

**Description**

This invention relates to a hydrovisbreaking process for hydrocarbon-containing feed streams, which substantially minimizes carbon formation. In one aspect, this invention relates to a process for removing metals from a hydrocarbon-containing feed stream. In another aspect, this invention relates to a process for removing sulfur or nitrogen from a hydrocarbon-containing feed stream. In still another aspect, this invention relates to a process for removing potentially cokeable components from a hydrocarbon-containing feed stream. In still another aspect, this invention relates to a process for reducing the amount of heavies in a hydrocarbon-containing feed stream.

10 It is well known that crude oil as well as products from extraction and/or liquefaction of coal and lignite, products from tar sands, products from shale oil and similar products may contain components which make processing difficult. As an example, when these hydrocarbon-containing feed streams contain metals such as vanadium, nickel and iron, such metals tend to concentrate in the heavier fractions such as the topped crude and residuum when these hydrocarbon-containing feed streams are fractionated. The  
15 presence of the metals make further processing of these heavier fractions difficult since the metals generally act as poisons for catalysts employed in processes such as catalytic cracking, hydrogenation or hydrodesulfurization.

The presence of other components such as sulfur and nitrogen is also considered detrimental to the processability of a hydrocarbon-containing feed stream. Also, hydrocarbon-containing feed streams may  
20 contain components (referred to as Ramsbottom carbon residue) which are easily converted to coke in processes such as catalytic cracking, hydrogenation or hydrodesulfurization. It is thus desirable to remove components such as sulfur and nitrogen and components which have a tendency to produce coke.

It is also desirable to reduce the amount of heavies in the heavier fractions such as the topped crude and residuum. As used herein the term heavies refers to the fraction having a boiling range higher than  
25 538°C (about 1000°F). This reduction results in the production of lighter components which are of higher value and which are more easily processed.

Hydrofining is a broad term used to describe a process to remove components such as metals, sulfur, nitrogen and Ramsbottom carbon residue from a hydrocarbon containing feed stream and to reduce the amount of heavies in the hydrocarbon containing feed stream. Hydrovisbreaking is a type of hydrofining  
30 and is generally characterized by a heat soak in the presence of hydrogen. Other hydrofining processes may contact the hydrocarbon containing feed stream with a fixed catalyst bed.

A number of different hydrovisbreaking processes are known. Some of these processes employ decomposable molybdenum compounds such as molybdenum hexacarbonyl, molybdenum naphthenate and molybdenum octoate. The decomposable molybdenum compound is mixed with the hydrocarbon  
35 containing feed stream and the hydrocarbon containing feed stream, which also contains molybdenum, is heated in the presence of hydrogen under suitable hydrovisbreaking conditions.

A major problem with prior hydrovisbreaking processes and particularly those which employ decomposable molybdenum compounds has been the formation of coke, which is extremely undesirable because of the loss of valuable hydrocarbon products. It is thus an object of this invention to provide a  
40 hydrovisbreaking process in which the production of coke is reduced with respect to previous hydrovisbreaking processes which employed the decomposable molybdenum compounds referred to above.

In accordance with the present invention, at least one decomposable molybdenum compound selected from the group consisting of molybdenum dithiophosphates and molybdenum dithiocarbamates  
45 is mixed with a hydrocarbon-containing feed stream in a hydrovisbreaking process. The hydrocarbon-containing feed stream, which also contains molybdenum, is heated in the presence of hydrogen under suitable hydrovisbreaking conditions. After being processed in such a manner, the hydrocarbon-containing feed stream will contain a significantly reduced concentration of metals, sulfur, nitrogen and Ramsbottom carbon residue as well as a reduced amount of heavy hydrocarbon components and only relatively small  
50 amounts of dispersed coke particles. Removal of these components from the hydrocarbon-containing feed stream in this manner provides an improved processability of the hydrocarbon-containing feed stream in processes such as catalytic cracking, hydrogenation or further hydrodesulfurization. Use of a molybdenum compound selected from the group consisting of molybdenum dithiophosphates and molybdenum dithiocarbamates results in improved suppression of coke formation with respect to the use of  
55 molybdenum compounds such as molybdenum hexacarbonyl, molybdenum naphthenate and molybdenum octoate.

Other objects and advantages of the invention will be apparent from the foregoing brief description of the invention and the appended claims as well as the detailed description of the invention which follows.

Any suitable hydrocarbon-containing feed stream may be processed using the above described  
60 catalyst composition in accordance with the present invention. Suitable hydrocarbon-containing feed streams include petroleum products, coal, pyrolyzates, products from extraction and/or liquefaction of coal and lignite, products from tar sands, products from shale oil and similar products. Suitable hydrocarbon feed streams include full range (untopped) crudes, gas oil having a boiling range from about 205°C to about 538°C, topped crude having a boiling range in excess of about 343°C and residuum. However, the present  
65 invention is particularly directed to heavy feed streams such as heavy full range crudes, heavy topped

crudes and residuum and other materials which are generally regarded as too heavy to be distilled. These materials will generally contain the highest concentrations of metals, sulfur, nitrogen and Ramsbottom carbon residues.

It is believed that the concentration of any metal in the hydrocarbon-containing feed stream can be reduced in accordance with the present invention. However, the present invention is particularly applicable to the removal of vanadium, nickel and iron.

The sulfur which can be removed in accordance with the present invention will generally be contained in organic sulfur compounds. Examples of such organic sulfur compounds include sulfides, disulfides, mercaptans, thiophenes, benzylthiophenes, dibenzylthiophenes, and the like.

