MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A
COMMONWEALTH OF AUSTRALIA

Patents Act

APPLICATION FOR A PATENT

X/We (a) THE DOW CHEMICAL COMPANY

33662/78

of (a) 2030 Abbott Road, Midland, Michigan, United States of America

hereby apply for the grant of a Patent for an invention entitled

(a) EMULSION CATALYST FOR HYDROGENTATION PROCESSES.

which is described in the accompanying (c) complete specification.

(Note: The following paragraph applies only to Convention applications)

This application is a Convention application based on the basic application(s) for a patent or similar protection identified by number, country, and filing date as follows:

(b) 772,874 United States of America 28 February 1977

Address for Service: PHILLIPS ORMONDE AND FITZPATRICK

Patent and Trade Mark Attorneys

NEW ADDRESS

N 367 Collins Street

Melbourne 3000 Australia

Telephone (03) 614 1944

Telex 6A 34210

Dated (e) 27th February 1978

(a) PHILLIPS ORMONDE AND FITZPATRICK

Attorneys for:

THE DOW CHEMICAL COMPANY.

PHILLIPS, ORMONDE AND FITZPATRICK

Patent and Trade Mark Attorneys

Melbourne, Australia
DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

3 3 6 6 2 /78

In support of the Convention application made for a patent for an invention entitled
Emulsion Catalyst for Hydrogenation of Hydrocarbonaceous Substances
of THE DOW CHEMICAL COMPANY, a corporation organized and existing under the
law of the State of Delaware, and having an office and place of business at 2030 Abbott Road, Midland, County of Midland, State of Michigan, United States of America, do solemnly and sincerely declare as follows:

1. I am authorized by THE DOW CHEMICAL COMPANY, the applicant for the patent, to make this declaration on its behalf.

2. The basic application(s) as defined by Section 141 of the Act was/were made

in United States of America on February 28

by NORMAN GLENN MOLL; GEORGE JOSEPH QUARDERER

in by

NORMAN GLENN MOLL, 2563 Daniels Road, Sanford, County of Midland, State of Michigan, United States of America;
GEORGE JOSEPH QUARDERER, 2725 Scott Street, Midland, County of Midland, State of Michigan, United States of America.

is/are the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The applicant Company is the assignee of the said invention from the said actual inventor(s).

4. The basic application(s) referred to in paragraph 2 of the Declaration was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared at Midland, Michigan this 17 day of February 1978.

To: The Commissioner of Patents.

By

Signature of Declarant.

WILLIAM MILLER YATES
General Patent Counsel
EMULSION CATALYST FOR HYDROGENATION PROCESSES

DOW CHEMICAL COMPANY

MOLL N.G. AND QUARDERER G.J.

CLAIM

1. A process for hydrogenating a hydrocarbonaceous substrate by contacting said substrate as a water-immiscible liquid phase with hydrogen in the presence of a metal-containing hydrogenation catalyst, characterized by adding the metal-containing catalyst initially to the water-immiscible liquid phase as an emulsion of a water solution of a compound of said metal in said liquid phase.
The following statement is a full description of this invention, including the best method of performing it known to the applicant(s):

EMULSION CATALYST FOR HYDROGENATION PROCESSES.

APPLICANT'S REF.: Case 18,292-F
Name(s) of Applicant(s):
THE DOW CHEMICAL COMPANY
Address(es) of Applicant(s):
2030 Abbott Road, Midland, Michigan, United States of America.
Actual Inventor(s):
Norman Glenn Moll and George Joseph Quarderer.
Address for Service is:
PHILLIPS, ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
37-41 Queen Street
Melbourne, Australia, 3000
Complete Specification for the invention entitled:

EMULSION CATALYST FOR HYDROGENATION PROCESSES.
The present invention relates to an improved method whereby a hydrogenation catalyst is conveniently and effectively dispersed in and contacted with a reaction mixture. It relates particularly to an improved method for dispersing such catalysts in heavy petroleum fractions and in liquid hydrocarbon slurries of coal prior to hydrogenation.

