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CRUDE OIL HYDROREFINING PROCESS

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The present application is a continuation-in-part of our copending application, Serial Number 207,072, filed July 2, 1962, now abandoned, which copending application is incorporated herein by specific reference thereto.

The present invention relates to a method for preparing a novel catalyst particularly adaptable for utilization in the hydrorefining of petroleum crude oils, heavy vacuum gas oils, heavy cycle stocks, crude oil residuum, topped crude oils, etc. More specifically, the present invention involves a process for hydrorefining petroleum crude oil and other heavy hydrocarbon charge stocks to effect the removal of nitrogen and sulfur therefrom, and affords unexpected advantages in the destructive removal of organo-metallic contaminants and/or the conversion of pentane-insoluble hydrocarbonaceous material.

Petroleum crude oil, and the heavier hydrocarbon fractions and/or distillates obtained therefrom, particularly heavy vacuum gas oils and topped crudes, generally contain nitrogenous and sulfurous compounds in large quantities. In addition, petroleum crude oils contain detrimentally excessive quantities of organo-metallic contaminants which exert deleterious effects upon the catalyst utilized in various processes to which the crude oil, topped crude oil, or heavy hydrocarbon fraction may be ultimately subjected. The more common of such metallic contaminants are nickel and vanadium, often existing in concentrations in excess of 50 p.p.m., although other metals including iron, copper, etc., may be present. These metals exist within the petroleum crude oil in a variety of forms: they may exist as metal oxides or as sulfides, introduced into the crude oil as a form of metallic scale; they may be present in the form of soluble salts of such metals; usually, however, they are present in the form of organo-metallic compounds such as metal porphyrins and 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 at least in part 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 organo-metallic contaminants, including metal porphyrins, crude oils contain greater quantities of sulfurous and nitrogenous compounds than are generally found in lighter 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 approximately 2700 p.p.m. of total nitrogen, calculated as the elements. The nitrogenous and sulfurous compounds are converted, upon being subjected to a catalytic hydrorefining process, into hydrocarbons, ammonia and hydrogen sulfide. However, the reduction in the concentration of the organo-metallic contaminants is not easily achieved, and to the extent that the same no longer exert a detrimental effect, particularly in regard to further processing of the 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 metal porphyrins, calculated as the elemental metals, subsequent processing

techniques will be adversely affected thereby. Thus, when a hydrocarbon charge stock containing metallic contaminants 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 such time as the composition of the catalytic composite is changed to the extent that undesirable results are obtained. That is to say, the composition of the cracking catalyst is closely 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 as a result of the deposition of the metallic contaminants thereupon, the changed composite resulting inherently in changed catalytic characteristics. Such an effect is undesirable with respect to the cracking process, since the deposition of metallic contaminants upon the catalyst results in a lesser quantity of valuable liquid product, as well as large amounts of hydrogen and coke, the latter also resulting in relatively rapid catalyst deactivation.

In addition to the foregoing described contaminating influences, 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 8.3% by weight of pentane-insoluble asphaltenes; these are hydrocarbonaceous compounds considered to be coke-precursors 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. Since this constitutes a large loss of charge stock, it is economically desirable to convert such asphaltenes into useful hydrocarbon oil fractions, thereby increasing the liquid yield of desired product, based upon the quantity of oil charged to the process.

The object of the present invention is to provide a much more efficient process for hydrorefining heavier hydrocarbonaceous material, and particularly petroleum crude oil, utilizing an unsupported catalyst prepared in a particular manner. The term "hydrorefining," as employed herein, 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 hereinabove set forth, metals are generally removed from the charge stock by deposition of the same onto the catalyst employed. This increases the amount of catalyst, actively shields the catalytically active surfaces and centers from the material being processed, and thereby generally precludes the utilization of a fixed-bed catalyst system for processing such contaminated crude oil. Various moving-bed processes, employing catalytically active metals deposited upon a carrier material consisting, for example, of silica and/or alumina, or other refractory inorganic oxide material, 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 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 suitable for further processing without experiencing the difficulties otherwise resulting from the presence of the foregoing contaminants. The process of the present invention is particularly advantageous for effecting the conversion of the organo-metallic contaminants without significant product yield loss, while simultaneously converting pentane-insoluble material into pentane-soluble liquid hydrocarbons.