The nitrogen which can be removed in accordance with the present invention will also generally be contained in organic nitrogen compounds. Examples of such organic nitrogen compounds include amines, diamines, pyridines, quinolines, porphyrins, benzoquinolines and the like.

Any suitable molybdenum dithiophosphate compound may be used in the hydrovisbreaking process. Generic formulas of suitable molybdenum dithiophosphates are:

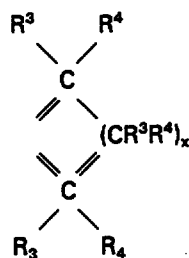
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wherein  $n=3, 4, 5, 6$ ;  $\text{R}^1$  and  $\text{R}^2$  are either independently selected from H, alkyl groups having 1—20 carbon atoms, cycloalkyl or alkylcycloalkyl groups having 3—22 carbon atoms and aryl, alkylaryl or cycloalkylaryl groups having 6—25 carbon atoms; or  $\text{R}^1$  and  $\text{R}^2$  are combined in one alkylene group of the structure

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with  $\text{R}^3$  and  $\text{R}^4$  being independently selected from H, alkyl, cycloalkyl, alkylcycloalkyl and aryl, alkylaryl and cycloalkylaryl groups as defined above, and  $x$  ranging from 1 to 10.

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wherein

$p=0, 1, 2$ ;  $q=0, 1, 2$ ;  $(p+q)=1, 2$ ;  
 $r=1, 2, 3, 4$  for  $(p+q)=1$  and  
 $r=1, 2$  for  $(p+q)=2$ ;

50



wherein

$t=0, 1, 2, 3, 4$ ;  $u=0, 1, 2, 3, 4$ ;  $(t+u)=1, 2, 3, 4$ ;  
 $v=4, 6, 8, 10$  for  $(t+u)=1$ ;  $v=2, 4, 6, 8$  for  $(t+u)=2$ ;  
 $v=2, 4, 6$  for  $(t+u)=3$ ;  $v=2, 4$  for  $(t+u)=4$ .

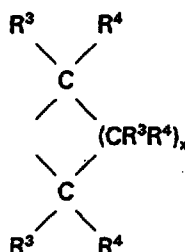
Sulfurized oxomolybdenum (V),  $0,0'$ -di(2-ethylhexyl)phosphorodithioate of the formula  $\text{Mo}_2\text{S}_2\text{O}_2[\text{S}_2\text{P}(\text{OC}_8\text{H}_{17})_2]_2$  is a particularly preferred additive.

Any suitable molybdenum dithiocarbamate compound may be used in the hydrovisbreaking process. Generic formulas of suitable molybdenum (III), (IV), (V) and (VI) dithiocarbamates are:

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wherein  $n=3, 4, 5, 6$ ;  $m=1, 2$ ;  $R^1$  and  $R^2$  are either independently selected from H, alkyl groups having 1—20 carbon atoms, cycloalkyl groups having 3—22 carbon atoms and aryl groups having 6—25 carbon atoms; or  $R^1$  and  $R^2$  are combined in one alkylene group of the structure



with  $R^3$  and  $R^4$  being independently selected from H, alkyl, cycloalkyl and aryl groups as defined above, and  $x$  ranging from 1 to 10.



wherein

$p=0, 1, 2$ ;  $q=0, 1, 2$ ;  $(p+q)=1, 2$ ;

$r=1, 2, 3, 4$  for  $(p+q)=1$  and

$r=1, 2$  for  $(p+q)=2$ ;



wherein

$t=0, 1, 2, 3, 4$ ;  $u=0, 1, 2, 3, 4$ ;  $(t+u)=1, 2, 3, 4$

$v=4, 6, 8, 10$  for  $(t+u)=1$ ;  $v=2, 4, 6, 8$  for  $(t+u)=2$ ;

$v=2, 4, 6$  for  $(t+u)=3$ ,  $v=2, 4$  for  $(t+u)=4$ .

Molybdenum (V) di(tridecyl)dithiocarbamate is a particularly preferred additive.

Any suitable concentration of the molybdenum additive may be added to the hydrocarbon-containing feed stream. In general, a sufficient quantity of the additive will be added to the hydrocarbon-containing feed stream to result in a concentration of molybdenum metal in the range of about 1 to about 1000 ppm and more preferably in the range of about 3 to about 300 ppm.

It is noted that one of the particular advantages of the present invention is the very small concentration of molybdenum which may be used. This substantially improves the economic viability of the process.

The hydrovisbreaking process can be carried out by means of any suitable apparatus whereby there is achieved a contact of the hydrocarbon containing feed stream, the decomposable molybdenum compound and hydrogen under suitable hydrovisbreaking conditions. The hydrovisbreaking process can be carried out as a continuous process or as a batch process. The hydrovisbreaking process is in no way limited to the use of any particular type of process or apparatus.

The molybdenum compound may be combined with the hydrocarbon-containing feed stream in any suitable manner. The molybdenum compound may be mixed with the hydrocarbon-containing feed stream as a solid or liquid or may be dissolved in a suitable solvent (preferably an oil) prior to introduction into the hydrocarbon-containing feed stream. Any suitable mixing time may be used. However, it is believed that simply injecting the molybdenum compound into the hydrocarbon-containing feed stream is sufficient. No special mixing equipment or mixing period are required.

