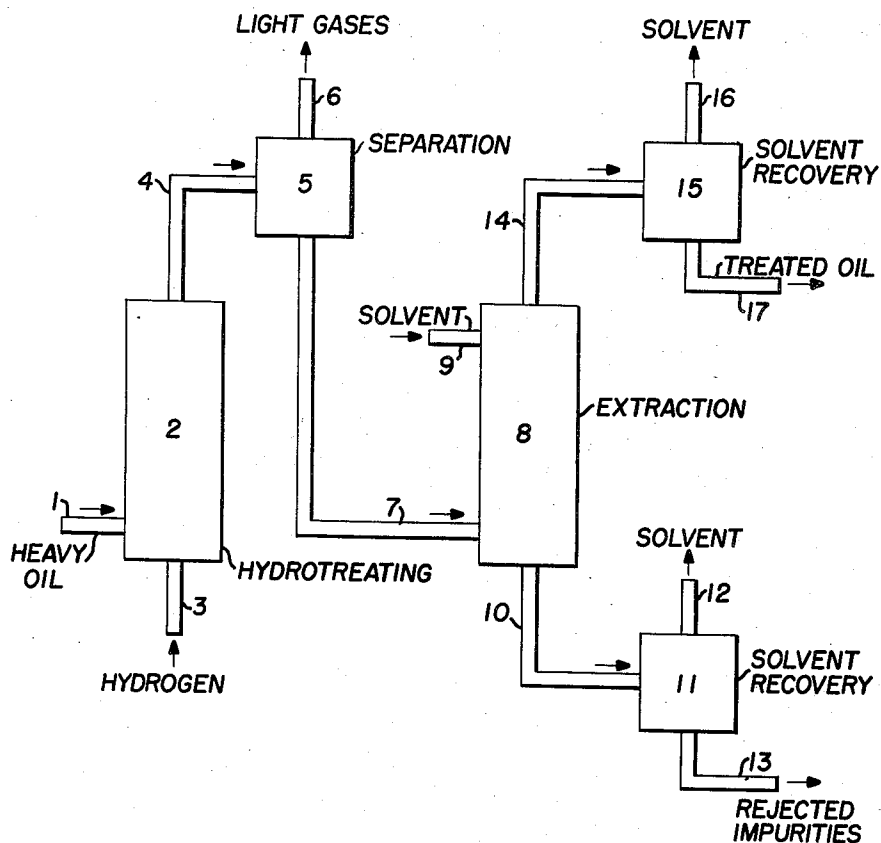


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BY HYDROGENATION FOLLOWED BY
SOLVENT EXTRACTION
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REMOVAL OF METAL CONTAMINANTS FROM HEAVY OILS BY HYDROGENATION FOLLOWED BY SOLVENT EXTRACTION

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The present invention relates to an improved process for the removal of metal contaminants, ash, and other impurities from heavy oils. It is more particularly concerned with an improved two-step process involving hydrotreating and liquid-liquid extraction for removal of contaminants from crude oils and residua to obtain improved fuel oils or cracking feed stocks. For example, vanadium, a source of corrosive ash in bunker fuels, and nickel, a catalyst poison in gas oils, are removed according to this invention.

In brief compass, this invention proposes to remove metal contaminants from a heavy oil by first hydrotreating the oil, and then extracting contaminants therefrom using a selective solvent.

It has been known that extraction processes, e. g., a phenol extraction process, will remove impurities such as metal contaminants and coke formers from heavy oils such as crudes and residua. The extent of removal of impurities, particularly from a crude or residual oil, has not been, however, nearly as effective as desired. Extraction removes only about 10 to 20% of the metal contaminants.

It has now been discovered that there is an unexpected advantage to be gained by first mildly hydrotreating an oil before extraction of contaminants. It has now been found that with a heavy oil, when first hydrotreated and then extracted with a suitable solvent, the extent of metal contaminants removal is far greater than would be expected from previous experience.

The types of metal contaminants present in heavy oils may be classified as those that are volatile and extractable (class I), and those that are non-volatile and non-extractable (class II). It is commonly believed that most of the metal contaminants present in heavy oil are associated with a porphyrin type of molecule or class of compounds (metallo-porphyrins).

Metallo-porphyrins are usually resistant to chemical breakdown and thermal decomposition, and some, e. g., nickel and vanadium, are extremely resistant. The class I contaminants are believed to be of the simple porphyrin class of compounds (monomers) and are readily removed from oils by extraction. Attempts to remove, by extraction, the class II types of metal contaminants, which are believed to be polymers (dimeric or polymeric) of porphyrins have previously been unsuccessful.

