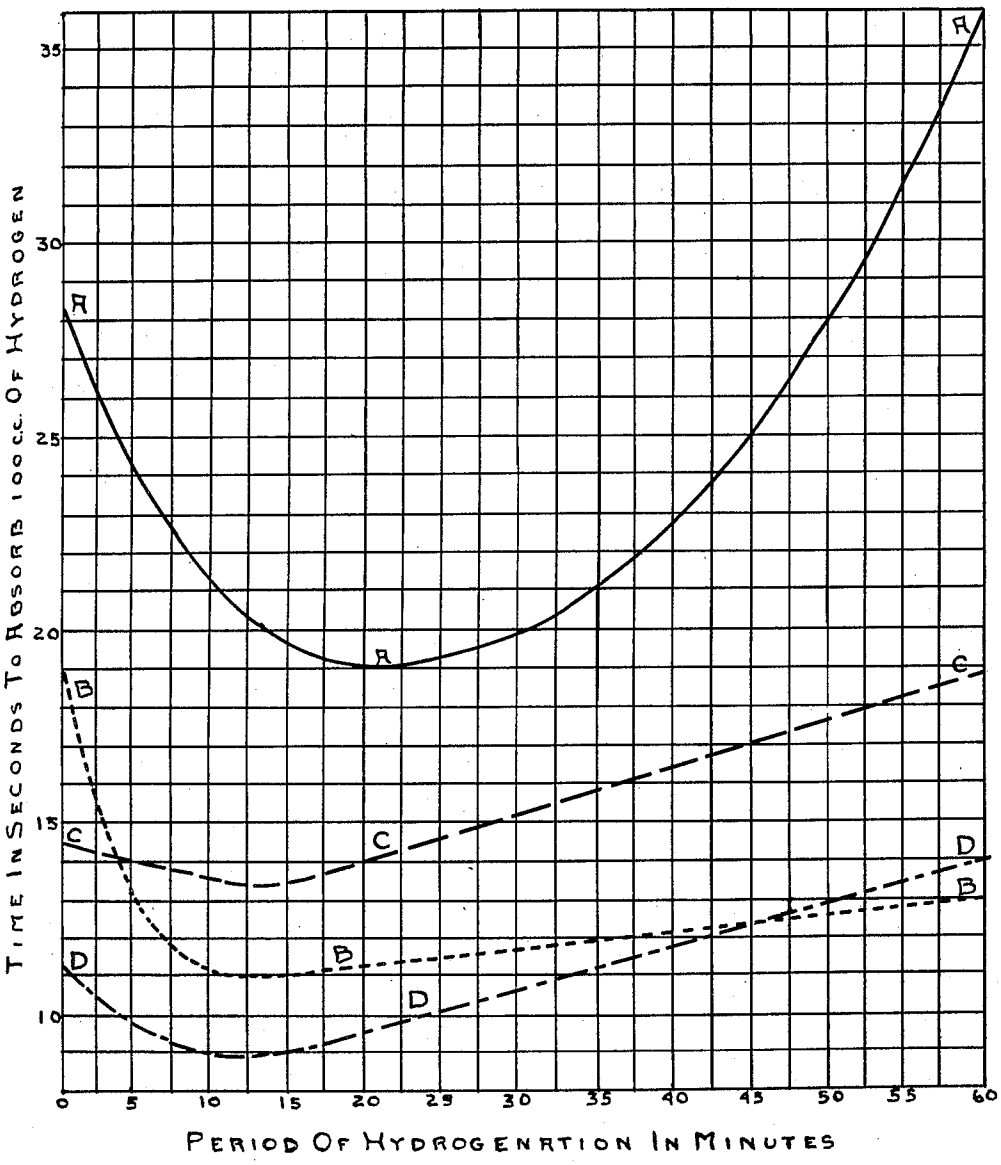
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C. ELLIS ET AL

CATALYZER AND METHOD OF MAKING SAME

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INVENTORS:

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UNITED STATES PATENT OFFICE.