In a continuous process, the molybdenum compound is mixed with the hydrocarbon containing feed stream prior to introducing the hydrocarbon containing feedstream into the reactor. For a batch process, it is also generally more convenient to add the molybdenum compound to the hydrocarbon-containing feed stream before the hydrocarbon containing feed stream is introduced into the reactor and the reactor is pressurized with hydrogen gas. However, if desired, the molybdenum compound may be added to the hydrocarbon containing feed stream after the hydrocarbon containing feed stream is introduced into the batch reactor but before the hydrovisbreaking process is begun.

The pressure and temperature at which the molybdenum compound is introduced into the hydrocarbon-containing feedstream is not thought to be critical. However, a temperature above 100°C is recommended.

Many hydrofining processes and some hydrovisbreaking processes are carried out using catalyst compositions. Such catalyst compositions generally comprise a support such as alumina, silica or silica/alumina. Catalyst compositions may also contain a promoter with typical promoters being the metals

group VIB, group VIIB, and group VIII of the Periodic Table. The hydrovisbreaking process of the present invention is distinguished from hydrofining or hydrovisbreaking processes which employ such catalyst composition in that such catalyst compositions are not employed in the hydrovisbreaking process of the present invention.

- 5 Any suitable reaction time in the hydrovisbreaking process may be utilized. In general, the reaction time will range from 0.01 hours to 10 hours. Preferably, the reaction time will range from 0.1 to 5 hours and more preferably from 0.25 to 3 hours. Thus, for a continuous process, the flow rate of the hydrocarbon containing feed stream should be such that the time required for the passage of the mixture through the reactor (residence time) will preferably be in the range of 0.1 to 5 hours and more preferably 0.25 to 3 hours.
- 10 For a batch process, the hydrocarbon-containing feed stream will preferably remain in the reactor for a time in the range of 0.1 hours to 5 hours and more preferably from 0.25 hours to 3 hours.

- The hydrovisbreaking process can be carried out at any suitable temperature. The temperature will generally be in the range of 250°C to 550°C and will preferably be in the range of 380° to 480°C. Higher temperatures do improve the removal of metals but temperatures should not be utilized which will have
- 15 adverse effects on the hydrocarbon-containing feed stream, such as increased coking, and also economic considerations must be taken into account. Lower temperatures can generally be used for lighter feeds.

- Any suitable hydrogen pressure may be utilized in the hydrovisbreaking process. The reaction pressure will generally be in the range of atmospheric to 69 mPa (atmospheric to 10,000 psig). Preferably, the pressure will be in the range of 3.55 to 20.8 mPa (500 to 3,000 psig). Higher hydrogen pressures tend to
- 20 reduce coke formation but operation at high pressure may have adverse economic consequences.

- Any suitable quantity of hydrogen can be added to the hydrovisbreaking process. The quantity of hydrogen used to contact the hydrocarbon-containing feed stock, either in a continuous or batch process, will generally be in the range of 17.8 to 3562 m<sup>3</sup> per m<sup>3</sup> fibers (100 to 20,000 standard cubic feet per barrel) of the hydrocarbon-containing feed stream and will more preferably be in the range of 89 to 891 m<sup>3</sup> per m<sup>3</sup>
- 25 (500 to 5,000 standard cubic feet per barrel) of the hydrocarbon-containing feed stream.

The following examples are presented in further illustration of the invention.

#### Example I

- In this example the experimental setup for batch-type hydrovisbreaking of heavy oils is described.
- 30 About 100 grams of a topped (510°C+) (950°F+) Hondo heavy crude (containing 18.2 weight-% Ramsbottom C, 6.2 weight-% S, 730 ppm (V+Ni), 0.55 weight-% xylene insolubles and a 538°C+ (1000°F+) fraction of 85.1 weight-%) plus appropriate amounts of a decomposable molybdenum compound were added to a 300 cc stirred autoclave (Autoclave Engineers, Inc., Erie, PA), which was preheated to about 93°C (200°F). The unit was sealed, alternately pressured with H<sub>2</sub> and vented so as to eliminate air, and finally
- 35 pressured with H<sub>2</sub> to the desired starting pressure (9.75 MPa) (about 1400 psig). Stirring at about 1000 r.p.m. and rapid heating up to the test temperature about 427°C (800°F) was carried out. During the test run, hydrogen gas was added so as to maintain a constant pressure of about 13.9—16.0 MPa (2000—2300 psig) at the final test temperature.

- After heating at about 427°C (800°F) for about 60 minutes, the unit was cooled as quickly as possible,
- 40 depressured and opened. The liquid product was collected and analyzed. Primarily, the amount of dispersed coke particles was determined (by filtration through a 0.45 µm membrane filter and weighing). Other test parameters were Ramsbottom carbon (ASTM D524), density of 15.6°C (60°F), xylene insoluble content and the amount of the 538°C+ (1000°F+) fraction of the liquid product.

#### 45 Example II

This example illustrates the results of hydrovisbreaking tests in accordance with the procedure outlined in Example I. The following decomposable molybdenum compounds were tested.

- A; Molyvan® 807, a mixture of about 50 weight-% molybdenum (V) ditridecyldithiocarbamate and about 50 weight-% of an aromatic oil (specific gravity: 0.963; viscosity at 99°C (210°F): 38.4 SUS); Molyvan®
- 50 807 contains about 4.6 weight-% Mo, it is marketed as an antioxidant and antiwear additive by R. T. Vanderbilt Company, Norwalk, CT;

B; Molyvan® L, a mixture of about 80 weight-% of a sulfided molybdenum (V) dithiophosphate of the formula Mo<sub>2</sub>S<sub>2</sub>O<sub>2</sub>[PS<sub>2</sub>(OR)<sub>2</sub>] wherein R is the 2-ethylhexyl group, and about 20 weight-% of an aromatic oil (see above); marketed by R. T. Vanderbilt Company;

- 55 C: Mo(CO)<sub>6</sub>, marketed by Aldrich Chemical Company, Milwaukee, Wisconsin;

D: Molybdenum (V) naphthenate, Mo(C<sub>10</sub>H<sub>2</sub>CO<sub>2</sub>)<sub>5</sub>; marketed by Shepherd Chemical Company, Cincinnati, Ohio;

E: Molybdenum (IV) octoate, MoO(C<sub>7</sub>H<sub>15</sub>CO<sub>2</sub>)<sub>2</sub>; containing about 8 weight-% Mo; marketed by Shepherd Chemical Company.