The hydrogenation of finely divided coal, residual oil, or other such heavy hydrocarbonaceous substances to mixtures of gaseous and liquid products has been studied for many years. In recent years, the liquefaction of coal in particular has become of more urgent interest because of dwindling petroleum resources. Although coal can be successfully hydrogenated to produce both gaseous and liquid products without the addition of a hydrogenation catalyst, since traces of catalytically active metals are normally present in coal, better yields of the desired products are obtained under more moderate reaction conditions when a metal hydrogenation catalyst is used.

Active catalysts for these processes constitute a known class including the metals or compounds of the metals iron, nickel, cobalt, molybdenum, tungsten, tin, zinc, vanadium, chromium, antimony, and a number of others, alone or in combination. Active metals such as palladium, platinum, andenium are also effective but are too expensive for the purpose. These hydrogenation catalysts can be added to the hydrogenation mixture as the finely divided
metals or as compounds thereof, either supported or unsupported. In the hydrogenation of coal and heavy petroleum fractions, the predominant stable form for most of these metal catalysts is the sulfide which can be formed during the hydrogenation process from the sulfur naturally present in these fossil hydrocarbonaceous substances or by presulfiding the catalyst.

Two well researched processes use a bed of particulate catalyst, usually a nickel or cobalt molybdate supported on alumina, through which are pumped a mixture of hydrogen and a dispersion of finely divided coal in a liquid hydrocarbon medium or a heavy hydrocarbon fraction at elevated temperature and pressure. A process developed at the U.S. Bureau of Mines for the hydrogenation of coal employs a stationary bed of pelleted or granular catalyst. The process is outlined by Yavorsky et al. in Chem. Eng. Progess 69(3), 51-2 (1973). The "ebullated bed" or H-Coal process employs a bed of similar but more finely divided catalyst which is maintained in the reactor in a turbulent or boiling state as the reaction mixture is passed through it, thereby maximizing contact with the catalyst particles. This process has been used both for the hydrogenation of coal and the hydrogenation of residual oil. Both of these processes are effective for the purpose but have inherent difficulties or disadvantages associated with the use of a bed of catalyst, that is, the necessity for specially designed apparatus, the need to avoid occlusion of the catalyst by feed material, the need to avoid caking or plugging in process equipment by particles
of catalyst, the deactivation of the catalyst by components of the feed material, and the problems of loading fresh catalyst in the reactor and the removal of spent catalyst. Loss of catalyst fines in the product oil is another problem in this process.

Other known coal and residual oil hydrogenation processes have added a catalyst directly to the reaction mixture as the finely divided metal or a metal compound, either of which may be converted to a catalytically active form under reaction conditions. Some processes have used the metal hydrogenation catalyst in the form of a water-soluble salt, with or without added water. Schuman, U.S. Patent 3,745,108 employs a liquid medium for a coal slurry which is part or all water containing a salt of the metal catalyst in solution, ammonium heptamolybdate [(NH₄)₂Mo₇O₂₄·4H₂O] being exemplified. This latter process is effective, but the maintenance of a liquid aqueous phase in the process imposes certain limitations on the process conditions and apparatus. Thus, the process temperature is necessarily rather low with resultant comparatively low conversion of coal and low yield of liquid hydrocarbons. In coal hydrogenation, more effective use of the catalyst has been obtained in some cases by prior impregnation of the coal with a catalyst compound.

The defects of the prior processes have been substantially overcome by the present invention, which is a process for hydrogenating a hydrocarbonaceous substrate by contacting said substrate as a water-immiscible liquid
phase with hydrogen in the presence of a metal-containing hydrogenation catalyst, characterized by adding the metal-containing catalyst initially to the water-immiscible liquid phase as an emulsion of a water solution of a compound of said metal in said liquid phase.

The metal compound is converted to the active hydrogenation catalyst under the conditions of hydrogenation. As a result of this technique, the active catalyst is thereby formed in situ as microscopically fine particles uniformly dispersed in the liquid reaction mixture.

