UNITED STATES PATENT OFFICE.

CARLETON ELLIS, OF MONTCLAIR, NEW JERSEY.

CATALYZER AND PROCESS OF MAKING SAME.

1,156,068. Specification of Letters Patent. Patented Oct. 12, 1915.

No Drawing. Application filed April 3, 1915. Serial No. 19,032.

To all whom it may concern:

Be it known that I, CARLETON ELLIS, a citizen of the United States, and a resident of Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Catalyzers and Processes of Making Same, of which the following is a specification.

This invention relates to catalyzers and to the process of making same and relates particularly to base metal catalyzers such as nickel, cobalt and copper material preferably formed in a liquid vehicle under suitable conditions as will be more fully hereinafter pointed out.

1. This application contains matter disclosed in pending application Serial No. 686,988 filed March 29, 1912 which was derived from Serial No. 656,100 filed Oct. 23, 1911 now Patent No. 1,026,156 of May 14, 1912 and also contains matter disclosed in the files of Serial No. 718,228 filed September 3, 1912, now Letters Patent No. 1,067,978 of July 22, 1913, Serial No. 732,943 filed November 22, 1912, now Letters Patent No. 1,097,308 of May 19, 1914 and copending application Serial No. 808,461 filed Dec. 23, 1913.

2. Hydrogenation by means of nickel oxid at ordinary pressure or at very high pressures is stated by Ipatiew (*Ber.* 1907, vol. 40, page 1290) to be effective as a catalyst. Nickel oxid which has been prepared by ignition and subsequently reduced to a somewhat lower oxid by the action of hydrogen on the ignited oxid alone or submerged in oil also is proposed as a catalyzer. The dense character of ignited nickel not infrequently makes its distribution through the liquid difficult and to render the operation easier it has been proposed to ignite nickel nitrate in the presence of carbonaceous material so as to form voluminous nickel oxid. The high temperature attained by this ignition while producing a voluminous product tends to densify the actual particles thereof. For these reasons among others it has been commonly regarded as desirable to use nickel in the metallic state as a catalyzer and to support it on some carrier by which it could be extended over such a surface that the densification due to ignition would not prejudice the activity of the resulting catalyst. The difficulties and expense of reduction to secure a uniform product have been found considerable. Such catalytic material is somewhat difficult to regenerate after it has become inactive from use owing to the mass of inert carrier which is often of an absorptive character. Catalyzers formed by reduction in an atmopshere of hydrogen gas are usually pyrophoric and great precaution is required to prevent ignition of the catalyzer with resultant inactivity or diminished catalytic action.

3. By my invention preferably no carrier or supporting material is used as the product is finely divided and does not require any extending support. As the catalytic material preferably is formed in a bath of the liquid vehicle it does not give trouble from pyrophoric action. Preferably the catalyzer is made from material which has not been ignited but is formed under such conditions as to avoid a dense form of material and conforming more or less to the original, preferably light flocculent freshly precipitated nature of the raw material. Owing to the fact that no carriers are essential and to the peculiar physical condition of the nickel or similar material, regeneration is brought about quickly and cheaply, when the catalyzer has lost its activity by use.

4. My invention in its preferred form embraces in its present form the heating of substantially a non-volatile compound of a metal such as a finely-divided solid or precipitate, preferably nickel material or nickel-containing material with a substantially fixed or relatively non-volatile compatible liquid bathing vehicle or suspensory agent such as fatty or mineral oil, glycerin and the like preferably in contact with a reducing gas such as hydrogen under high pressure or preferably at about atmospheric pressure and ordinarily with removal of water as formed during the reducing operation, until the nickel material has been brought to a substantially or completely pure metallic state or to any other desired stage of reduction.

5. Nickel material prepared under some circumstances may contain chlorids which heretofore have been known to act deleteriously as catalyzer poisons to prevent or reduce the activity of the catalytic material. In the present case, however, such bodies as sodium chlorid may be present even in considerable amount without causing material injury to the catalyzer. This is an impor-

tant consideration in preparing nickel hydrate from nickel chlorid under conditions aiming to produce a highly flocculent precipitate so as to secure a large amount of surface action. Such flocculent material is of course difficult to wash free from chlorids and the expense attached to purifying this material is not inconsiderable. The present process enables material to be used which has not been subjected to expensive washing operations and hence enables a cheapening of the operation to be effected.

6. The gas used for reduction is preferably pure hydrogen and this preferably should be free from oxygen. If prepared by the electrolytic process the hydrogen gas may contain some oxygen and if so it is desirable to pass the gas over heated copper oxid to cause the oxygen to unite with some of the hydrogen, thereby forming water which may be removed by a drying agent. Other reducing gases such as carbon monoxid also, may be employed, likewise vapors of organic compounds, such as alcohol or gasolene which also have a reducing action. Under some circumstances the reducing gas may be dispensed with altogether and the nickel material heated with the liquid vehicle under such temperature and pressure conditions as will effect the desired degree of reduction. With respect to the pressure of the reducing gas it may be stated that the process is most simply carried out by using gas at approximately atmospheric pressure but when rapid action is desired or when it is desired to free some difficultly reducible material from every trace of oxygen higher pressures may be employed.