In copending application, Serial Number 207,072, we have described an unsupported, colloidally dispersed cat-

alytic material particularly adaptable for slurry-type processing of heavy oil fractions. The unsupported catalyst is a decomposed heteropoly acid selected from the metals of Group VI–B of the periodic table having an atomic number greater than 24. We have now found that significantly improved results are afforded when the hydrorefining reactions are effected in the presence of hydrogen sulfide, added prior to initiating any of the hydrorefining reactions.

Therefore, a broad embodiment of the present invention involves a process for hydrorefining a hydrocarbon charge stock, which process comprises admixing said charge stock with at least one heteropoly acid selected from the metals of Group VI–B having an atomic number greater than 24, heating the resulting mixture to decompose said heteropoly acid, reacting the resulting colloidal suspension with hydrogen in the presence of added hydrogen sulfide at a temperature above about 225° C. and at a pressure greater than about 500 pounds per square inch gauge, and recovering a hydrorefined liquid product.

A specific embodiment of the present invention encompasses a process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes, which process comprises admixing said crude oil with phosphomolybdic acid and an alcohol containing less than about eleven carbon atoms, heating the resulting mixture at a temperature below about 310° C. and for a time sufficient to decompose said phosphomolybdic acid and to remove the solvent alcohol, reacting the resulting colloidal suspension with hydrogen in the presence of added hydrogen sulfide 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, and recovering said crude oil substantially free from pentane-insoluble asphaltenes.

From the foregoing embodiments, it is noted that the method of the present invention involves the preparation of a catalyst utilizing metals selected from Group VI–B of the periodic table. Reference is herein made to the Periodic Chart of the Elements, pages 448 and 449, 43rd edition of Handbook of Chemistry and Physics. It is further noted, that the metals from Group VI-B, namely molybdenum and/or tungsten, have an atomic number greater than 24. It has been found that heteropoly acids of chromium, in addition to other chromium complexes, upon decomposition within the hydrocarbon charge stock, do not yield comparable results, and particularly with respect to the conversion of the pentane-insoluble fraction and the organo-metallic compounds including nickel and/or vanadium porphyrins. Furthermore, the decomposition of chromium complexes is effected above about 310° C., resulting in premature cracking of the crude oil. Briefly, the catalyst is preferably prepared by dissolving heteropoly molybdic acids and/or heteropoly tungstic acids, such as phosphomolybdic acid, silicomolybdic acid, phosphotungstic acid, arsenomolybdic acid, and antimonomolybdic acid and silicotungstic acid in an appropriate solvent such as alcohols containing up to and including ten carbon atoms per molecule. The solution is added to the petroleum crude oil and the mixture distilled with stirring, at a temperature less than about 310° C., to remove the solvent and decompose the heteropoly acid, thereby creating a colloidally dispersed catalyst suspended within the petroleum crude oil. The quantity of the heteropoly acid employed is such that the colloidal suspension, or dispersion, which results when the acid is decomposed within the hydrocarbon charge stock, comprises from about 1.0% to about 10.0% by weight, calculated, however, as the elemental metal.