CARLETON ELLIS, OF MONTCLAIR, AND HARRY M. WEBER, OF BLOOMFIELD, NEW JERSEY; SAID WEBER ASSIGNOR OF HIS ENTIRE RIGHT TO ELLIS-FOSTER COMPANY, A CORPORATION OF NEW JERSEY.

CATALYZER AND METHOD OF MAKING SAME.

Application filed July 15, 1920. Serial No. 396,599.

To all whom it may concern:

Be it known that we, CARLETON ELLIS and HARRY M. WEBER, citizens of the United States, and residents, respectively, of Montclair, in the county of Essex and State of New Jersey, and Bloomfield, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Catalyzers and Methods of Making Same, of which the following is a specification.

This invention relates to a method of making catalyzers adapted for use as hydrogen carriers and particularly useful in the hydrogenation of fatty oils and like purposes.

The invention involves the comminution of the catalytic raw material in a suitable medium preferably one of a liquid character or one which becomes liquid on exposure to heat; such comminution being carried out to an extent sufficient to yield catalytic material having the desired catalytic activity such as will be more fully hereinafter explained.

As a suitable source of catalytic material various compounds of nickel may be employed. Of such compounds the basic compounds of nickel yield satisfactory results Nickel carbonate or the basic carbonate of nickel, nickel hydroxid and in some cases the oxide may be used. Corresponding compounds of copper and cobalt similarly may be utilized. In some cases mixed catalyzers consisting of nickel and copper, cobalt or other metal may be used. The employment of the rare metals such as platinum, palladium, osmium and the like is not excluded although generally speaking not recommended for making a catalyzer of the type described herein. The rare metals are quite expensive and satisfactory results are obtained from base metals such as those indicated. In addition to the foregoing organic salts of these metals such for example as nickel formate, acetate, benzoate and the like or mixtures or combinations involving both inorganic and organic radicals may be utilized such for example as nickel carbonate and formate.

As a material or vehicle in which to carry out the comminution preferably there is employed a hydrocarbon such as a petroleum oil of high boiling point and also waxes, for example paraffin wax, petroleum jelly, petrolatum free from sulphur compounds and the like. It is also possible to employ vegetable oils although in the final reduction operation vegetable oils are usually not as desirable as the high temperatures necessary bring about more or less decomposition. Besides these oily, fatty or waxy materials other vehicles may be employed such as volatile substances like ether or gasoline or mixtures of gasoline with the less volatile material kerosene. In some cases glycerine may be used or glycerine diluted with water. Good results have been obtained by grinding with water alone and subsequently evaporating to dryness and carrying out reduction under suitable conditions.

In carrying out the comminution various apparatus may be employed to enable the process to be carried through effectively. Preferably a ball mill or pebble mill is employed and when preparing the nickel catalyzer such a ball mill may be lined with brick or porcelain or may be made of nickel, when the presence of any other metal might prove objectionable in the product. Steel rolls also may be used for grinding and comminution may be carried out with the Chilian mill, edge runner or putty chaser, also with burr mills.

The temperature of the mass during grinding may vary, whether hot or cold makes little difference in some cases but in other cases as for example when paraffin wax is used as the medium preferably a temperature should be maintained above the melting point of the wax. In other cases as for example with volatile materials the temperature is preferably lower, or cooling of the mill may be resorted to in some cases.

It is important to have the proportion of oil or other vehicle such that the grinding may be carried out effectively. When grinding nickel carbonate for example a plastic mass may be prepared which grinds readily for a time but as the carbonate becomes finer the mass stiffens and finally clings to the sides of the ball mill and is not so easily ground. In fact in a small laboratory mill considerable difficulty has been found with percentages of oil which origi-

nally made a good flowing mass of soft putty like material. In a general way the proportion of oil to material may be varied to say one part of oil to two parts of the material up to six parts of oil to one part of material; but of course such proportions depend in part at least on the character of the original material which is being ground, some compounds have much greater absorptive capacities for oil than others.