7. The temperature of reduction may vary considerably depending on the liquid vehicle used for reduction and on the character of the reducing gas. The physical condition of the nickel material also influences the rate of reduction and the temperature should be adjusted with reference to these several factors. Specifically temperatures between 200° C. and 300° C. are most desirable as the physical form of the nickel material in a proper vehicle ordinarily is but little effected by reduction between this range of temperature. Below 200° the action is slow as a rule especially with hydrogen gas while carbon monoxide sometimes is somewhat more rapid and effective at lower temperatures. Above 300° decomposition of the liquid vehicle may occur with unfavorable action on the catalyzer. This however depends on the character of the said liquid vehicle. No limitation is intended to be expressed by setting forth the range of temperature as conditions may modify the temperature within narrower or wider ranges. Between 260° or better 270° and 290° C. however the most desirable results, when using nickel hydrate, are attained, due no doubt, to the physical as well as chemical form of the product. When employing a glycerin as a liquid vehicle a temperature near the boiling point of glycerin, that is 290° C., is desirable. The glycerin and catalyzer may be contained in a receptacle fitted with a reflux condenser which enables the vapors of glycerin carried away in the gas to be condensed more or less and returned to the receptacle while moisture formed by the reaction or present in the original material is allowed to escape. At times, hydrogenation of the glycerin occurs forming more volatile products.

8. The submersion or bathing liquid preferably should be of a viscous nature in order to hinder the contraction of the particles of catalytic material during its formation. It may be a material which is solid at ordinary temperatures, as, for instance, hardened oil. Also, the liquid preferably should be of a substantially fixed or relatively non-volatile character within the range of temperature employed for reduction under the particular conditions of operation. Liquids of thin body are prone to allow undue contraction of the catalytic particles and such liquids are also generally highly volatile so that the necessary temperature of reduction cannot be attained without resorting to high pressure using an autoclave which involves expensive apparatus and which may be attended with some danger to the operator. A compatible vehicle such as a fatty oil specially a neutral fat substantially free from fatty acid is well adapted for the purpose. Heavy petroleum oils if of sufficient purity may also be employed. An oil of this character of as stable a nature as possible under the thermal conditions imposed preferably should be employed. Glycerin although boiling below 300° C. can be used successfully for reduction within a carefully adjusted temperature range. In a similar manner other vehicles which are liquid under the conditions of operation may be employed as the submersion media. Care should be taken however that the medium does not react unfavorably with the solid material to form inert compounds etc.

9. Generally speaking, water formed during the reducing operation should be removed promptly from the zone of reaction. If allowed to accumulate and create back pressure the tendency will exist to hinder further reduction so that poorly reduced material results. On this account a copious current of hydrogen should be passed through the reacting mass or conditions be otherwise adjusted to secure the removal of the water vapor. This of course applies when the material employed evolves water or the latter is formed by the reaction.

10. The reduced catalytic material may be

removed from the liquid vehicle by filtration or deposition or if desired separation may be effected by centrifuging the mixture. In the case of glycerin which is soluble in both water and alcohol either of these or similar solvents may be employed to wash the catalyzer free from vehicle. Or the glycerin may be removed by distillation preferably under diminished atmospheric pressure or in a current of hydrogen. In a strong current of hydrogen glycerin may be volatilized very readily at elevated temperatures. When a fatty oil is used as the vehicle and the pressure of this fatty material is not objectionable in the subsequent operation of hydrogenating a larger body of oil the mixture of oil and catalyzer may be directly added to the oil to be hardened. Or the catalyzer may be formed in the entire body of oil to be hydrogenated.

10. Materials suitable as a source of the catalytic body are as stated preferably basic inorganic compounds of the base metals particularly nickel, cobalt and copper or mixtures thereof. The compounds of these metals which are preferred are the oxids or hydrates, carbonates, and the like. Nickel carbonate especially when employed in a basic and somewhat hydrated condition is capable of being reduced to form a fairly satisfactory catalyzer in some cases but has the disadvantage of contaminating the excess of hydrogen with more or less carbon dioxid, when heating under conditions giving rise to this gas. Nickel hydrate, especially when employed in a moist condition is particularly adapted for the present purpose. Nickelous hydroxid $Ni(OH)_2H_2O$ affords a highly efficient catalytic basis. Other forms are $mNi(OH)_2.nH_2O$. It may be prepared by precipitation from nickel sulfate or chlorid solution by means of caustic soda solution for example. The hydrate may if desired be dissolved in ammonia water and evaporated in the presence of the liquid vehicle so as to form the the nickel hydrate in intimate contact with said vehicle. A fatty oil which would be saponified under the circumstances and form emulsions is not as suitable for these substances as petroleum oil or glycerin. The source of catalytic material herein is therefore preferably a finely-divided solid material preferably an inorganic basic compound; illustratively nickel hydrate which preferably is used in the form of the perhydrate or moist hydrate as distinct from ignited or strongly dried material. Such a product may be obtained by drying a precipitate of nickel hydrate as prepared above at a temperature approximating or slightly below, 100° C. This material is especially susceptible to the reducing action of hydrogen or other reducing gas and from it may be obtained a catalytic material comprising or consisting of finely-divided metallic nickel having in some cases substantially the form of the original precipitate and possessing a highly active catalytic character.