Suitable heteropoly acids, selected from the metals of Group VI–B having an atomic number greater than 24, include phosphomolybdic, phosphotungstic acid, silicomolybdic acid, silicotungstic acid, and mixtures thereof including phosphomolybdic acid-phosphotungstic acid, etc. The process is effected, as hereinafter set forth in specific examples, by initially dissolving the desired quantity of the heteropoly acid, such as phosphomolybdic acid, in the hydrocarbon charge stock. Although the use of the phosphomolybdic acid, as is, in a finely divided state does effect a significant degree of removal of sulfurous compounds, reduces the concentration of the nickel and vanadium porphyrins, and converts approximately 75% of the pentane-insoluble asphaltenes into pentane-soluble hydrocarbons, the concentration of nitrogenous compounds continues to be considerably high, and further treatment would appear to be indicated. However, when phosphomolybdic acid is dissolved in water, prior to the addition thereto of the petroleum crude oil, the concentration of nitrogenous compounds is significantly decreased, in addition to a more effective removal of the other contaminating influences. When the phosphomolybdic acid is initially dissolved in an alcohol containing up to and including about ten carbon atoms per molecule, in ketones, esters, etc., the contaminating influences within the petroleum crude oil are removed to the extent that the future processing of such crude oil no longer involves consideration of the detrimental effects otherwise resulting from the presence of large quantities of the contaminating influences. Typical of the alcohols suitable for use in preparing the solution of the desired heteropoly acid include isopropyl alcohol, isopentyl alcohol, methyl alcohol, amyl alcohol, mixtures thereof, etc. The mixture of the alcohol solution of phosphomolybdic acid and the petroleum crude oil is heated at a temperature below about 310° C. for the purpose of distilling the alcohol, leaving the phosphomolybdic acid as a decomposed colloidal dispersion within the crude oil. Temperatures above about 310° C. tend to result in premature cracking reactions whereby the effectiveness of the process to convert pentane-insoluble asphaltenes becomes adversely affected. The colloidal dispersion is then passed into a suitable reaciton 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 about 500 to about 500 pounds per square inch gauge. The process may be conducted as 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. The normally liquid hydrocarbons are separated from the total reaction zone 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 being combined with fresh petroleum crude oil, and recycled to the reaction zone. In order to maintain the highest possible 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 the catalyst-containing sludge removed from the process will be dependent upon the desired degree of contaminant removal. However, it is further desirable to add a quantity of fresh phosphomolybdic acid to the petroleum crude oil in order to compensate for that quantity of molybdenum, calculated as the elemental metal, removed from the catalyst-containing sludge.

The colloidal dispersion of decomposed phosphomolybdic acid and crude oil is reacted with hydrogen under the operating conditions aforesaid, and in the presence of added hydrogen sulfide. When dispersed in the crude oil, the phosphomolybdic acid, or other heteropoly acid, appears to be reduced to form a crystalline structure as yet unidentified. As such, the catalyst is capable of hydrogenating, and/or hydrocracking, the more easily reduced sulfur compounds in the crude oil, thereby producing hydrogen sulfide. However, when the reactions are initiated in the presence of added hydrogen sulfide a more active form of catalyst is produced im-

mediately, which form of catalyst is capable of the destructive removal of the less easily reduced sulfur compounds. As hereinafter indicated by specific example, the more active form of catalyst is also capable of a greater degree of nitrogenous compound removal, yields a hydrorefined product effluent containing lesser quantities of metallic contaminants and effects the conversion of a greater portion of the pentane-insoluble fraction. Since this more active form of catalyst appears to have the same crystalline structure, also not identified, as the catalyst used in the absence of added hydrogen sulfide, the precise physical and/or chemical change effected therein is not known with accuracy. In a specific example, an atmosphere completely devoid of hydrogen and consisting solely of hydrogen sulfide caused the concentration of sulfurous compounds to increase from 2.8% to 3.4% by weight, while only reducing the nitrogen concentration from 2700 p.p.m. to about 1800 p.p.m. Thus, it may be surmised that the beneficial effects of the added hydrogen sulfide occur only when the latter is present at the time the hydrogenation is being initiated; the hydrogen sulfide is added in an amount of from 1.0 to about 15.0 mol percent.

The following examples are given to illustrate the present invention, and to indicate the effectiveness thereof in hydrorefining a petroleum crude oil to remove the various contaminating influences. It is not intended to limit the present invention to the catalyst, concentrations of material, charge stock and/or conditions of operation.

The crude oil employed to illustrate the benefits afforded through the utilization of the present invention, was a Wyoming sour crude oil having a gravity of 23.2° API at 60° F., 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, computed as the elemental metal. In addition, the sour crude consisted of about 8.3% by weight of pentane-insoluble asphaltenes. As hereinafter indicated, the process of the present invention not only effects the conversion of a significant proportion of the 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 product effluent.