Under the conditions of this hydrogenation process, there is no longer a separate aqueous phase and the dissolved metal compound is decomposed and converted to an active form of the metal catalyst, probably a sulfide.

Thus the invention is essentially an improved method whereby a catalyst is more conveniently and efficiently dispersed and utilized so that a very small quantity can provide optimum results.

The present method for catalyst addition and dispersion in the reaction mixture is particularly advantageous in the hydrogenation of a heavy hydrocarbonaceous substance such as coal, heavy petroleum fractions, residual oil, and tar or pitch, either of natural origin or derived from petroleum or coal, to obtain more useful lower boiling products, gaseous or liquid although largely liquid products are usually more desirable. The conditions for hydrogenation of these substances are well-known. Process pressures may range from about 1000 psi (71 kg./cm²) to as high as 10,000 psi (710 kg./cm²) but are usually in the range...
from about 1500 to about 3000 psi (106-212 kg./cm.²).

Process temperatures can be as low as 300°C to as high as 600°C, but a range of about 400°C to about 500°C is more commonly used, depending upon the particular catalyst, the type of substance being hydrogenated, and the kind of product desired, i.e., larger or smaller proportions of gaseous hydrocarbons, lower boiling liquids, or relatively higher boiling liquid hydrocarbons.

This new method is of special interest in the liquefaction of coal, more particularly, coal crushed and dispersed in a liquid hydrocarbon medium to provide a pumpable slurry.

The catalyst, which is introduced in the form of a water-soluble salt is chosen from the metals iron, cobalt, nickel, molybdenum, tungsten, tin, zinc, vanadium, chromium and antimony.

The quantity of catalyst used in this improved process can be significantly less than the quantities preferred in somewhat similar prior art processes because of the better dispersion thereby provided throughout the reaction mixture. For molybdenum in the form of ammonium or alkali metal heptamolybdate, proportions of about 0.01-1 percent molybdenum based on coal or other substance being hydrogenated give good results and about 0.02-0.5 percent molybdenum is preferred whereas comparable prior art processes commonly employ much more catalyst. Similar low proportions of other coal and residual oil hydrogenation catalysts are also effective in the improved
process. Less active catalysts such as iron may require somewhat higher proportions, up to about 1 percent, for example. The proportion of catalyst in the reaction mixture is a variable which affects the product distribution and degree of conversion. Normally, relatively high proportions of catalyst result in higher conversion but also higher yields of gases and light oil which may be undesirable. The smaller proportions of catalyst made possible by this invention with better catalyst dispersion can provide both high conversion and high yields of higher boiling oil. The convenient mode of catalyst addition and the broad applicability of the method are other principal advantages of the invention.

The proportions of metal compound to water and of water solution to emulsifying oil have a significant effect on the characteristics of the catalyst. Good results are obtained when a concentrated aqueous solution is emulsified but generally a somewhat more active catalyst is formed when a relatively dilute solution is used, probably because smaller particles of catalyst are produced. It is also desirable to maintain a high proportion of emulsifying oil to water solution in order to make a relatively stable emulsion of small aqueous droplets and consequently a finely dispersed catalyst.
Since a liquid feed mixture is ordinarily passed to the hydrogenation process soon after being made up with the emulsified catalyst solution, the emulsion does not have to be of very high stability and the use of an emulsifier or emulsion stabilizer may not be necessary. In some systems, however, such an additive may be of advantage in facilitating the formation of an emulsion or in obtaining very small aqueous droplets in the emulsion. Any convenient method can be used to emulsify the salt solution in the hydrocarbon medium. To obtain the optimum fine dispersion of catalyst throughout the reaction mixture, it is important that the droplet size of aqueous phase in the emulsion be very small. This condition can be achieved by initially forming a dispersion of oil in the aqueous solution, then causing the dispersion to invert by slowly adding more oil so that the oil becomes the continuous phase and the aqueous solution is very finely dispersed in it. Other methods of forming the emulsion have given satisfactory results, however.