In the present invention it is one object to prepare a catalyzer concentrate as for example a mixture of nickel and for example hydrocarbon vehicle containing only enough of the latter to seal the particles of nickel so that they will not oxidize and thus enable the shipment of the catalyzer in a concentrated form to long distances without substantial deterioration. A hydrocarbon vehicle is quite satisfactory for this purpose as it is comparatively inert. Thus for example paraffin wax is a very satisfactory sealing medium and enables the product to be pressed or molded into the form of cakes which are convenient for handling and shipping. In like manner petroleum jelly serves to protect the nickel particles from oxidation but in this case a more plastic product is secured. However there is no value in having excessive amounts of wax, vaseline or other vehicle present when a nickel concentrate is desired as shipping of any excess quantities of the grinding and sealing medium is sometimes objectionable. Moreover to properly grind the material it is usually necessary to have an excess of the medium and in order to secure a high degree of concentration in the final product the excess of hydrocarbon may be removed by distillation when sufficiently volatile for the purpose. Thus mixtures of petroleum jelly and gasoline may be used and the gasoline subsequently distilled. Or the petroleum jelly may be distilled at a high temperature and the distillation is accelerated by agitating the mass during heating. In making a permanent form of catalyzer for shipping purposes saponifiable oils are not as satisfactory because some part of the nickel may react with any free fatty acid forming nickel soap or a soap of whatever metal may be present and this action may affect the quality of the catalyzer. In addition to keeping the amount of hydrocarbon vehicle down to a minimum from the above standpoint, it may also be mentioned that when hydrogenating vegetable oils it is not desirable to introduce more than a small per cent of unsaponifiable matter and the presence of any large amount of hydrocarbon oil or wax would be objectionable in some cases.

The grinding may be carried out until the originally rather coarse material is so fine or so flocculated through the vehicle as to be very slowly settling and in one case for example, using a magnification of between 1700 and 1800 diameters the particles of nickel obtained from nickel carbonate appear quite irregular and flocculent, the largest particles being approximately the size of the head of a pin.

In carrying out the foregoing operations it should be understood that for most cases as, for example, in the hydrogenation of oils it is a consideration to have the materials free or substantially free from catalyzer poisons so that pains are taken to exclude hydrocarbon oils containing sulphur or raw material such as nickel hydrate which contains sulphur, arsenic or other bodies having a depressing action on the catalytic process.

The grinding of the material such for example as nickel carbonate in a vehicle as above described has a very decided effect on the catalytic activity, when for example nickel carbonate of ordinary commercial grade is used. Grinding such nickel carbonate in a dry state without the presence of a vehicle is not effective in yielding a catalyzer of the highest type of efficiency at least under any conditions which would be practical in the usual type of hydrogenation plant. Nickel carbonate which has passed through the finest bolting cloth, as for example, 200 mesh cloth does not give the efficiency that the same material affords when ground in oil. It is a rather remarkable fact that grinding in this manner does achieve the results observed but by reference to the accompanying sheet or diagram it will be seen that the effect of grinding is distinctly noticeable.

Before considering the chart in detail, the method of making observations, whereby the curves here presented were obtained, will be first noted.

A description of the apparatus used for determining the efficiency of the various catalysts tested is as follows: A small maple board platform was mounted on a jointed standard in such a manner as to allow the platform to be oscillated rapidly. The platform was held in a horizontal position, when at rest, by means of 4 springs attached to each corner of the platform. The lower leg of the jointed standard was attached to a solid table and the lower end of the springs were also attached to the table. Mounted on the platform was a small electric hot plate used for maintaining the temperature of the oil and catalyst being tested, at the desired point namely between 180 and 190° C. A suitable receptacle for holding the flask containing a definite quantity of oil and catalyst in position, was placed on the hot plate the walls of which were heat insulated by means of asbestos board. At one edge of the wooden platform there was attached an iron