Example I

Phosphomolybdic acid, in an amount of 6.34 grams, as received from the manufacturer thereof, and without further treatment, was added to 200 grams of the Wyoming sour crude. The mixture was placed in an 850 cc. rocker-type autoclave, pressured to 100 atmospheres with hydrogen, and the temperature increased to a level of 400° C., resulting in a pressure of 205 atmospheres. These conditions were maintained for a period of 12 hours, and the normally liquid hydrocarbon portion of the total product effluent, following centrifugal separation, indicated 1790 p.p.m. of nitrogen, 0.86% by weight of sulfur, 2.50% by weight of pentane-insoluble asphaltenes, 6.0 p.p.m. of nickel and 3.0 p.p.m. of vanadium. The normally liquid hydrocarbon portion indicated a gravity, ° API at 60° F., of 29.8.

Sufficient phosphomolybdic acid, to provide 2.4% by weight of molybdenum in admixture with 200 grams of the Wyoming sour crude, was ground to a finely-divided powder and added to the crude. The mixture was distilled to remove the fraction of the crude oil boiling within the normal gasoline boiling range, and thereafter placed within the rocker autoclave at a temperature of 400° C., resulting in a pressure of 191 atmospheres of hydrogen, for a period of about 8 hours. The analysis of the normally liquid hydrocarbon portion of the total product effluent indicated at least partial improvement over the results obtained when the phosphomolybdic acid was employed as received. The concentration of nitrogen remained about the same at 1790 p.p.m., sulfur contamination decreased to 0.77% by weight, 1.87% by weight of pentane-insoluble asphaltenes remained, and the liquid portion contained 1.9 p.p.m. of nickel and 5.4 p.p.m. of vanadium, existing as metallic porphyrins.

Example II

In order to illustrate the substantial improvement resulting when the phosphomolybdic acid is added to the crude oil in solution, a sufficient amount of phosphomolybdic acid (to yield 2.3% molybdenum) was dissolved in 150 grams of isopropyl alcohol. The solution was added dropwise to 100 grams of the Wyoming sour crude, the mixture being heated at a temperature of 120° C., thereby distilling off the alcohol as the solution of phosphomolybdic acid was added. Upon complete addition of the solution, the sample was distilled to remove the normally liquid hydrocarbons boiling within the gasoline boiling range. The colloidal suspension was placed within the rocker autoclave, pressured to 100 atmospheres with hydrogen and heated to a temperature of 400° C., resulting in a pressure of 212 atmospheres. These conditions prevailed for a period of 8 hours. Following a centrifugal separation from the catalyst-containing sludge, the normally liquid hydrocarbon portion of the product effluent indicated 309 p.p.m. of nitrogen, 0.23% by weight of sulfur, 0.09% by weight of pentane-insoluble asphaltenes, 0.03 p.p.m. of nickel and 0.20 p.p.m. of vanadium. The normally liquid hydrocarbon portion also indicated a gravity, ° API at 60° F., of 32.8. It will be noted, notwithstanding the relatively high degree of nitrogenous compounds remaining in the normally liquid portion of the product effluent, that there has been a substantial improvement with respect to the contaminating influence exhibited by sulfur, the asphaltenes, and the nickel and vanadium porphyrins. Furthermore, the increase in gravity, ° API at 60° F., from 23.2 to about 32.8, indicates a significant degree of conversion to lower-boiling hydrocarbon components.

Example III

Phosphomolybdic acid, in an amount of 12.68 grams, was dissolved in 300 grams of isopropyl alcohol over a steam bath. The solution was added to 500 grams of the sour Wyoming crude dropwise and with stirring; the mixture was subjected to distillation, during the dropwise addition of the phosphomolybdic acid solution, to remove the isopropyl alcohol, leaving the phosphomolybdic acid as a finely divided, colloidally dispersed material within the crude oil. Of the resulting colloidal suspension, 100 grams were charged to the rocker autoclave. While at room temperature, the autoclave was pressured to 3.0 atmospheres with hydrogen sulfide, then to 100 atmospheres with hydrogen. The temperature was raised to 400° C., resulting in a pressure of 206 atmospheres, which conditions were maintained for 8 hours. The normally liquid product effluent, having a gravity, ° API at 60° F., of 33.9, following centrifugal separation from the catalyst-containing sludge indicated 232 p.p.m. of nitrogen, 0.32% by weight of sulfur, 0.09% by weight of pentane-insoluble asphaltenes, 0.05 p.p.m. of nickel, the vanadium concentration being 0.06 p.p.m.