In some coal and residual oil hydrogenation processes, a separate sulfiding step is used to make the metal catalyst more active. In the present improved process, the smaller quantities of catalyst are effectively sulfided and activated during operation by the small amounts of sulfur normally present in coal and petroleum. No specific catalyst sulfiding step is needed, therefore.
The liquid hydrocarbon medium in which the powdered coal is slurried or a residual oil or tar is dispersed (when such a diluent is desirable) can be any convenient petroleum fraction or similar liquid, but preferably it is the liquid hydrocarbon obtained from the hydrogenation process or recycle oil fraction as used in most prior art hydrogenation processes. For best results, such recycle oil has been treated to remove at least some of the low boilers and insoluble components. In coal liquefaction, the proportion of oil to coal in the process slurry is also generally as shown in the art, that is, sufficient to provide a pumpable mixture. Proportions of 55-75 parts by weight of oil to 45-25 parts of coal are typical. For the hydrogenation of residual oil, tar, or pitch, somewhat lower proportions of the liquid hydrocarbon medium or none at all may be preferred.

The water-soluble salt of the catalytic metal can be essentially any such salt. For metal catalysts such as those of the iron group, tin, or zinc, the nitrate or acetate may be most convenient whereas for molybdenum, tungsten, or vanadium, more complex salts, such as an alkali metal or ammonium molybdate, tungstate, or vanadate may be preferable. Mixtures of two or more metal salts can be used.

A particular advantage of the present process is the fact that it may not be necessary to include a catalyst recovery step as in many prior
art processes because of the very small amounts of catalyst that are used.

Other advantages derived from the small amounts of catalyst used in this process and the high dispersion of catalyst that is achieved are simpler reactor design because there is no need for high internal circulation rates and the elimination of costly shutdowns for removal of catalyst deposits in process equipment.

**Analytical Procedures**

In the working examples described below, the analytical procedures employed were as follows:

**Viscosity**

Viscosities of oil samples were measured at 25°C using a Brookfield viscometer. Ash was not removed from the oil prior to the measurement.

**Toluene Insolubles and Ash**

A 40 g sample was shaken with 160 g of toluene and centrifuged. The supernatant liquid was decanted and the remaining residue of toluene-insoluble hydrocarbons and ash was vacuum dried at 100°C and weighed. The ash content of the residue was determined by standard procedures.

**Asphaltenes**

A 25 g sample was shaken with 100 g of n-hexane and centrifuged. The supernatant liquid was decanted and the residue, a mixture of ash, toluene insolubles, and toluene soluble hydrocarbons which are insoluble in n-hexane (asphaltenes), was vacuum
dried at 100°C and weighed. The asphaltene content was determined by subtracting toluene insolubles and ash from the total hexane insolubles.

**Coal Analysis**

The coal used in the examples was Pittsburgh No. 8 Allison Mine bituminous coal crushed, dried, and pulverized to pass a 120 mesh screen (U.S. Sieve Series). The sulfur content was about 3.9 percent.

**Example 1**

In a 55 U.S. gallon (208 l.) makeup tank, 73 pounds (33.2 kg.) of bituminous coal, pulverized and dried with a mean particle size of less than 75 microns, was stirred with 109.5 pounds (49.5 kg.) of cycle oil from the coal hydrogenation process until a smooth slurry was obtained. To this slurry was added an emulsified catalyst solution prepared as follows: 36.5 g of ammonium heptamolybdate tetrahydrate, \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}\), was dissolved in 109.5 g of water at room temperature. An emulsion of this solution in oil was prepared by slowly adding 350 g of filtered recycle oil to the solution while mixing over a period of about 5 minutes. The catalyst emulsion was then added to the slurry of coal in oil and the whole was stirred for about one hour.