11. A further feature of my invention involves the use of composite catalytic material such as may be obtained by reducing a mixture of for example nickel and cobalt or copper compounds. A mixture of equal parts of soluble salts of nickel and cobalt may be dissolved in water and precipitated with alkali to give hydrated material in a suitable form. Similarly, three parts of nickel sulfate and one part of copper sulfate may be put into solution and precipitated with, for example, caustic soda, forming a co-precipitated mixture of nickel and copper hydrates in a very intimate state. These composite bodies are reduced in the manner aforesaid and afford catalyzers which are useful in treating oils that oftentimes are resistant to hydrogenation with a simple nickel catalyzer. The nickel and copper composition is especially suited for the hydrogenation of fish and whale oils.

What I claim is:—

1. The process of preparing catalyzer adapted for hydrogenating fatty oils and the like which comprises forming catalytic material comprising an active metal by reduction of a reducible hydrated compound of said metal in a compatible substantially fixed liquid vehicle in the presence of a reducing gas.

2. The process of making catalyzer adapted for hydrogenating fatty oils and the like which comprises mixing a flocculent precipitate comprising nickel hydrate $Ni(OH)_2.H_2O$ with a compatible substantially fixed liquid vehicle, in heating and passing hydrogen through the mixture; whereby finely-divided catalytic material results.

3. The process of making catalyzer adapted for hydrogenating fatty oils and the like which comprises incorporating nickel and copper hydrate with a compatible substantially fixed oily medium, in heating and passing hydrogen through the mixture; whereby finely-divided catalytic material results.

4. The process of making catalyzer adapted for use in hydrogenating fatty oils and the like which comprises incorporating a finely-divided reducible solid compound of nickel and a similar compound of copper with a compatible substantially fixed oily vehicle, in heating and exposing to the action of a reducing gas while removing moisture formed by reduction; whereby finely-divided catalytic material capable of hardening resistant oils results.

5. The process of making catalyzer adapted for use in hydrogenating fatty oils and the like which comprises incorporating a finely-divided reducible solid compound of

nickel and a similar compound of another catalysis-aiding element, in heating and exposing to the action of a reducing gas while removing moisture formed by reduction; whereby finely-divided catalytic material capable of hardening resistant oils results.

6. The process of making catalyzer adapted for use in hydrogenating fatty oils and other unsaturated material which comprises exposing a finely-divided reducible solid compound of nickel and another catalysis element to the action of a reducing gas; whereby finely-divided catalytic material results.

7. The process of making catalyzer adapted for use in hydrogenating fatty oils and other unsaturated material which comprises mixing a finely-divided reducible solid compound of nickel with a compatible substantially fixed oily vehicle and exposing to the action of a reducing gas at a temperature approaching 300° C., whereby voluminous finely-divided catalytic material results.

8. The process of making catalyzer adapted for use in hydrogenating fatty oils and the like which comprises exposing a finely-divided reducible solid compound of nickel and another catalysis-aiding metal at normal atmospheric pressure and at a temperature between 270° and 290° C., to the action of a reducing gas.

9. A catalytic material comprising finely-divided metallic nickel and copper and active as a hydrogen carrier in the catalytic hydrogenation of fatty oils.

10. A catalytic material comprising finely-divided metallic nickel having substantially the form of freshly precipitated nickel hydrate.

11. A catalytic agent comprising finely-divided reduced nickel material whose particles possess substantially the form of precipitated nickel hydrate, and are active as a hydrogen carrier in the catalytic hydrogenation of fatty oils.

12. A catalytic material adapted as a hydrogen carrier comprising finely-divided metallic nickel and another catalysis-aiding metal and active as a hydrogen carrier in the catalytic hydrogenation of fatty oils.

13. A catalytic material of a metallic character comprising nickel and copper substantially free from oxids.

14. A catalytic agent adapted for hydrogenating fatty oils which comprises a voluminous flocculent active composite, comprising base metal powder substantially free from oxids and specifically active as a hydrogen carrier for unsaturated fatty oils.

15. A catalytic agent adapted specifically as a hydrogen carrier for fatty oils and consisting of an active base metal and another catalysis-aiding metal, all in the form of a voluminous powder.

Signed at Montclair in the county of Essex and State of New Jersey this 2nd day of April A. D. 1915.

CARLETON ELLIS.

Witnesses:
W. O. HENKE,
B. M. ELLIS.