When the autoclave was pressured to 6.0 atmospheres of hydrogen sulfide, then to 100 atmospheres with hydrogen, the normally liquid hydrocarbon product effluent indicated 71 p.p.m. of nitrogen, 0.05% by weight of sulfur, 0.05% by weight of pentane-insoluble asphaltenes, less than 0.03 p.p.m. of nickel and less than 0.03 p.p.m. of vanadium, the gravity, ° API at 60° F. being 34.9.

With the autoclave pressured to 12.0 atmospheres with hydrogen sulfide, then to 100 atmospheres with hydrogen, the liquid product effluent had a gravity of 34.0 ° API at 60° F., and contained 113 p.p.m. of nitrogen, 0.05%

by weight of sulfur, 0.04% by weight of pentane-insolubles, 0.06 p.p.m. of nickel and less than 0.06 p.p.m. of vanadium.

This example indicates the improved results obtained when the phosphomolybdic acid is dispersed as an alcohol solution within the petroleum crude oil, and the additional activity imparted to the catalyst as a result of the added hydrogen sulfide.

The foregoing specification and examples indicate the method of the present invention, by which method the hydrorefining of severely contaminated petroleum crude oils is effected. The utilization of heteropoly acids in the presence of added hydrogen sulfide has been shown to result in a liquid hydrocarbon product suitable for further processing without the accompanying detrimental effects otherwise resulting through the presence of the various contaminating influences.

We claim as our invention:

1. A process for hydrorefining a hydrocarbon charge stock which comprises admixing said charge stock with at least one heteropoly acid of a metal of Group VI–B having an atomic number greater than 24, heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said heteropoly acid, reacting the resulting colloidal suspension with hydrogen and added hydrogen sulfide at a temperature above above 225° C. and at a pressure greater than about 500 pounds per square inch gauge, said reaction being initiated in the presence of the added hydrogen sulfide, and recovering a hydrorefined liquid product.

2. The process of claim 1 further characterized in that said colloidal suspension is reacted with hydrogen and hydrogen sulfide at a temperature within the range of from about 225° C. to about 500° C. and under an imposed pressure of from about 500 to about 5000 pounds per square inch gauge.

3. The process of claim 1 further characterized in that said heteropoly acid comprises phosphomolybdic acid.

4. The process of claim 1 further characterized in that said heteropoly acid comprises phosphotungstic acid.

5. A process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes which comprises admixing said crude oil with at least one heteropoly acid of a metal of Group VI–B having an atomic number greater than 24, heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said heteropoly acid, reacting the resulting colloidal suspension with hydrogen and added hydrogen sulfide at a temperature above about 225° C. and at a pressure greater than about 500 pounds per square inch gauge, said reaction being initiated in the presence of the added hydrogen sulfide, and recovering said crude oil substantially free from pentane-insoluble asphaltenes.

6. The process of claim 5 further characterized in that said heteropoly acid comprises phosphomolybdic acid.

7. The process of claim 5 further characterized in that said heteropoly acid comprises phosphotungstic acid.

8. The process of claim 5 further characterized in that said heteropoly acid comprises silicomolybdic acid.

9. The process of claim 5 further characterized in that said heteropoly acid comprises silicotungstic acid.

10. A process for hydrorefining a petroleum crude oil containing pentane-insoluble asphaltenes which comprises admixing said crude oil with phosphomolybdic acid and an alcohol containing less than about eleven carbon atoms, heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to decompose said phosphomolybdic acid, reacting the resulting colloidal suspension with hydrogen and added hydrogen sulfide at a temperature within the range of about 225° C. to about 500° C. and at a pressure of from about 500 to about 5000 pounds per square inch guage, said reaction being initiated in the presence of the added hydrogen sulfide, and recovering said crude oil substantially free from pentane-insoluble asphaltenes.

11. The process of claim 10 further characterized in that said hydrogen sulfide is added in an amount within the range of from about 1.0 to about 15.0 mol percent.

References Cited by the Examiner

UNITED STATES PATENTS

2,554,597 5/1951 Starnes et al. ..... 208—213

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