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HYDROREFINING OF PETROLEUM CRUDE OIL AND CATALYST THEREFOR

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The present invention relates to a method for preparing a novel catalyst particularly adaptable for utilization in a slurry-type process for the hydrorefining of petroleum crude oils, heavy vacuum gas oils, heavy cycle stocks, crude oil residuum, black oils, topped crude oils, visbreaker effluent, and other heavy hydrocarbonaceous mixtures boiling above the normal gasoline boiling range. More specifically, the present invention involves a process for hydrorefining a petroleum crude oil for the purpose of effecting the removal of nitrogen and sulfur, affording unexpected advantages in the destructive removal of organo-metallic contaminants and the conversion of the pentane-insoluble fraction of the petroleum crude oil.

Petroleum crude oils and the heavy hydrocarbon fractions and/or distillates obtained therefrom, particularly heavy vacuum gas oils and topped crudes, contain nitrogenous and sulfurous compounds in exceedingly large quantities. In addition, petroleum crude oils contain detrimental quantities of organo-metallic contaminants which exert deleterious effects upon the catalysts utilized in various processes to which the crude oil, topped crude oil, or heavy hydrocarbon fraction may be subjected. The more common of these metallic contaminants are nickel and vanadium, generally existing in concentrations in excess of about 50 p.p.m., although other metals including iron, copper, etc. are often present. Metallic contaminants may occur within the petroleum crude oil in a variety of forms; they may exist as metal oxides or sulfides, introduced into the crude oils as metallic scale or particles; they may be present in the form of soluble salts of such metals; usually, however, they exist in the form of high molecular weight organometallic compounds such as metal porphyrins and the various derivatives thereof. Although the metallic contaminants, existing as oxide or sulfide scale, may be removed, at least in part, by a relatively simple filtering technique, and the water-soluble salts are removable by washing and a subsequent dehydration procedure, a much more severe treatment is required to effect the destructive removal of the organo-metallic compounds, particularly to the degree necessary to produce a crude oil or heavy hydrocarbon fraction which is suitable for further processing.

In addition to the organo-metallic contaminants, including metal porphyrins and derivatives thereof, crude oils generally contain greater quantities of sulfurous and nitrogenous compounds than are found in lighter, normally liquid hydrocarbon fractions such as gasoline, kerosene, light gas oil, etc. For example, a Wyoming sour crude, having a gravity of 23.2° API at 60° F., contains about 2.8% by weight of sulfur and 2700 p.p.m. of nitrogen, 18 p.p.m. of nickel and about 81 p.p.m. of vanadium. The nitrogenous and sulfurous compounds are converted, upon being subjected to catalytic hydrorefining, into hydrocarbons, ammonia and hydrogen sulfide; similarly, any oxygenated compounds will be converted into water and the hydrocarbon counterpart. However, a reduction in the concentration of the organometallic contaminants is not as easily achieved, and to the extent that that the same no longer exert a detrimental effect with respect to further processing of the

petroleum crude oil. Notwithstanding that the total concentration of these metallic contaminants may be relatively small, for example, less than about 10 p.p.m. of metallic porphyrins, calculated as the elemental metals, subsequent processing techniques will be adversely affected thereby. Thus, when a hydrocarbon charge stock, containing metals in excess of about 3.0 p.p.m., is subjected to a cracking process for the purpose of producing lower-boiling components, the metals become deposited upon the catalyst employed, steadily increasing in quantity until the composition of the catalytic composite is changed to the extent that undesirable side effects result. That is to say, the composition of the cracking catalyst is controlled with respect to the nature of the charge stock being processed and to the desired product quality and quantity. This composition is changed considerably due to the deposition of the metallic contaminants thereupon, the changed composite resulting in changed catalytic characteristics. This particular effect is highly undesirable with respect to the cracking process since the deposition of metallic contaminants upon the catalyst also tends to result in a lesser quantity of liquid product, and large amounts of hydrogen and coke, the latter also producing a relatively rapid degree of catalyst deactivation.