The coal-oil slurry was fed by a high pressure pump to a point where hydrogen was mixed with it and the mixture was fed at 13.6 pounds (6.04 kg.) slurry and 0.265 pound-mole (0.117 kg.-mole) \(\text{H}_2\) per hour under 2,000 psi (140 kg./cm.\(^2\)) pressure through a preheater and a 0.286 cu ft (8.1 l.) capacity elongated tubular reactor maintained
at 460°C. The effluent from the reactor was let down to atmospheric pressure and then separated by conventional means into gas, light oil boiling below 150°C, a small amount of aqueous phase, and oil boiling above 150°C plus residue. Product distribution based on the slurry feed was as follows:

<table>
<thead>
<tr>
<th></th>
<th>wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>gases</td>
<td>7.7</td>
</tr>
<tr>
<td>light oil</td>
<td>2.5</td>
</tr>
<tr>
<td>aqueous phase</td>
<td>1.9</td>
</tr>
<tr>
<td>150°C oil + residue</td>
<td>87.9</td>
</tr>
</tbody>
</table>

Hydrogen conversion was better than 50 percent and total product recovery was greater than 98 percent based on the slurry feed.

**Example 2**

Using the apparatus and general procedure described in Example 1, a two-stage experiment was carried out to demonstrate the effect of the emulsified catalyst system in a coal hydrogenation process. In the first stage which was of 28.75 hours duration, a 40 weight percent coal-60 weight percent recycle oil slurry with no added catalyst was pumped through the reactor with average rates of 21.4 pounds (9.7 kg.) slurry and 0.35 pound-mole (0.16 kg.-mole) hydrogen per hour at reactor pressure and temperature levels of Example 1. The recycle oil contained 70 ppm Mo (equivalent to 0.01 percent
Mo based on the coal remaining from previous operation. At the end of the first stage, an emulsion of aqueous ammonium molybdate in oil was added to the slurry feed to provide a Mo level of 0.12 percent based on the coal. This slurry mixture was run through the reactor as before for 8.75 hours. Samples of effluent were taken for analysis at several points during the two stages of the run and larger quantities of effluent were collected for material balance determinations, two in the first stage and one in the second.

The recycle oil was 150+°C product with the following analysis:

**TABLE II**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>93 cps</td>
</tr>
<tr>
<td>Ash content</td>
<td>0.074%</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>29.65%</td>
</tr>
<tr>
<td>Mo content</td>
<td>70 ppm</td>
</tr>
</tbody>
</table>

The coal used in this run had an average ash content of 11.7 percent.

**TABLE III**

Analytical Samples

<table>
<thead>
<tr>
<th>Time, min.</th>
<th>No Mo Added</th>
<th>Mo Added</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>368 1,045 1,675</td>
<td>2,040 2,220</td>
</tr>
<tr>
<td>Viscosity, cps</td>
<td>1,105 367 515</td>
<td>80 78</td>
</tr>
<tr>
<td>Asphaltenes in 150+°C oil</td>
<td>32.68 - 30.40</td>
<td>24.42 23.78</td>
</tr>
<tr>
<td>ppm Mo in 150+°C oil</td>
<td>- - 8</td>
<td>- 840</td>
</tr>
<tr>
<td>Time, min.</td>
<td>No Mo Added</td>
<td>Mo Added</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td>A55</td>
<td>1186</td>
</tr>
<tr>
<td>Pressure, psi (kg/cm.²)</td>
<td>2307(162)</td>
<td>2000(140)</td>
</tr>
<tr>
<td>Slurry feed, lb/hr (kg/hr.)</td>
<td>21.9(9.9)</td>
<td>21.0(9.5)</td>
</tr>
<tr>
<td>H₂ feed, SCF/hr (liters/hr.)</td>
<td>134.9(3820)</td>
<td>124.4(3530)</td>
</tr>
<tr>
<td>Effluent Light Oil</td>
<td>7.8</td>
<td>7.9</td>
</tr>
<tr>
<td>Weight % Aqueous phase</td>
<td>2.7</td>
<td>3.1</td>
</tr>
<tr>
<td>150+°C oil</td>
<td>86.3</td>
<td>85.3</td>
</tr>
<tr>
<td>% Recovery on slurry</td>
<td>98.8</td>
<td>101.6</td>
</tr>
<tr>
<td>lb H₂ conv/100 lb coal (kg H₂ conv.)</td>
<td>3.77(1.71)</td>
<td>3.38(1.53)</td>
</tr>
<tr>
<td>% Mo in slurry (based on coal)</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>% Conversion* of coal to toluene-soluble material</td>
<td>66.9</td>
<td>66.2</td>
</tr>
</tbody>
</table>