The present invention is predicated upon the discovery that during mild or moderate hydrotreating of heavy oils, class II metal contaminants are converted to the extractable class I type. The hydrotreating is not carried out to an extent sufficient to cause appreciable or complete degradation of the class II compounds. While not being limited, of course, to this theory, a possible explanation may be that sulfur linkages account for the polymeric structure of the class II compounds and that during mild hydrogenation of the oil, sulfur is removed thereby destroying the sulfur linkages and leaving an extractable monomer type of metal contaminant.

The present invention, based upon this discovery, comprises relatively mild hydrotreating of a heavy oil followed by liquid-liquid extraction to obtain a surprisingly high degree of metal contaminant removal, besides improving other properties such as lowering the nitrogen, sulfur, MNI and Conradson carbon contents. In some cases the hydrotreating step may be preceded by an additional extraction or asphalt precipitation step.

The following explanation of the drawing attached to and forming a part of this specification will serve to make this invention clear. The drawing schematically depicts a simplified version of this process.

In light of the above explanation, it can be seen that this invention is primarily applicable, and is limited in utility, to heavy oils containing constituents non-vaporizable at atmospheric pressure, such as petroleum crudes, shale oils, tar sands, asphalts, tars, etc., and residua therefrom. Well fractionated distillate oils usually contain only class I metal contaminants which are volatilizable and readily extractable. Most distillate oils, being free of non-vaporizable constituents, do not require, therefore, the presently proposed treatment.

The hydrotreating process as used in the present invention comprises one where the heavy oil is contacted under mild hydrogenation conditions in the presence of a hydrogenation catalyst, preferably a catalyst that is resistant to sulfur contamination. Hydrogenation catalysts such as platinum, palladium, nickel, vanadium, etc. can be used, although cobalt and/or molybdenum are preferred. Mixtures of catalysts may be used, and the catalyst may exist as an oxide or sulfide. Promoters such as fluorine, chlorine, rare earth, etc., can be used.

These catalysts may, of course, be distended on suitable carriers such as natural or synthetic aluminas, silicas, metal hydrides, etc. The catalytic component can be deposited on the carrier in place if desired. For example, V_2O_5 , obtained from the feed oil itself, can be deposited on an alumina base in the reactor and used as a catalyst. The catalysts can be used in the form of fixed, fluid, or gravitating beds, or be used in a suspensoid or slurry type of process. The catalysts can be used on a once-through basis or can be regenerated continuously or intermittently, either within or externally of the unit by burning, hydrotreating, chemical treating, reworking, etc. It is preferred to use a fixed bed type of hydrotreating unit with periodic oxygen regeneration of the catalyst.

With the preferred sulfur resistant catalysts, e. g., a cobalt molybdate catalyst, the range of hydrotreating conditions preferred are:

Pressure	200 to 2000 p. s. i.
Temperature	600 to 950° F.
Space velocity	0.25 to 4.0 v./v./hr.
Hydrogen partial pressure	100 to 2000 p. s. i.

The solvent extraction step involves contacting, preferably countercurrently in a staged unit, the hydrotreated oil with a selective solvent to obtain a raffinate and an extract phase; and recovering solvent for reuse and product from these phases. The contacting may be effected in a plate, packed or positive mechanical mixing tower (e. g., Scheibel tower), or similar units known in the art. The solvent used is one having an affinity for aromatic and nitrogen type compounds and is preferably one that is predominantly selective to the class I type of highly aromatic metal contaminants. Preferred solvents include: butyrolactone, phenol, furfural, pyridine, acetic acid saturated with bromine, and dimethylsulfoxide.

Preferred solvent extraction conditions are:

Temperature	° F. 150 to 300
Oil solvent ratio	1:1 to 4:1

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Conventional extraction aids such as anti-solvents and reflux can, of course, be used.