rod which served as a handle for shaking the apparatus and which was also used as a support for a clamp to hold the flask in an upright position when being shaken. The neck of the flask was closed by means of a three hole rubber stopper, one of these holes being used for the insertion of a thermometer to determine the temperature of the oil and the other two holes for the insertion of tubes for the inlet and outlet of hydrogen from the flask. The inlet tube extended to the bottom of the flask and was attached to the hydrogen supply, the hydrogen supply being regulated by means of a needle valve. The outlet tube was attached by means of rubber tubing to an aspirator bottle. Inserted in the rubber tubing between the outlet tube and the aspirator bottle was a glass T, the third leg of which served as an outlet for the waste hydrogen during the passage of the hydrogen into the oil during hydrogenation and also as an outlet for flushing the air from the flask when the hydrogenation was first started. During the determination of the time required to absorb a definite volume of hydrogen the outlet is closed by means of rubber tubing and a clamp. The outlet of the aspirator bottle was connected by means of rubber tubing to a burette which was graduated to $\frac{1}{10}$ c. c. and had a capacity of 100 c. c. The aspirator bottle was filled with water with a layer of oil on top of the water to act as a seal and prevent moisture from getting into the hydrogen supply.

The operation of the above apparatus was as follows: The oil and catalyst was first heated to a temperature of between 180–190° C. and the flask then clamped in position on the hot plate. Sufficient hydrogen was then passed from the hydrogen supply to flush out the air which was in the flask primarily, with the outlet tube from the T open. After the air had been entirely removed from the flask 100 c. c. of hydrogen was allowed to flow into the aspirator bottle, the outlet tube from the T closed and the liquid in the burette leveled with the liquid in the aspirator bottle. The flask was then rapidly shaken back and forth and the time required to absorb the 100 c. c. of hydrogen in the aspirator bottle determined, maintaining the level of the liquid in the burette and the aspirator bottle throughout the operation; the determination being therefore made at atmospheric temperature and pressure.

The time required to absorb 100 c. c. of hydrogen while the oil was being shaken was taken every 5 minutes. During these 5 minute intervals a fairly rapid stream of hydrogen was allowed to pass through the oil which approximates commercial practice.

In order that a comparison of the efficiency of various catalysts might be made, a standard quantity, 250 grams of prime summer yellow cottonseed oil and a standard quantity of catalytically active material based on its nickel content was used. .5 of 1% of the weight of the oil used or the equivalent of 1.25 grams of nickel being the quantity of catalytic material used in all of the determinations of catalytic activity which follow. The weighed quantity of catalyzer is first added to the cottonseed oil and the mixture brought up to a temperature of between 180 and 190° C., this procedure being a common practice in the industry. The flask containing the cottonseed oil and catalyst was then placed in the apparatus which is more fully described above, the air flushed from the flask with hydrogen, and the time of absorption of 100 c. c. of hydrogen by the cottonseed oil in the presence of the catalyst being tested was immediately determined and the time in seconds required for the absorption noted as the zero point.

A steady stream of hydrogen was then allowed to pass through the oil for a period of five minutes and the time required for the oil to absorb 100 c. c. of hydrogen was again determined. The procedure of allowing a steady stream of hydrogen to pass through the oil for a period of five minutes and the determination of the time required to absorb 100 c. c. of hydrogen at the expiration of each five minute interval was carried out for a period of one hour's time of hydrogenation and the results plotted.

In the accompanying chart the curve marked A was prepared from the performance of the catalyst prepared from dry nickel carbonate which had been ground in a pebble mill to pass 200 mesh bolting cloth and then reduced in paraffin to an active catalytic state at a temperature of 350–360° C. for a period of one hour. One hour is a somewhat longer period of time than is required to reduce small quantities of nickel carbonate to a catalytically active state but in order to standardize the reduction of the raw material we reduced the nickel salt at the desired temperature for this period of time in all cases. 50 parts by weight of dry nickel carbonate and 100 parts by weight of paraffin was used in this case and after reduction a quantity of the reduced material equivalent to 1.25 grams of nickel was used for testing the catalytic activity of the reduced material.