*Percent conversion of coal was calculated according to the following formula:

\[
\text{Conversion} = 100 \left(1- \frac{z (1 + s.h) (l-y_2)x_3}{s (1-y_2) + (1-s) x_1 (1-y_1)}\right)
\]

where:
- \(s\) = weight fraction of coal in the slurry
- \(x_1\) = fraction of toluene insolubles in slurry oil
- \(y_1\) = fraction of ash in \(x_1\)
- \(y_2\) = fraction of ash in coal
- \(y_3\) = fraction of ash in toluene insolubles from 150+°C oil
- \(x_3\) = fraction of toluene insolubles in 150+°C oil
- \(h\) = lb \(H₂\) (2.2)(kg.) consumed per lb coal (2.2)(kg.)
- \(z\) = fraction of product as 150+°C oil
Examples 3–7

Using the apparatus and general procedure described in Example 1, 60-40 oil-coal slurries containing different metal salt solutions emulsified in the oil were pumped through the reactor at 460°C and 2,000 psi (140 kg./cm.²). In Examples 3 and 4, the catalyst salts were respectively 0.11 percent (based on coal) of a mixture of Co(NO₃)₂·6H₂O and ammonium heptamolybdate tetrahydrate and 0.11 percent of a similar mixture of Ni(NO₃)₂·6H₂O and ammonium heptamolybdate tetrahydrate, in each of which mixtures the metals were present in an equal atomic ratio. In Example 5, the catalyst salt was 0.5 percent of FeSO₄·7H₂O, in Example 6, the catalyst salt was 0.1 percent of Na₂WO₄·2H₂O, and in Example 7, the catalyst salt was 0.11 percent of ammonium heptamolybdate tetrahydrate as in Example 1. Samples of effluent were analyzed as before after several hours of operation in each case. The conditions and results found are listed in Table V.
TABLE V

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Co/Mo</th>
<th>Ni/Mo</th>
<th>Fe</th>
<th>W</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry rate, lb/hr (kg./hr.)</td>
<td>12.15</td>
<td>13.62</td>
<td>19.82</td>
<td>19.51</td>
<td>17.86</td>
</tr>
<tr>
<td>H₂ rate, SCF/hr (l./hr.)</td>
<td>103.7</td>
<td>103.9</td>
<td>128.3</td>
<td>140.3</td>
<td>147.2</td>
</tr>
<tr>
<td>% H₂ consumed</td>
<td>54.2</td>
<td>54.5</td>
<td>62.7</td>
<td>46.6</td>
<td>54.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effluent</th>
<th>% Gas</th>
<th>% Light oil</th>
<th>% Ag. phase</th>
<th>% 150°C oil &amp; residue</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.4</td>
<td>4.0</td>
<td>2.8</td>
<td>84.8</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>2.6</td>
<td>2.4</td>
<td>86.7</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>9.9</td>
<td>3.2</td>
<td>2.3</td>
<td>84.5</td>
<td>102.0</td>
</tr>
<tr>
<td></td>
<td>9.3</td>
<td>2.9</td>
<td>2.4</td>
<td>85.4</td>
<td>101.1</td>
</tr>
<tr>
<td></td>
<td>6.9</td>
<td>2.8</td>
<td>2.2</td>
<td>98.1</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Example 8