- 60 Results are summarized in Table I.

TABLE I

| Run No                                          | 1<br>(Invention) | 2<br>(Invention) | 3<br>(Control) | 4<br>(Control) | 5<br>(Control) |
|-------------------------------------------------|------------------|------------------|----------------|----------------|----------------|
| Mo Additive                                     | A                | B                | C              | D              | E              |
| Mo Concentration (ppm) in Feed                  | 50               | 50               | 50             | 50             | 50             |
| Formed Coke (Wt-% of Liquid Product)            | 3.2              | 4.1              | 8.9            | 8.4            | 7.8            |
| Conversion of 538°C+ (1000°F+) Fraction (%)     | 67.0             | 65.5             | 68.9           | 70.7           | 73.1           |
| Ramsbottom C (Wt-% of Liquid Product)           | 10.2             | 9.9              | 10.1           | 10.7           | 10.1           |
| Xylene Insol. (Wt-% of Liquid Product)          | 0.5              | 0.4              | 0              | 0.3            | 0.2            |
| Density of Liquid Product (15.6°C (60°F); g/cc) | 0.930            | 0.931            | 0.926          | 0.925          | 0.919          |
| API Gravity of Liquid Product 15.6°C (60°F)     | 20.4             | 20.3             | 21.1           | 21.3           | 22.3           |

Data in Table I show that, unexpectedly, molybdenum dithiocarbamate (compound A) and molybdenum dithiophosphate (compound B) caused significantly lower coke formation than three other molybdenum compounds during the hydrovisbreaking of the 510°C+ (950°F+) topped crude at about 427°C/13.9—16.0 MPa H<sub>2</sub> (800°F/2000—2300 psig H<sub>2</sub>) during a period of about 60 minutes. Ramsbottom carbon and xylene insoluble contents in the liquid product were comparable for all runs. The API gravity of the product was slightly lower in the invention runs and so was the 538°C+ (1000°F+) conversion.

#### Example III

- In this example the experimental setup for the continuous hydrovisbreaking of heavy oils is described.
- 10 A topped 343°C+ (650°F+) Hondo heavy crude (containing 12.1 weight-% Ramsbottom C, 5.6 weight-% S, 480 ppm (Ni+V), a 538°C+ (1000°F+) fraction of 62.0 weight-%, and having an API gravity of 9.0) plus, when desired, molybdenum compounds were stirred in a heated feed vessel. The oil feed was pumped at a rate of about 2 liters per hour into a stainless steel pipe of about 1/2" inner diameter and was mixed with hydrogen gas (pressure: 12.5 MPa (1800 psig)). The oil-gas mixture was heated to a temperature of almost
- 15 438°C (820°F) in a 18.3 m (60 feet) long coiled stainless steel tube surrounded by an electric furnace and charged through an induction tube extending close to the bottom of a heated reactor 10.2 cm (4 inch) diameter and 0.66 m (26 inch) length) where it mixed with the reactor contents. The product exited through an eduction tube, which was positioned so as to provide a liquid volume, of about 1 liter and thus an average residence time of the oil-gas mixture of about 30 minutes at the reaction temperature of about
- 20 438°C (820°F).

The product passed through a pressure let-down valve into a series of phase separators and coolers. All liquid fractions were combined, and were analyzed as described in Example I. A tracer was introduced in the gaseous product stream. The tracer was analyzed in a gas chromatograph so as to calculate gas flows and hydrogen consumption. Results are summarized in Table II.

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TABLE II

| Run No                                                                                      | 6<br>(Invention) | 7<br>(Invention) | 8<br>(Control) | 9<br>(Control) | 10<br>(Control) |
|---------------------------------------------------------------------------------------------|------------------|------------------|----------------|----------------|-----------------|
| Mo Additive                                                                                 | A                | B                | C              | D              | E               |
| Mo Concentration (ppm) in Feed                                                              | 80               | 80               | 80             | 80             | 80              |
| Formed Coke (Wt-% of Liquid Product)                                                        | 3.1              | 3.5              | 6.6            | 7.7            | 7.5             |
| Conversion of 538°C+ (1000°F+) Fraction (%)                                                 | 53.4             | 54.6             | 60.4           | 59.1           | 59.9            |
| Gas Formation m <sup>3</sup> /m <sup>3</sup> of oil feed (SCF/bbl. of Oil Feed)             | 47.2(265)        | 45.2(254)        | 52.0(292)      | 54.1(304)      | 55.6(312)       |
| H <sub>2</sub> Consumption m <sup>3</sup> /m <sup>3</sup> of Oil Feed (SCF/bbl of Oil Feed) | 81(455)          | 76.6(430)        | 43.8(246)      | 53.4(300)      | 46.7(262)       |

Data in Table II confirm the results of Table I: lower coke formation when molybdenum dithiocarbamate and dithiophosphate (compounds A and B, Runs 6 and 7) were employed. Hydrogen consumption was significantly higher in Runs 6 and 7, whereas 538°C+ (1000°F+) conversion and gas formation were somewhat lower in these runs than in control runs (Runs 8, 9 and 10).