The results obtained from a catalyst prepared from one part by weight of nickel carbonate which was ground in a pebble mill for a period of four hours with 6 parts by weight of mineral oil is noted on the chart as curve B. The product obtained after the grinding operation was of the consistency of a thin cream and a small quantity when rubbed between the fingers did not show any

signs of grittiness. The apparent size of some of the particles of nickel carbonate when examined under the microscope with a magnification of 1750 diameters was about the size of a head of a pin but the majority of the particles were smaller. The reduction of the finely divided nickel carbonate in the mineral oil vehicle was then carried out at a temperature of 350–360° C. for a period of one hour and the catalytic efficiency determined in the manner described above.

The initial efficiency of the nickel carbonate which was ground in oil is very much higher than that of the nickel carbonate which was ground dry. The nickel carbonate ground in oil attained its greatest efficiency after 12 to 13 minutes of hydrogenation; while the nickel carbonate which was ground dry only attained its maximum efficiency after 20 minutes time of hydrogenation. The efficiency of the nickel carbonate ground in oil decreased very slowly until at the end of one hour's time of hydrogenation the time required to absorb 100 c. c. of hydrogen was but 13 seconds while in the case of the nickel carbonate which was ground dry the time required to absorb 100 c. c. of hydrogen was 36 seconds. It is evident therefore that the efficiency of the nickel carbonate when ground in oil and then reduced is much greater than when nickel carbonate is finely ground without the use of oil.

Nickel formate when ground dry in a pebble mill to pass 200 mesh bolting cloth and then reduced in paraffin at a temperature between 250–260° C. has a somewhat higher efficiency than that of the particular sample of nickel carbonate when treated in the same manner. The curve marked C on the chart was prepared from the results obtained from the performance of nickel formate when treated in this manner and tested in the apparatus described above.

Curve D represents the results obtained from a catalyst prepared by grinding one part by weight of nickel formate in a pebble mill with 6 parts by weight of mineral oil for a period of four hours and in reducing the resultant product at a temperature of 250–260° C. for a period of one hour. The general appearance of the nickel formate ground in the oil was similar to the appearance of the product obtained from grinding nickel carbonate in oil, the size of the ground particles and the consistency of the product being approximately the same and there was no evidence of grittiness when a small sample of the ground product was rubbed between the fingers. The efficiency of the reduced catalyst was then determined and the results noted on the accompanying chart and marked curve D.

The initial efficiency of the nickel formate which was ground in oil was materially higher than that of the nickel formate which was ground dry and in both cases the catalysts had worked up to their maximum efficiency after 12 to 13 minutes of hydrogenation. The efficiency of both catalysts then gradually decreased until at the expiration of 60 minutes hydrogenation the nickel formate catalyst which had been ground dry required 18.8 seconds to absorb 100 c. c. of hydrogen while the nickel formate catalyst which had been ground in oil required but 13 seconds time to absorb 100 c. c. of hydrogen.

The reduction of the catalytic raw material in the medium as aforesaid may take place in various ways as for example in the case of nickel formate by simply heating the mass to say 240° C. whereby decomposition occurs and catalytic nickel is formed. Or a mixture of nickel and copper carbonates which have been ground in vaseline may be heated to 250° or higher and a current of hydrogen or other reducing gas passed therethrough until reduction is effected.

Another method which is preferred because of its simplicity and cheapness is that of heating the hydrocarbon vehicle with its ground up catalytic raw material to a temperature at which cracking takes place whereby reduction occurs and the catalytic concentrate is obtained. Under these conditions a distillation and consequent removal of more or less of the vehicle results. A temperature of 340 to about 400° is usually satisfactory for making a catalyzer under the latter conditions. Agitation of the mass while being heated is useful. The product may contain various percentages of nickel from that required in ordinary catalytic operations that is usually less than 1%, up to say 75% of nickel. A useful form of concentrate is one containing 25 to 30% of nickel or nickel and cobalt material, while a more desirable one for shipping to long distances contains 60 to 70% of the catalytic material. The nickel made by reduction in a vehicle is not strictly speaking of a pyrophoric character and in fact by extraction of the hydrocarbon with benzol or other solvent a metal powder may be obtained which may be exposed to the air for a considerable period without substantial loss in catalytic power. However for shipping purposes as aforesaid it is desirable to have a certain amount of sealing material and preferably this should be from 25 to 50%.