Referring now to the drawing, a heavy oil to be treated, which may be suitably preheated, is injected by line 1 into a hydrotreating zone 2, which contains a fixed bed of a hydrogenation sulfur resistant catalyst. The catalyst is in the form of particles having a size in the range of 10 to 14 mesh. A free hydrogen containing gas, containing preferably over 50 volume percent hydrogen, is introduced into the base of zone 2 by line 3. The zone is maintained under mild hydrotreating conditions. The conditions are such that any substantial conversion of class II contaminants to free metals is avoided, because this results in rapid deactivation of the catalyst, low yields, and excessive hydrogen consumption. The treated oil is removed by line 4 and passed to a separation zone 5. Some distillate gas oils and naphtha, formed during the hydrotreating, can be removed in zone 5 but as shown, it is simply used to separate light gases, which are removed by line 6. The remainder of the hydrotreated liquid product is passed from separation zone 5 by line 7 to the bottom of a conventional extraction zone 8, which may comprise a tower containing a plurality of vertically spaced perforated plates. A suitable solvent, e. g., phenol, is admitted to the top of the tower by line 9, and flows countercurrently to the oil, extracting metal contaminants and other undesirable constituents. The solvent and impurities are removed from the base of tower 8 by line 10 and sent to a solvent recovery zone 11 which may comprise a distillation or steam stripping zone. Solvent is removed from zone 11 by line 12 for reuse. The impurities rejected from the oil are recovered from zone 11 by line 13 and may be disposed of as desired.

The raffinate from zone 8 is recovered overhead via line 14 and passed to a solvent recovery zone 15, similar to zone 11. Separated solvent is removed for reuse from zone 15 by line 16, and the treated oil is recovered by line 17. Besides having an extremely low metals content, this oil is greatly improved in other respects, i. e., sulfur, nitrogen, Conradson carbon and aromatic contents, etc. have been substantially reduced. This oil product in line 17, depending upon the feed stock, may be used as a fuel oil and will be superior in this respect because of its extremely low ash content. It will make an excellent feedstock for catalytic cracking or lube oil manufacturing processes.

EXAMPLE 1

The following data were collected to demonstrate the surprising results obtained by the present invention. The same feed stock was used for each of the three examples and comprised a residuum from Bachaquero crude having the following inspections:

Initial boiling point.....	1000° F.
Percent on crude.....	31.
Gravity.....	1.9° A. P. I.
Sulfur.....	3.78 wt. percent.
Conradson carbon.....	32 wt. percent.

The hydrotreating of this residuum was carried out with a downflow operation in a fixed bed type of reactor having a volume of about one gallon. The conditions of hydrotreating were: 800° F., one v./v./hr., 1600

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p. s. i. g., 17.1 wt. percent conversion to 1100° F.—on feed, and 3440 s. c. f. of added hydrogen/bbl. The catalyst was 13% CoMoO₄ carried on spray dried alumina, with 5% fluorine added.

The extraction of the oils was carried out on a laboratory bench scale basis in a flask. Five successive batch contacts were made at 150° F. using each time 100 vol. percent (on oil) pyridine and 20 vol. percent water.

Table I

Process	None	Pyridine Extraction Only	After Hydrotreating	After Hydrotreating and Pyridine Extraction
Yield, Wt. Percent.....	100	95	95	90
Metals, p. p. m.:				
Ni.....	136		70	5
V.....	1,188	1,070	501	24
Fe.....			12	10

* Probably mostly insoluble rust.

The above table shows that for the same yield loss in each step, the combination process according to this invention removed 96.6% of the nickel and 98% of the vanadium at a yield of 90%. This is to be compared with the only 10% vanadium removal for extraction alone, and the 58% vanadium removal for hydrotreating alone. From previous experience it is known that hydrotreating or extracting to a yield of 90% does not even approach the extent of removal obtained by the combined steps. Optimum conditions were not maintained by these tests. By slightly altering the hydrotreating and/or extraction conditions, essentially complete metal and ash removal can be accomplished.

Having described this invention and presented specific examples thereof, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A process for improving the quality of heavy oils containing constituents non-vaporizable at atmospheric pressure which comprise mildly catalytically hydrogenating said oil in the presence of hydrogen and a sulfur resistant catalyst at a pressure in the range of 200 to 2000 p. s. i., a temperature in the range of 600° to 950° F., a space velocity of 0.25 to 4.0 v./v./hr. and a hydrogen partial pressure of 100 to 2000 p. s. i. to convert non-volatile and non-extractable polymeric metal contaminants to volatile and extractable monomeric compounds, and treating the hydrogenated product with a solvent selected from the group consisting of butyrolactone, phenol, furfural, pyridine, acetic acid saturated with bromine, and dimethylsulfoxide to remove the extractable monomeric compounds.

2. The process of claim 1 wherein said catalyst is in the form of a fixed bed in a hydrogenation zone, and is periodically oxidatively regenerated.

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