# Claims

1. A process for hydrovisbreaking a hydrocarbon-containing feed stream characterized by the steps of: introducing at least one decomposable molybdenum compound selected from molybdenum dithiophosphates and molybdenum dithiocarbamates into said hydrocarbon-containing feed stream; and contacting said hydrocarbon-containing feed stream containing said decomposable molybdenum compound under hydrovisbreaking conditions with hydrogen, wherein said contacting is carried out in the absence of a catalyst composition containing alumina, silica or silica alumina.

2. The process of claim 1 characterized in that said decomposable molybdenum dithiophosphate compound is selected from the generic formulas (1), (2) and (3)



wherein  $n=3, 4, 5, 6$ ;  $\text{R}^1$  and  $\text{R}^2$  are either independently selected from H, alkyl groups having 1—20 carbon atoms, cycloalkyl or alkylcycloalkyl groups having 3—22 carbon atoms and aryl, alkylaryl, or cycloalkylaryl groups having 6—25 carbon atoms; or  $\text{R}^1$  and  $\text{R}^2$  are combined in one alkylene group of the structure



with  $\text{R}^3$  and  $\text{R}^4$  being independently selected from H, alkyl, cycloalkyl, alkylcycloalkyl, aryl, alkylaryl and cycloalkylaryl groups as defined above, and  $x$  ranging from 1 to 10;



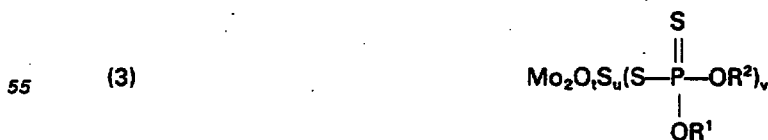
wherein

$p=0, 1, 2$ ;  $q=0, 1, 2$ ;  $(p+q)=1, 2$ ;

$r=1, 2, 3, 4$  for  $(p+q)=1$ ;

$r=1, 2$  for  $(p+q)=2$ ; and

$\text{R}^1$  and  $\text{R}^2$  are as defined before:



wherein

$t=0, 1, 2, 3, 4$ ;  $u=0, 1, 2, 3, 4$ ;  $(t+u)=1, 2, 3, 4$ ;

$v=4, 6, 8, 10$  for  $(t+u)=1$ ;  $v=2, 4, 6, 8$  for  $(t+u)=2$ ;

$v=2, 4, 6$  for  $(t+u)=3$ ;  $v=2, 4$  for  $(t+u)=4$ ; and

$\text{R}^1$  and  $\text{R}^2$  are as defined before.

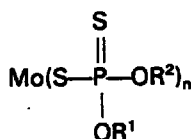
3. The process of claim 2 characterized in that said decomposable molybdenum dithiophosphate compound is oxymolybdenum (V) 0,0' - di(2 - ethylhexyl)phosphorodithioate.

Data in Table II confirm the results of Table I: lower coke formation when molybdenum dithiocarbamate and dithiophosphate (compounds A and B, Runs 6 and 7) were employed. Hydrogen consumption was significantly higher in Runs 6 and 7, whereas 538°C+ (1000°F+) conversion and gas formation were somewhat lower in these runs than in control runs (Runs 8, 9 and 10).

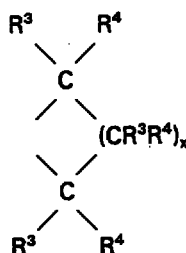
# Claims

1. A process for hydrovisbreaking a hydrocarbon-containing feed stream characterized by the steps of: introducing at least one decomposable molybdenum compound selected from molybdenum dithiophosphates and molybdenum dithiocarbamates into said hydrocarbon-containing feed stream; and contacting said hydrocarbon-containing feed stream containing said decomposable molybdenum compound under hydrovisbreaking conditions with hydrogen, wherein said contacting is carried out in the absence of a catalyst composition containing alumina, silica or silica alumina.

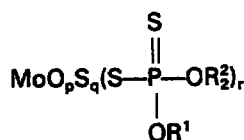
2. The process of claim 1 characterized in that said decomposable molybdenum dithiophosphate compound is selected from the generic formulas (1), (2) and (3)



wherein  $n=3, 4, 5, 6$ ;  $\text{R}^1$  and  $\text{R}^2$  are either independently selected from H, alkyl groups having 1—20 carbon atoms, cycloalkyl or alkylcycloalkyl groups having 3—22 carbon atoms and aryl, alkylaryl, or cycloalkylaryl groups having 6—25 carbon atoms; or  $\text{R}^1$  and  $\text{R}^2$  are combined in one alkylene group of the structure



with  $\text{R}^3$  and  $\text{R}^4$  being independently selected from H, alkyl, cycloalkyl, alkylcycloalkyl, aryl, alkylaryl and cycloalkylaryl groups as defined above, and  $x$  ranging from 1 to 10;



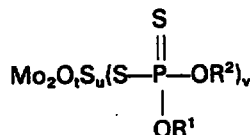
wherein

$p=0, 1, 2$ ;  $q=0, 1, 2$ ;  $(p+q)=1, 2$ ;

$r=1, 2, 3, 4$  for  $(p+q)=1$ ;

$r=1, 2$  for  $(p+q)=2$ ; and

$\text{R}^1$  and  $\text{R}^2$  are as defined before:



wherein

$t=0, 1, 2, 3, 4$ ;  $u=0, 1, 2, 3, 4$ ;  $(t+u)=1, 2, 3, 4$ ;

$v=4, 6, 8, 10$  for  $(t+u)=1$ ;  $v=2, 4, 6, 8$  for  $(t+u)=2$ ;

$v=2, 4, 6$  for  $(t+u)=3$ ;  $v=2, 4$  for  $(t+u)=4$ ; and

$\text{R}^1$  and  $\text{R}^2$  are as defined before.