After the catalytic material or concentrate has been obtained there is no objection to subjecting it to grinding as in some cases the particles of nickel may have been caked together slightly and grinding of the catalyzer may improve its quality. However this does not apply in most cases and very active catalyzer maintaining its power over the hydrogenation period in the desired manner

may be readily obtained without resorting to the extra step or expense of grinding the reduced nickel or other metallic powder.

When a large amount of oil or other vehicle has been used in the grinding operation it may be reduced in other ways than by distillation. For example centrifuging or filtration may be utilized. The oil obtained from this operation may be used again.

When nickel carbonate is the source of the raw material it may be advantageously formed by precipitation from the sulphate of nickel by means of soda ash, drying with sodium sulphate present and washing the dried product. In this manner by far the largest proportion of sulphates are removed whereas by simple washing of the wet precipitate basic sulphates are liable to be retained to an objectionable degree.

The following represent a series of tests made with different materials under different conditions in carrying out the foregoing invention.

Example #1.—50 parts by weight of nickel carbonate was ground with 300 parts by weight of mineral oil in a pebble mill for a period of 4 hours. The ground product on removal from the pebble mill had a consistency of a thin cream. The ground material in oil was heated to a temperature of 350–360° C. and maintained at this point for a period of one hour or until the carbonate had been reduced to a catalytically active material. Upon testing the catalyst in the apparatus described previously in the specification we found that the initial time required for 250 grams of cottonseed oil to absorb 100 c. c. of hydrogen required in the presence of .5 of 1% of the catalytically active material produced by the above operation was 19 seconds. The mean time of absorption over a period of one hour's hydrogenation was 13.3 seconds. The time required for the absorption of the same volume of hydrogen at the end of one hour's hydrogenation was 13 seconds.

Example #2.—50 parts by weight of nickel carbonate was ground in a pebble mill with 150 parts by weight of water for a period of 4 hours. At the expiration of this time the ground material was of the consistency of a thin putty and there was no evidence of grittiness when a small portion of the material was rubbed between the fingers. Under a microscope with a magnification of 1750 diameters the largest of the particles appeared to be about the size of an ordinary pin head while the majority of the particles were smaller than this. The initial time required to absorb 100 c. c. of hydrogen using standard quantities of cottonseed oil and catalytically active material was 22 seconds. The mean time of absorption for the same volume of hydrogen during one hour's period of hydrogenation was 13.1 seconds and the time required to absorb 100 c. c. of hydrogen at the end of one hour's period of hydrogenation was 14 seconds.

Example #3.—50 parts by weight of nickel carbonate was ground in a pebble mill with 100 parts by weight of petrolatum or petroleum jelly for a period of 4 hours. The pebble mill was heated during the grinding to a temperature above that of the melting point of the petrolatum. The product was of a putty like consistency. The ground nickel carbonate in petrolatum was then heated for a period of one hour at a temperature of 350–360° C. and during this operation 63% of the petrolatum distilled off leaving a product containing 40% of nickel and 60% of petrolatum. The catalytically active product was then tested in the regular manner. The initial time required for 250 grams of cottonseed oil to absorb 100 c. c. of hydrogen in the presence of this catalyst was 30 seconds. The mean time required to absorb this volume of hydrogen during a period of one hour's hydrogenation was 12.7 seconds. The time required to absorb the same volume of hydrogen at the end of one hour's hydrogenation was 11 seconds. In this case the catalyst worked up to its maximum efficiency somewhat more slowly than in the examples cited previously, requiring between 15 and 16 minutes of hydrogenation to work up to its maximum efficiency.

Example #4.—In this case 50 parts by weight of nickel carbonate was ground in a pebble mill with 75 parts by weight of kerosene and 25 parts by weight of petrolatum. The resultant product was of a putty-like consistency. The ground carbonate in the oily vehicle was then reduced to a catalytically active state at a temperature of 350–360° C. for a period of one hour. Using the standard quantities of oil and catalyst the initial time required to absorb 100 c. c. of hydrogen was 30 seconds. The mean time during a period of one hour's hydrogenation to absorb the same volume of hydrogen was 13.1 seconds. The time required to absorb the same volume of hydrogen at the end of one hour's hydrogenation was 13 seconds.