In addition to the foregoing contaminating influences, petroleum crude oils and other heavier hydrocarbon fractions contain excessive quantities of pentane-insoluble material. For example, the Wyoming sour crude described above consists of about 8.39% by weight of a pentane-insoluble asphaltenic fraction, a hydrocarbonaceous material considered as a coke-precursor and having the tendency to become immediately deposited within the reaction zone and onto the catalytic composite in the form of a high molecular weight, gummy residue. At the conditions of operation necessary to effect a reasonably efficient, successful process, it is virtually impossible to avoid the conversion of asphaltenic compounds into hydrocarbonaceous coke. Since the deposition of this material constitutes a large loss of charge stock, it is further economically desirable to convert such asphaltenes into useful hydrocarbon oil fractions, thereby increasing the liquid yield of valuable product as based upon the quantity of oil charged to the process. Furthermore, the presence of high-boiling, pentane-insoluble asphaltenes, and excessive quantities of organo-metallic contaminants, tends to interfere with the removal of sulfur and nitrogen, and in particular, the latter.

The object of the present invention is to provide a much more efficient process for hydrorefining heavier hydrocarbonaceous material and particularly pertoleum crude oils containing pentane-insoluble asphaltenes in addition to metallic contaminants, utilizing an unsupported catalyst prepared in a particular manner. The term "hydrorefining" as employed herein, and in the appended claims, connotes the catalytic treatment, in an atmosphere of hydrogen, of a hydrocarbon fraction or distillate for the purpose of eliminating and/or reducing the concentration of the various contaminating influences previously described. As hereinbefore set forth, metals are removed from the charge stock by deposition of the same on the catalyst employed, and asphaltenes are deposited in the form of coke. This increases the amount of catalyst within the reaction zone, actively shields the catalytically active surfaces and centers of the catalyst from the material being processed, and generally precludes the utilization of an efficient fixed-bed system for processing such highly contaminated crude oil. Various moving-bed process, employing catalytically active metals deposited upon a carrier material consisting of silica

and/or alumina, for example, or other refractory inorganic oxide material, such as alumina-zirconia, silica-zirconia, etc., are extremely erosive, causing plant maintenance to become difficult and expensive. The present invention teaches the preparation of a colloidally dispersed, unsupported catalytic material useful in a slurry-type process, which catalytic material will not effect extensive erosion or corrosion of the reaction system. The present process yields a liquid hydrocarbon product which is more adaptable for further processing without experiencing the difficulties otherwise resulting from the presence of the foregoing contaminants. The present invention affords a process which is particularly advantageous for effecting the conversion or organo-metallic compounds without significant product yield loss, while simultaneously converting pentane-insoluble material into pentane-soluble liquid hydrocarbons.

A broad embodiment of the present invention encompasses a hydrorefining catalyst comprising a colloidal suspension of a peroxymolybdate in a hydrocarbon. More specifically, the hydrorefining catalyst of the present invention comprises a colloidal suspension of the reaction product of an oxide of molybdenum and hydrogen peroxide in a hydrocarbon, which suspension consists of from 0.1% to about 10.0% by weight of molybdenum, calculated as the element thereof.

Another broad embodiment of the present invention affords a process for hydrorefining a hydrocarbon charge stock, which process comprises forming the reaction product of an oxide of molybdenum and hydrogen peroxide, combining said reaction product with said hydrocarbon charge stock, distilling the resulting mixture to remove water, thereby forming a colloidal suspension of said reaction product within said charge stock, and thereafter reacting said colloidal suspension with hydrogen at a temperature above about 225° C. and at a pressure greater than about 500 pounds per square inch gauge.

A more limited embodiment of the present invention involves a process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes, which process comprises forming the reaction product of molybdenum trioxide and hydrogen peroxide in a molar ratio of from 1:1 to about 8:1, commingling said reaction product with said charge stock, distilling the resulting mixture to remove water, thereby forming a colloidal suspension of said reaction product in said charge stock, and thereafter reacting said colloidal suspension with hydrogen at a temperature within the range of from about 225° C. to about 500° C. and at a pressure of from about 500 to about 5000 pounds per square inch gauge.

From the foregoing embodiments, it is noted that the present invention involves the preparation of a colloidally dispersed, unsupported catalyst within the hydrocarbonaceous material from which the contaminating influences are to be removed. The catalyst is prepared by initially forming a mixture of an oxide of molybdenum and hydrogen peroxide, adding the resulting reaction product to the material intended for processing. As hereinafter indicated by specific examples, the reaction product is formed from the oxide of molybdenum and a molar ratio of hydrogen peroxide to said oxide of molybdenum within the range of from 1:1 to about 8:1. The molybdenum oxide is employed in an amount such that the colloidal suspension comprises from about 0.1% to about 10.0% by weight of molybdenum, calculated as if the molybdenum component existed in the form of elemental molybdenum. Intermediate concentrations of hydrogen peroxide are preferred, and lie within the range of from about 3:1 to about 6:1.