3. The process of claim 2 characterized in that said decomposable molybdenum dithiophosphate compound is oxymolybdenum (V) 0,0' - di(2 - ethylhexyl)phosphorodithioate.



4. The process of claim 1 characterized in that said decomposable molybdenum dithiocarbamate compound is selected from the generic formulas (1), (2) and (3)



wherein  $n=3, 4, 5, 6$ ;  $m=1, 2$ ;  $R^1$  and  $R^2$  are either independently selected from H, alkyl groups having 1—20 carbon atoms, cycloalkyl groups having 3—22 carbon atoms and aryl groups having 6—25 carbon atoms; or  $R^1$  and  $R^2$  are combined in one alkylene group of the structure and the meaning identified in claim 2;



wherein

$p=0, 1, 2$ ;  $q=0, 1, 2$ ;  $(p+q)=1, 2$ ;

$r=1, 2, 3, 4$  for  $(p+q)=1$ ;

$r=1, 2$  for  $(p+q)=2$ ; and

$R^1$  and  $R^2$  are as defined before;



wherein

$t=0, 1, 2, 3, 4$ ;  $u=0, 1, 2, 3, 4$ ;  $(t+u)=1, 2, 3, 4$ ;

$v=4, 6, 8, 10$  for  $(t+u)=1$ ;  $v=2, 4, 6, 8$  for  $(t+u)=2$ ;

$v=2, 4, 6$  for  $(t+u)=3$ ;  $v=2, 4$  for  $(t+u)=4$ ; and

$R^1$  and  $R^2$  are as defined before.

5. The process of claim 4 characterized in that said decomposable molybdenum dithiocarbamate compound is molybdenum (V) di(tridecyl)dithiocarbamate.

6. The process of any of the preceding claims characterized in that said decomposable molybdenum compound is added in an amount to result in a concentration of molybdenum in said hydrocarbon-containing feed stream in the range of 1 to 1000 ppm.

7. The process of claim 6 characterized in that said decomposable molybdenum compound is added in an amount to result in a concentration of molybdenum in said hydrocarbon-containing feed stream in the range of 3 to 300 ppm.

8. The process of any of the preceding claims characterized in that said hydrovisbreaking conditions comprise a reaction time in the range of 0.01 to 10 hours, a temperature in the range of 250 to 550°C, a pressure in the range of atmospheric to 69 MPa and a hydrogen addition in the range of 17.8 to 3562 m<sup>3</sup> per m<sup>3</sup> of said hydrocarbon-containing feed stream.

9. The process of claim 8 characterized in that said reaction time is in the range of 0.1 to 5 hours, said temperature is in the range of 380 to 480°C, said pressure is in the range of 3.55 to 20.8 MPa and said hydrogen addition is in the range of 89 to 891 m<sup>3</sup> per m<sup>3</sup> of said feed stream.

10. The process of claim 9 characterized in that said reaction time is in the range of 0.25 to 3 hours.

# Patentansprüche

1. Hydrovisbreaking-Verfahren für ein kohlenwasserstoffhaltiges Einsatzmaterial, gekennzeichnet durch folgende Stufen:

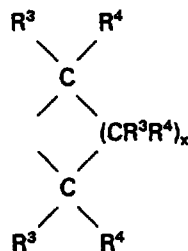
Einführen von mindestens einer zersetzbaren Molybdänverbindung, ausgewählt unter Molybdändithiophosphaten und Molybdändithiocarbamaten, in das kohlenwasserstoffhaltige Einsatzmaterial; und

Kontaktieren des kohlenwasserstoffhaltigen Einsatzmaterials mit einem Gehalt an der zersetzbaren Molybdänverbindung unter Hydrovisbreaking-Bedingungen mit Wasserstoff, wobei das Kontaktieren in Abwesenheit einer Katalysatorzusammensetzung mit einem Gehalt an Aluminiumoxid, Siliciumdioxid oder Siliciumdioxid-Aluminiumoxid durchgeführt wird.

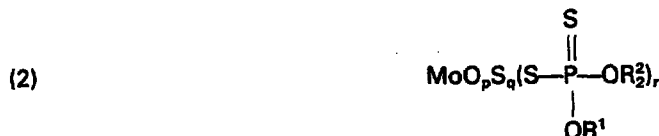
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das zersetzbare Molybdändithiophosphat unter Verbindungen der allgemeinen Formeln (1), (2) und (3) ausgewählt ist.



wobei  $n=3, 4, 5$  oder  $6$ ;  $R^1$  und  $R^2$  unabhängig voneinander unter M, Alkylresten mit 1—20 Kohlenstoffatomen, Cycloalkyl- oder Alkylcycloalkylresten mit 3—22 Kohlenstoffatomen und Aryl-, Alkylaryl- oder Cycloalkylarylresten mit 6—25 Kohlenstoffatomen ausgewählt sind; oder  $R^1$  und  $R^2$  zu einem Alkylrest der Formel



kombiniert sind, wobei  $R^3$  und  $R^4$  unabhängig voneinander unter H, Alkyl-, Cycloalkyl-, Alkylcycloalkyl-, Aryl-, Alkylaryl und Cycloalkylarylresten gemäß der vorstehenden Definition ausgewählt sind und  $x$  im Bereich von 1—10 liegt;



worin

$p=0, 1, 2$ ;  $q=0, 1, 2$ ;  $(p+q)=1, 2$ ;