Example #5.—In order to illustrate the increase of efficiency of the catalytically active material prepared from nickel carbonate ground in oil and then reduced and nickel carbonate which was reduced as received the following example is cited. Nickel carbonate as purchased and which was screened to pass a 60 mesh screen was reduced in paraffin wax at a temperature of 350–360° C. for a period of one hour. Using standard quantities of cottonseed oil and catalytically active material for determining the efficiency of the catalyst the initial

time required for the absorption of 100 c. c. of hydrogen was 170 seconds. The mean time for the absorption of the same volume of hydrogen over a period of one hour's hydrogenation was 70 seconds. The time required to absorb this volume of hydrogen at the end of one hour's hydrogenation was 55 seconds. In this case the maximum efficiency of the catalytic material was only obtained after fifteen minutes of hydrogenation.

Example #6.—A small quantity of the reduced catalytic material obtained from Example #5 was ground in a pebble mill for a period of 4 hours and the efficiency of the ground material then determined. The pebble mill was heated to a temperature above the melting point of the paraffin during the grinding operation. The initial time required to absorb 100 c. c. of hydrogen using standard quantities of oil and catalytically active material was 30 seconds. The mean time during a period of one hour's hydrogenation to absorb the same volume of hydrogen was 19.4 seconds and the time required to absorb the above volume of hydrogen at the end of one hour's hydrogenation was 20 seconds. In the case of this catalyst it required 10 minutes time of hydrogenation to bring the catalyst up to its maximum efficiency of 14 seconds.

Example #7.—50 parts by weight of nickel formate was ground with 300 parts by weight of white mineral oil in a pebble mill for a period of 4 hours. At the end of this time the product was of the consistency of a thin cream. The particles of ground nickel formate when viewed under a microscope with a magnification of 1750 diameters the largest of them was approximately the size of the head of a pin while the majority of the particles were smaller. The ground material was then reduced at a temperature of 250–260° C. for a period of one hour. On testing the reduced catalytic material in the apparatus which was described above the initial time required for the standard volume of oil with the standard quantity of catalytic material was 15 seconds. The mean time was 11.2 seconds. The time required over a period of one hour's hydrogenation for the absorption of 100 c. c. of hydrogen was 11.1 seconds. The time required to absorb the same volume of hydrogen at the end of one hour's hydrogenation was 14 seconds.

Example #8.—Nickel formate was ground dry to pass 200 mesh bolting cloth and was reduced in paraffin at a temperature of 250–260° C. for a period of one hour. Upon testing the reduced catalytic material in the above testing apparatus we found that the initial time for the absorption of 100 c. c. of hydrogen was 15 seconds, the mean time required over a period of one hour's hydrogenation for the absorption of the same volume of hydrogen was 15.5 seconds. The time required to absorb 100 c. c. of hydrogen at the end of one hour's period of hydrogenation was 18 seconds. Standard quantities of oil and catalyzer was used in the above example.

In comparison with the foregoing and indicative of results which may be obtained by grinding nickel alone the following test was made: Nickel flake such as is obtained by the Edison process and which in itself has been recommended as catalytic material was subjected to grinding for a period of 72 hours in a ball mill. Although the nickel flake is itself extremely thin and light this great length of grinding was necessary in order to secure a catalyzer which had a mean time of absorption over a period of one hour's hydrogenation of only 65 seconds in comparison with one made from nickel carbonate by grinding the latter in oil and then reducing, which under like conditions had a mean time of absorption over a period of one hour's hydrogenation of 13 seconds.