Briefly, the process is effected, as hereinafter set forth in the specific examples, by initially dissolving the desired quantity of molybdenum trioxide or molybdenum dioxide, or a mixture thereof, in a solution of hydrogen peroxide in a molar ratio as hereinabove stated. The resulting reaction product, a peroxymolybdate, is then intimately commingled with the petroleum crude oil or other heavy hydrocarbon fraction, from which mixture water is removed, for example by heating the mixture, during dropwise addition, at at temperature sufficiently high to remove the same by distillation. That is to say, the water is removed in a continuous manner as the peroxymolybdate is added to the petroleum crude oil, for example, by adding benzene which forms an azeotropic mixture with water and permits the distillation to be effected at a sufficiently low temperature. Other suitable solvents, in addition to benzene, would include various alcohols, esters and ketones and such as isopropyl alcohol, isopentyl alcohol, methyl alcohol, amyl alcohol, methyl ethyl ketone, ethyl acetate, etc. Temperatures below about 310° C., and preferably less than 100° C., are preferred for the purpose of removing the water, leaving the molybdenum component dispersed within the crude oil as a colloidal suspension. The colloidal dispersion is then passed into a suitable reaction zone maintained at a temperature within the range of from about 225° C. to about 500° C. and under a hydrogen pressure within the range of from about 500 to about 5000 pounds per square inch gauge.

Although the exact physical and/or chemical state of the colloidally dispersed particles is not known precisely it is believed that the oxide of molybdenum reacts with the hydrogen peroxide to form a peroxymolybdate which, when added to the petroleum crude oil, in turn forms particles having an unidentified crystalline structure. The hexavalent molybdenum is possibly reduced to a lower valence state, resulting in a form which may be similar to molybdenum blue.

When the colloidal suspension is reacted with hydrogen under the aforementioned conditions of operation, the more readily reducible sulfurous compounds are caused to form hydrogen sulfide which reacts with the catalyst particles to produce a new catalyst state believed to be a form of sulfided molybdenum, although X-ray analysis of the used catalyst indicates a somewhat different crystalline structure. Also, there is some evidence of enhanced catalytic activity when the hydrorefining reactions are initiated in the presence of from 1.0% to about 15.0% by volume of added hydrogen sulfide, particularly in regard to the elimination of virtually all the nitrogeneous compounds. As hereinbefore stated, exceedingly large quantities of asphaltenes and organo-metallic contaminants appear to restrict somewhat the activity of the catalyst with respect to the conversion of nitrogenous compounds.

The process may be conducted in a batch-type procedure, or in an enclosed vessel through which the colloidal suspension is passed; when effected in a continuous manner, the process may be conducted in either upward flow or downward flow. Normally liquid hydrocarbons are separated from the total reaction zone product effluent by any suitable means, for example, through the use of a centrifuge or settling tanks, at least a portion of the resulting catalyst-containing sludge with or without regeneration, being combined with fresh petroleum crude oil, and recycled through the reaction zone. In order to maintain a high degree of catalytic activity, it is preferred that at least a portion of the catalyst-containing sludge be removed from the process prior to combining the remainder with fresh crude oil. The precise quantity of catalyst-containing sludge removed will be dependent upon the desired degree of contaminant removal. However, it is desirable to add a quantity of fresh molybdenum oxide and hydrogen peroxide to the petroleum crude oil to compensate for that quantity removed from the catalyst-containing sludge, maintaining, however, the concentration of the dispersed material within the crude oil from about 0.1% to about 10.0% by weight calculated as elemental molybdenum.

The following examples are given to illustrate the process of the present invention and the effectiveness

thereof in removing nickel and vanadium contaminating influences from a petroleum crude oil, and in converting the pentane-insoluble asphaltenes while simultaneously effecting the conversion of sulfurous and nitrogenous compounds into sulfur and nitrogen-free hydrocarbons. It is not intended that the present invention be unduly limited to the reagents, charge stock and/or operating conditions employed.