As described in the foregoing examples, a 60-40 recycle oil-coal slurry was pumped through the reactor at a constant rate of 20 lb/hr (9.1 kg./hr.) with 0.36 pound-mole (0.163 kg.-mole) per hour of hydrogen at a reactor pressure of 2000 psig (140 kg./cm.²). The coal slurry feed contained ammonium heptamolybdate solution emulsified in the oil at a concentration of 0.027 percent molybdenum based on the coal. During this run, the reactor temperature controller was set at 475°C. As can be seen from the data in Table VI, the proportions of gas, light oil, water, and toluene insolubles are higher at higher
temperatures while the asphaltene content and viscosity of the 150+°C oil fraction are lower.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>475</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat'l Balance, wt. %</td>
<td>99.1</td>
</tr>
<tr>
<td>Lb H₂ converted per 100 lb coal</td>
<td>4.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product, wt. %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>150+°C oil</td>
<td>78.2</td>
</tr>
<tr>
<td>light oil</td>
<td>5.2</td>
</tr>
<tr>
<td>gas</td>
<td>13.4</td>
</tr>
<tr>
<td>aqueous phase</td>
<td>3.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition of 150+°C oil, wt. %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ash</td>
<td>5.3</td>
</tr>
<tr>
<td>toluene insoluble</td>
<td>13.4</td>
</tr>
<tr>
<td>asphaltenes</td>
<td>24.9</td>
</tr>
<tr>
<td>hexane soluble</td>
<td>56.4</td>
</tr>
</tbody>
</table>

| Viscosity of 150+°C oil, cps  | 173 |

In a manner similar to that shown in the above examples, a solution or dispersion of residual oil, tar, or pitch in a hydrocarbon oil containing an emulsified water solution of a metallic catalyst salt is hydrogenated to obtain lower boiling hydrocarbon products. Where the viscosity of the residual oil or other such fraction is sufficiently low, no lighter oil need be added as a diluent, of course, the oil fraction then constituting its own liquid
medium. As previously shown, the proportion of gas and lower boiling liquid hydrocarbons in the product is favored by higher temperatures, longer residence time, and also to some extent by higher proportions of catalyst.

As previously noted, the process described herein for the addition and dispersion of a hydrogenation catalyst as an emulsion of an aqueous metal compound solution in a water-immiscible liquid reaction mixture is similarly applicable to other such hydrogenation processes. Examples of such processes include the hydrogenations of benzene and naphthalene to cycloparaffins and vegetable or animal oils to saturated fats.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for hydrogenating a hydrocarbonaceous substrate by contacting said substrate as a water-immiscible liquid phase with hydrogen in the presence of a metal-containing hydrogenation catalyst, characterized by adding the metal-containing catalyst initially to the water-immiscible liquid phase as an emulsion of a water solution of a compound of said metal in said liquid phase.

2. The process of Claim 1 and further characterized in that a hydrocarbonaceous substance is hydrogenated to lower boiling products by contacting a dispersion of said substance in a liquid hydrocarbon medium with hydrogen at elevated temperature and pressure.

3. The process of Claim 1 or 2 and further characterized in that the hydrocarbonaceous substance is coal.

4. The process of Claim 1 and further characterized in that the metal is chosen from iron, cobalt, nickel, molybdenum, tungsten, tin, zinc, vanadium, chromium and antimony.

5. The process of Claim 4 and further characterized in that the metal is molybdenum.

6. The process of Claim 5 and further characterized in that the molybdenum compound is ammonium heptamolybdate.

7. The process of Claims 4, 5 or 6 and further characterized in that 0.01-1 percent of molybdenum is present in the slurry based on the weight of coal.
8. The process of claim 7 and further characterized in that the hydrogenation temperature is 400°C-500°C.

9. The process of claim 7 and further characterized in that the metal is a mixture of nickel and molybdenum.

10. The process of claim 7 and further characterized in that the metal is a mixture of cobalt and molybdenum.

11. The process of claim 7 and further characterized in that the metal is iron.

12. The process of claim 7 and further characterized in that the metal is tungsten.

13. The process of claims 1, 2 or 3 and further characterized in that the metal is a mixture of cobalt and molybdenum.

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PHILLIPS ORMONDE AND FITZPATRICK

ATTORNEYS FOR:

THE DOW CHEMICAL COMPANY

DANIEL