wash and dry it. Then at a temperature of 250–300° C. pass a mixture of gases containing one volume of carbon monoxid and three volumes of hydrogen over the mixture until the reduction of the nickel oxid is complete, and the conversion of the carbon monoxid into methane is taking place. The temperature can then be reduced to about 150° C. or even less without the catalytic agent becoming inactive. If desired, the entire reduction of the nickel oxid can be carried out with pure hydrogen. The precipitation can, for instance, be carried out by means of alkali hydroxid. Instead of beryllium nitrate, zirconium nitrate or thorium nitrate, can be employed.

Example 2.

Pour an aqueous solution of 1 part of aluminium nitrate over 5 parts of nickel oxalate, evaporate the mixture and dry and reduce it in a current of hydrogen at from 300–350° C.

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° C., hydrogenization 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° C. 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° C. and allow

hydrogen to act at a pressure of twenty atmospheres while suitably mixing the constituents.

The hydrogenization takes place very rapidly. If desired the pressure can be increased, for instance, up to 50 atmospheres, or higher. In this example, if iron nitrate be employed instead of nickel nitrate, good results can be obtained. The reduction to metallic nickel or iron can be carried out in the autoclave itself, for instance, at 250–300° C. and 80 atmospheres pressure.

Example 4.

Mix 13 parts of nickel hydroxid with 2 parts of magnesium hydroxid, and warm them gently with concentrated formic acid which is free from sulfur, until the formates are obtained. Heat the mixture gently, and then treat with hydrogen at 300° C. On treating olive oil with hydrogen in the presence of this catalytic mixture at say from 80–100° C. a more rapid hydrogenization is brought about than is the case when pure nickel is used. In this example the hydroxids can be replaced by the corresponding carbonates if desired, 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 solution, together with the promoter, and then treated as hereinbefore described.

Example 5.

Bring nickel wire netting into the form of loose spheres, rolls or the like, and clean these with pure dilute nitric acid, then wash them and moisten with a moderately concentrated solution of aluminium nitrate, then dry and treat with hydrogen at from 300–350° C. The contact mass containing alumina can, for instance, be employed for the hydrogenization 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 is effected.

Example 6.

Dissolve 85 parts of nickel nitrate and 15 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° C. add the catalytic mixture containing titanium oxid to cotton seed oil, and then treat with hydrogen at from 100–120° C. while maintaining the mixture in a state of motion.

If desired, the reaction can be carried out under increased pressure, for instance, 100 atmospheres, and in this case the hydrogenization takes place very rapidly and completely even at a temperature of 90° C. 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.

Add 2 parts of dissolved potassium aluminate to a solution containing 30 parts of nickel nitrate and 1½ parts of calcium nitrate and introduce the whole into a boiling solution of sodium carbonate. Then filter, wash well, dry and reduce. The nickel catalytic agent containing calcium aluminate can be employed for hydrogenization purposes, for instance, it may be introduced into an oil resulting from cracking petroleum residues and which is rich in unsaturated compounds, whereupon hydrogen is allowed to react at a temperature of 100° C. and at a pressure of 80 atmospheres. The iodine number is rapidly reduced and at the same time the color and unpleasant odor diminish.

In a similar manner other contact mixtures can be employed, which contain as a promotor, for instance, calcium vanadate, barium chromate and barium tungstate, or the compounds which result by the reduction of these compounds.

Now what we claim is:—

1. The process of hydrogenizing compounds containing carbon by treating such compounds with hydrogen in the presence of a heated intimate mixture of a common metal acting as a catalyzer for the said reactions, and a precipitated difficultly reducible oxygen-containing compound of a metal which is capable of forming only a weak basic oxid.

2. The process of hydrogenizing compounds containing carbon by treating such compounds with hydrogen in the presence of a heated intimate mixture of a metal of the iron group and a precipitated difficultly reducible oxygen-containing compound which is capable of forming only a weak basic oxid.

3. The process of hydrogenizing compounds containing carbon by treating such compounds with hydrogen in the presence of a heated intimate mixture of nickel and a precipitated difficultly reducible oxygen-containing compound of a metal which is capable of forming only a weak basic oxid.

4. The process of hydrogenizing compounds containing carbon by treating such compounds with hydrogen in the presence of a heated intimate mixture of nickel and a precipitated oxygen-containing compound of aluminium.

5. The process of hydrogenizing compounds containing carbon by treating such

compounds with hydrogen in the presence of a heated intimate mixture of nickel and aluminium oxid prepared by precipitation.

6. The process of hydrogenizing compounds containing carbon by treating such compounds with hydrogen under a pressure exceeding that of 50 atmospheres, in the presence of a heated intimate mixture of a common metal and a precipitated difficultly reducible oxygen-containing compound of a metal which is capable of forming only a weak basic oxid.

7. The process of hydrogenizing unsaturated oils by treating them with hydrogen in the presence of a heated intimate mixture of a common metal acting as a catalyzer for the said reactions and a precipitated difficultly reducible oxygen-containing compound of a metal which is capable of forming only a weak basic oxid.

8. A catalyst comprising co-precipitated nickel and a difficultly reducible oxygen compound of a metal which is capable of forming only a weak basic oxid, said nickel having the catalytic powers of nickel reduced at temperatures around 300° C.

9. A catalyst comprising co-precipitated nickel and alumina, said nickel having the catalytic powers of nickel reduced at temperatures around 300° C.

In testimony whereof we have hereunto set our hands in the presence of two subscribing witnesses.

CARL BOSCH.
ALWIN MITTASCH.
CARL KRAUCH.

Witnesses:
CH. TRUNCIDER,
J. ALEC. LLOYD.