The crude oil utilized to illustrate the benefits afforded through the use of the present invention was a Wyoming sour crude oil having a gravity of 23.2° API at 60° F., and containing about 2.8% by weight of sulfur, approximately 2700 p.p.m. of nitrogen, 18 p.p.m. of nickel and 81 p.p.m. of vanadium as metal porphyrins, calculated as the elemental metals. In addition, the sour crude consisted of about 8.39% by weight of pentane-insoluble asphaltenes. As hereinafter indicated, the process of the present invention not only effects conversion of a significant proportion of pentane-insoluble asphaltenes, but also results in a substantial production of lower-boiling hydrocarbons as indicated by an increase in the gravity, ° API at 60° F., of the normally liquid hydrocarbon portion of the total reaction zone product effluent.

Example I

In this example, 5.76 grams of molybdenum trioxide were added to 200 grams of boiling water and heated for 10 minutes. A finely divided slurry of molybdenum trioxide in water resulted, and this slurry was added dropwise to 500 grams of the Wyoming sour crude and 250 grams of benzene, the resulting mixture being continuously distilled during admixing for the purpose of removing water. 200 grams of the resulting colloidal suspension, containing 0.5% by weight of molybdenum, was placed in a rotating autoclave under 100 atmospheres of pressure, the temperature being increased to a level of 400° C., resulting in a final pressure of 200 atomspheres. After eight hours at these conditions, the effluent was subjected to centrifugal separation to provide a catalyst-containing sludge and a normally liquid hydrocarbon product. The normally liquid hydrocarbon product, upon analysis, indicated 1990 p.p.m. of nitrogen, 0.68% by weight of sulfur, 1.48% by weight of pentane-insoluble asphaltenes, 2.0 p.p.m. of nickel and 1.6 p.p.m. of vanadium.

Molybdenum dioxide in an amount of 10.0 grams was added to 200 grams of water and heated to a temperature of about 100° C. The solution was added dropwise to 200 grams of the sour Wyoming crude, accompanied by vigorous stirring with a vibromixer and distillation of water as the solution was added. A total of 227 grams of a colloidal suspension containing 2.37% by weight of molybdenum, calculated as the element was sealed in the rotating autoclave. After eight hours, at a temperature of 400° C. and a hydrogen pressure of 192 atmospheres, the contents were subjected to centrifugal separation to provide a normally liquid product effluent. Analyses indicated a concentration of 2750 p.p.m. of nitrogen, 1.68% by weight of sulfur, 24.8 p.p.m. of nickel, 11.5 p.p.m. of vanadium, a gravity of 25.2° API at 60° F. and 4.58% by weight of pentane-insoluble asphaltenes. This example is presented to show the inadequate results obtained through the use of molybdenum trioxide and molydenum dioxide alone.

When utilized in combination, 2.8% by weight of molybdenum, derived from molybdenum trioxide and molybdenum dioxide added to 200 grams of the sour crude as above, and under the foregoing conditions, offered little improvement, resulting in a normally liquid product effluent having a gravity of 24.9° API at 60° F., and containing 2110 p.p.m. of nitrogen, 1.74% by weight of sulfur, 4.06% by weight of pentane-insoluble asphaltenes, 4.6 p.p.m. of nickel and 4.3 p.p.m. of vanadium.

Example II

Molybdenum dioxide, in an amount of 10 grams, was added to 35 grams of 30.0% by weight solution of hydrogen peroxide, a 4:1 molar ratio of hydrogen peroxide to molybdenum dioxide, and 300 grams of water, the resulting solution being heated at a temperature of 100° C. The solution was added to 250 grams of Wyoming sour crude and 250 grams of benzene, accompanied by stirring with the vibromixer and removal of water by distillation as added. Upon complete addition, the material was subjected to distillation to remove the benzene solvent. 229 grams of charge stock, having a concentration of 3.06% of molybdenum, calculated as elemental molybdenum, were placed in the rotating autoclave and pressured to 10 atmospheres with hydrogen. The autoclave was heated to a temperature of 400° C., the resulting pressure being 200 atmospheres, which conditions were maintained for a period of eight hours. Following centrifugal separation from the sludge, the normally liquid portion of the product effluent indicated a gravity of 34.5° API at 60° F., and contained 0.12% by weight of sulfur, less than 0.03 p.p.m. of nickel, less than 0.07 p.p.m. of vanadium and 618 p.p.m. of nitrogen.