From the foregoing it will be observed that catalyzers may be rated on the basis of the time taken to absorb a definite amount of hydrogen gas for example in the present case 100 c. c., and such rating or numerical expression may be used to indicate the initial absorptive power or the average absorptive power over a given period, say one hour. Both ratings are used in the consideration of the activity of the catalyzer, namely, its initial speed of absorption and its average speed over 60 minutes duration. The former may be misleading because some catalyzers start off briskly absorbing the gas and then fall rapidly in power after a few minutes hydrogenation. Others gain in speed as the hydrogenation progresses then after a certain point show perhaps uniform absorption over a considerable subsequent period. The average absorption over one hour is therefore perhaps the best index of the quality of the catalyzer.

A rather interesting method of making catalyzer which may be employed in special cases is that of grinding the catalytic raw material, for example, nickel hydroxid in water. The hydroxid may be freshly precipitated and in its moist state placed in a ball mill or edge runner and ground to the requisite condition of fineness. Then this moist putty may be projected in small quantities at a time into a tank of heated oil so as to expel the moisture quickly. The tank should be capacious in order to permit of foaming. When the oil contains a sufficient quantity of the hydroxid or dried product the mixture may be reduced either by treatment with a reducing gas or by the cracking process aforesaid or in any other suitable manner.

In the foregoing operations the description has referred mainly to grinding the catalytic material without the presence of any abrasive body but it should be understood that in all such cases it is possible to have present a quantity of abrasive substance such as finely powdered pumice, silex, quartz dust, carborundum and the like. The presence of such an abrasive facilitates the grinding more or less but has the disadvantage that it increases the wear and tear on the grinding apparatus and frequently in the case of steel grinding vessels introduces so large a percentage of iron in the catalyzer that its activity is impaired and the iron in this finely divided state may be taken up by the oil causing discoloration of the material. Thus while abrasive may be used it is not necessary and is frequently objectionable. There is no objection however to the addition to the finished catalyzer of a sufficient amount of bulking material such as silex to enable the catalyzer to be readily filtered. By protracted grinding of the catalyzer raw material in the oil to produce the fine suspensions referred to above the reduced nickel partakes to a considerable extent of the more or less colloidal condition of the original unreduced ground material and such colloidal material is, in the hydrogenation process, not easily filtered from oils in some cases without the presence of suitable bulking material aforesaid.

In the foregoing reference has been made to extraction of the catalyzer with a solvent such as benzol, ether, and the like and by such method or any other suitable extraction method the dry powdered catalytic metal such as nickel which is obtained retains, as stated, for a considerable time its catalytic activity when exposed to the air. It will however oxidize quickly when heated slightly or when a portion is ignited, this oxidation frequently spreading throughout the mass. If moistened with water the catalytic activity is usually impaired in some cases. Thus by the foregoing method a dry powdered catalyzer may be obtained which may be introduced into any other sealing medium if desired or may be packaged in containers which if desired are filled with an inert gas such as hydrogen or nitrogen.

What we claim is:

1. The process of making a catalyzer concentrate which comprises grinding nickel formate in an oil vehicle, continuing the grinding operation until the potential-catalytic properties are very substantially enhanced, and subjecting the ground material to reducing conditions whereby catalyzer is obtained.

2. In the process of making a hydrogenating catalyst by reducing catalytic raw material in a vehicle the steps which comprise first grinding the catalytic raw material in petroleum jelly, continuing the grinding operation until the potential-catalytic properties are very substantially enhanced, and reducing to form the catalytic substance in the vehicle.

3. In the process of making a hydrogenating catalyst by reducing potentially catalytic raw material comprising a readily reducible sulfur-free compound of a metal having an atomic weight between 58 and 64 in a vehicle the steps which comprise first grinding the catalytic raw material in a vehicle which is substantially liquid at the temperature of the grinding operation, reducing to form the catalytic substance in the vehicle and finally grinding said catalytic substance while in said vehicle.

4. In the process of making a hydrogenating catalyst by reducing a basic potentially catalytic metallic compound readily reducible sulfur-free compound of a metal having an atomic weight between 58 and 64 in a vehicle the steps which comprise first grinding the catalytic raw material in the vehicle, reducing to form the catalytic substance in the vehicle and finally grinding said catalytic substance while in said vehicle.

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