$r=1, 2, 3, 4$  für  $(p+q)=1$ ;

$r=1, 2$  für  $(p+q)=2$ ;

und  $R^1$  und  $R^2$  die vorstehend definiert Bedeutung haben;



worin

$t=0, 1, 2, 3, 4$ ;  $u=0, 1, 2, 3, 4$ ;  $(t+u)=1, 2, 3, 4$ ;

$v=4, 6, 8, 10$  für  $(t+u)=1$ ;  $v=2, 4, 6, 8$  für  $(t+u)=2$ ;

$v=2, 4, 6$  für  $(t+u)=3$ ;  $v=2, 4$  für  $(t+u)=4$ ;

und  $R^1$  und  $R^2$  die vorstehend definierte Bedeutung haben.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, dass es sich beim zersetzbaren Molybdändithiophosphat um Oxymolybdän (V) - 0,0' - di - (2 - ethylhexyl) - phosphorodithioat handelt.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das zersetzbare Molybdändithiocarbamat aus den allgemeinen Formeln (1), (2) und (3) ausgewählt ist



worin  $n=3, 4, 5, 6$ ;  $m=1, 2$ ;  $R^1$  und  $R^2$  unabhängig voneinander unter H, Alkylresten mit 1—20 Kohlenstoffatomen, Cycloalkylresten mit 3—22 Kohlenstoffatomen und Arylresten mit 6—25 Kohlenstoffatomen ausgewählt sind, oder  $R^1$  und  $R^2$  zu einem Alkylrest kombiniert sind, der im Hinblick auf Struktur und Bedeutungen der Reste den Angaben in Anspruch 2 entspricht;



worin

$p=0, 1, 2$ ;  $q=0, 1, 2$ ;  $(p+q)=1, 2$ ;

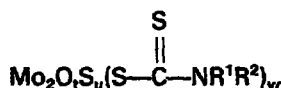
$r=1, 2, 3, 4$  für  $(p+q)=1$ ;

$r=1, 2$  für  $(p+q)=2$ ;

und  $R^1$  und  $R^2$  die vorstehend definierte Bedeutung haben;



(3)



5 worin

t=0, 1, 2, 3, 4; u=0, 1, 2, 3, 4; (t+u)=1, 2, 3, 4;

v=4, 6, 8, 10 für (t+u)=1; v=2, 4, 6, 8 für (t+u)=2;

v=2, 4, 6 für (t+u)=3, v=2, 4 für (t+u)=4;

und R<sup>1</sup> und R<sup>2</sup> die vorstehend definierte Bedeutung haben.

10 5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, dass es sich beim zersetzbaren Molybdändithiocarbamat um Molybdän- (V) - di - (tridecyl) - dithiocarbamat handelt.

6. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die zersetzbare Molybdänverbindung in einer solchen Menge zugesetzt wird, dass sich im kohlenwasserstoffhaltigen Einsatzmaterial eine Molybdänkonzentration im Bereich von 1—1000 ppm ergibt.

15 7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, dass die zersetzbare Molybdänverbindung in einer solchen Menge zugesetzt wird, dass sich im kohlenwasserstoffhaltigen Einsatzmaterial eine Molybdänkonzentration im Bereich von 3—300 ppm ergibt.

20 8. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Hydrovisbreaking-Bedingungen eine Reaktionszeit im Bereich von 0,01—10 Stunden, eine Temperatur im Bereich von 250—550°C, einen Druck im Bereich von Atmosphärendruck bis 69 MPa und eine Wasserstoffzugabe im Bereich von 17,8 bis 3562 m<sup>3</sup> pro m<sup>3</sup> des kohlenwasserstoffhaltigen Einsatzmaterials umfassen.25 9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, dass die Reaktionszeit im Bereich von 0,1—5 Stunden, die Temperatur im Bereich von 380—480°C, der Druck im Bereich von 3,55—20,8 MPa und die Wasserstoffzugabe im Bereich von 89—891 m<sup>3</sup> pro m<sup>3</sup> des Einsatzmaterials liegen.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, dass die Reaktionszeit im Bereich von 0,25—3 Stunden liegt.

## Revendications

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1. Procédé d'hydroviscoréduction d'un courant d'alimentation contenant des hydrocarbures, caractérisé par les étapes de:

introduction d'au moins un composé de molybdène décomposable choisi parmi des dithiophosphates de molybdène et des dithiocarbamates de molybdène dans le courant d'alimentation contenant des hydrocarbures; et

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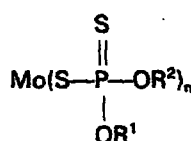
mise en contact du courant d'alimentation contenant des hydrocarbures, contenant le composé de molybdène décomposable, dans des conditions d'hydroviscoréduction, avec de l'hydrogène, sachant que l'on effectue la mise en contact en l'absence d'une composition catalytique contenant de l'alumine, de la silice ou de la silice alumine.