When utilizing hydrogen peroxide in a molar ratio of 6:1 with respect to molybdenum dioxide, the colloidal suspension charged to the autoclave was in an amount of 231 grams, and had a concentration of 3.09% by weight of molybdenum. The normally liquid product effluent recovered following centrifugal separation indicated a gravity of 34.6° API at at 60° F., 0.15% by weight of sulfur, 0.02% by weight of pentane-insoluble asphaltenes, 645 p.p.m. of nitrogen, there being no indication of the continuing presence of nickel and/or vanadium.

When utilizing a colloidal suspension containing 2.42% by weight of molybdeum, having resulted from the reaction product of molybdenum trioxide and a 2:1 molar ratio of hydrogen peroxide, the normally liquid product effluent had a gravity of 33.7° API at 60° F. and contained 0.03 p.p.m. of nickel, 0.1 p.p.m. of vanadium, 0.16% by weight of sulfur, 200 p.p.m. of nitrogen and 0.38% by weight of pentane-insoluble asphaltenes.

This example illustrates the benefits afforded the hydrorefining of petroleum crude oils containing excessive amounts of pentane-insoluble asphaltenes and organometallic contaminants through the utilization of the reaction product of an oxide of molybdenum and a molar ratio of hydrogen peroxide within the range of about 1:1 to about 8:1. Such results are surprisingly unexpected in view of the fact that an effective unsupported hydrogenation catalyst functions to catalyze reduction reactions whereas peroxymolybdates, the reaction product of an oxide of molybdenum and hydrogen peroxide, normally function to catalyze oxidation reactions.

The foregoing examples and specification clearly indicate the method of effecting the process of the present invention and the preparation of the unsupported catalyst employed therein. The petroleum crude oil has been hydrorefined to the extent that it is extremely suitable for further processing; the benefits afforded a process for hydrorefining such petroleum crude oils will be readily recognized by those possessing skill within the art of petroleum refining.

I claim as my invention:

1. A method of catalyst preparation which comprises reacting an oxide of molybdenum and aqueous solution of hydrogen peroxide, adding the resultant reaction product to a hydrocarbon liquid and distilling water from the mixture to form a colloidal suspension of molybdenum compound in said liquid.

2. The method of claim 1 further characterized in that said oxide of molybdenum is molybdenum dioxide.

3. The method of claim 1 further characterized in that said oxide of molybdenum is molybdenum trioxide.

4. The method of claim 1 further characterized in that

the molar ratio of hydrogen peroxide to said oxide of molybdenum is within the range of from about 1:1 to about 8:1.

5. A process of hydrorefining a hydrocarbon charge stock which comprises forming the reaction product of an oxide of molybdenum and hydrogen peroxide, commingling said reaction product with said hydrocarbon charge stock, distilling the resulting mixture to remove water, thereby forming a colloidal suspension of said reaction product within said charge stock and thereafter reacting said colloidal suspension with hydrogen at a temperature above about 225° C. and at a pressure greater than about 500 pounds per square inch gauge.

6. The process of claim 5 further characterized in that said colloidal suspension is reacted with hydrogen at a temperature within the range of from about 225° C. to about 500° C. and at a pressure of from about 500 to about 5000 pounds per square inch gauge.

7. The process of claim 5 further characterized in that said colloidal suspension comprises from about 0.1% to about 10.0% by weight of molybdenum, calculated as the element.

8. The process of claim 5 further characterized in that the molar ratio of hydrogen peroxide to the oxide of molybdenum is within the range of from about 1:1 to about 8:1.

9. A process for hydrorefining a hydrocarbon charge stock which comprises forming the reaction product of molybdenum trioxide and from 1:1 to about 8:1 molar ratio of hydrogen peroxide, commingling said reaction product with said hydrocarbon charge stock, distilling the resulting mixture to remove water, thereby forming a colloidal suspension of said reaction product in said charge stock, and thereafter reacting said colloidal suspension with hydrogen at a temperature within the range of from about 225° C. to about 500° C. and at a pressure of from about 500 to about 5000 pounds per square inch gauge.

10. The process of claim 9 further characterized in that said hydrocarbon charge stock comprises a petroleum crude oil containing pentane-insoluble asphaltenes.

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