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2. Procédé selon la revendication 1, caractérisé en ce que le composé de dithiophosphate de molybdène décomposable est choisi parmi les formules génériques (1), (2) et (3)

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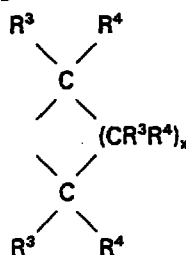
(1)



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dans laquelle n=3, 4, 5, 6; R<sup>1</sup> et R<sup>2</sup> sont indépendamment choisis parmi H, des groupes alkyles ayant de 1 à 20 atomes de carbone, des groupes cycloalkyles ou alkylcycloalkyles ayant de 3 à 22 atomes de carbone et des groupes aryles, alkylaryles ou cycloalkylaryles ayant de 6 à 25 atomes de carbone, ou R<sup>1</sup> et R<sup>2</sup> sont combinés en un groupe alkylène présentant la structure:

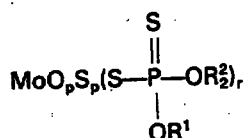
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65 R<sup>3</sup> et R<sup>4</sup> étant indépendamment choisis parmi H, des groupes alkyles, cycloalkyles, alkylcycloalkyles, aryles, alkylaryles et cycloalkylaryles tels qu'on les a définis plus haut, et x étant compris entre 1 et 10;

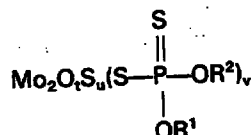
(2)



dans laquelle

 $p=0, 1, 2; q=0, 1, 2; (p+q)=1, 2;$  $r=1, 2, 3, 4$  si  $(p+q)=1;$  $r=1, 2$  si  $(p+q)=2;$  et $\text{R}^1$  et  $\text{R}^2$  sont tels qu'on les a définis précédemment;

(3)



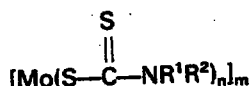
dans laquelle

 $t=0, 1, 2, 3, 4; u=0, 1, 2, 3, 4; (t+u)=1, 2, 3, 4;$  $v=4, 6, 8, 10$  si  $(t+u)=1; v=2, 4, 6, 8$  si  $(t+u)=2;$  $v=2, 4, 6$  si  $(t+u)=3; v=2, 4$  si  $(t+u)=4;$  et $\text{R}^1$  et  $\text{R}^2$  sont tels qu'on les a définis précédemment.

3. Procédé selon la revendication 2, caractérisé en ce que le composé de dithiophosphate de molybdène décomposable est l'0,0' - di(2 - éthylhexyl)phosphorodithioate d'oxymolybdène (V).

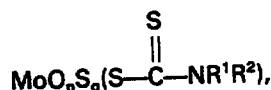
4. Procédé selon la revendication 1, caractérisé en ce que le composé de dithiocarbamate de molybdène décomposable est choisi parmi les formules génériques (1), (2) et (3)

(1)



dans laquelle  $n=3, 4, 5, 6; m=1, 2; \text{R}^1$  et  $\text{R}^2$  sont indépendamment choisis parmi H, des groupes alkyles ayant de 1 à 20 atomes de carbone, des groupes cycloalkyles ayant de 3 à 22 atomes de carbone, et des groupes aryles ayant de 6 à 25 atomes de carbone, ou  $\text{R}^1$  et  $\text{R}^2$  sont combinés en un groupe alkylène présentant la structure et la signification indiquées dans la revendication 2;

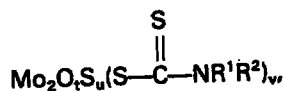
(2)



dans laquelle

 $p=0, 1, 2; q=0, 1, 2; (p+q)=1, 2;$  $r=1, 2, 3, 4$  si  $(p+q)=1;$  $r=1, 2$  si  $(p+q)=2;$  et $\text{R}^1$  et  $\text{R}^2$  sont tels qu'on les a définis précédemment.

(3)



dans laquelle

 $t=0, 1, 2, 3, 4; u=0, 1, 2, 3, 4; (t+u)=1, 2, 3, 4;$  $v=4, 6, 8, 10$  si  $(t+u)=1; v=2, 4, 6, 8$  si  $(t+u)=2;$  $v=2, 4, 6$  si  $(t+u)=3; v=2, 4$  si  $(t+u)=4;$  et $\text{R}^1$  et  $\text{R}^2$  sont tels qu'on les a définis précédemment.

5. Procédé selon la revendication 4, caractérisé en ce que le composé de dithiocarbamate de molybdène décomposable est le di(tridécyl)dithiocarbamate de molybdène (V).

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'on ajoute le composé de molybdène décomposable en une quantité permettant d'obtenir une concentration en molybdène dans le courant d'alimentation contenant des hydrocarbures comprise entre 1 et 1000 ppm.

7. Procédé selon la revendication 6, caractérisé en ce que l'on ajoute le composé de molybdène décomposable en une quantité permettant d'obtenir une concentration en molybdène dans le courant d'alimentation contenant les hydrocarbures comprise entre 3 et 300 ppm.

8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les



conditions d'hydroviscoréduction comprennent un temps de réaction compris entre 0,01 et 10 heures, une température comprise entre 250 et 550°C, une pression comprise entre la pression atmosphérique et 69 MPa et une addition d'hydrogène comprise entre 17,8 et 3562 m<sup>3</sup> par m<sup>3</sup> de courant d'alimentation contenant des hydrocarbures.

5 9. Procédé selon la revendication 8, caractérisé en ce que le temps de réaction est comprise entre 0,1 et 5 heures, la température est comprise entre 380 et 480°C, la pression est comprise entre 3,55 et 20,8 MPa et l'addition d'hydrogène est comprise entre 89 et 891 m<sup>3</sup> par m<sup>3</sup> de courant d'alimentation.

10 10. Procédé selon la revendication 9, caractérisé en ce que le temps de réaction est compris entre 0,25 et 3 heures.

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