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REMOVAL OF METAL CONTAMINANTS FROM PETROLEUM

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This invention relates to a process for removing metal contaminants from petroleum. More particularly, the invention involves a process for effectively reducing the vanadium, nickel and iron contents of petroleum fractions.

Metal contaminants, particularly vanadium, iron and nickel, are present in almost all crude petroleum in the form of hydrocarbon-soluble metallo-organic complex nitrogen compounds. The concentration of the metal contaminants varies widely with the source of the crude, but is very small, that is, in the order of parts per million. Because of the very small concentration of the metal contaminants, their removal from the crude petroleum or any fraction thereof is extremely difficult.

Attention has been focused on the necessity of removing metal contaminants from petroleum by the almost universal adoption of catalytic cracking for the production of high octane gasoline. The presence of metal contaminants, particularly vanadium, iron and nickel, in cracking charge not only seriously shortens the life of cracking catalysts, but also changes the selectivity of the catalysts with the result that more of the hydrocarbon charge is converted to carbon and to gas. In addition to their harmful action on cracking catalysts when present in cracking charge, metal contaminants present in petroleum fractions also cause pitting and corrosion of turbine blades and fuel oils burners.

Present procedures for removing metal contaminants from petroleum either result in a substantial loss of hydrocarbon or concentrate the metal-containing compounds in a particular fraction. One of the means presently used to free cracking charge of metal contaminants involves distillation of the crude under conditions which prevent entrainment of the high boiling metal-containing nitrogen complexes with the result that the metal contaminants concentrate in the heavy residual fractions. This method does not solve the problem of metal contaminants because the dense concentration of metal contaminants in the heavy residual fractions causes pitting and corrosion of the burners utilizing this fuel.

The process of this invention provides a simple direct procedure for removing metal contaminants from the crude petroleum. In accordance with the process of the invention, crude petroleum or a fraction thereof is contacted with iodine with the resulting conversion of the soluble metal-containing complexes to hydrocarbon-insoluble compounds which are simply removed from the hydrocarbon fraction by conventional means of separating a solid material from a liquid fraction. Filtration is normally utilized to effect the separation of hydrocarbon-insoluble complexes resulting from contact with iodine, but it is possible to effect the separation by centrifugal means or by passage of the hydrocarbon fraction through an adsorbent such as alumina or silica gel.

Contact of a petroleum fraction with iodine under the conditions prescribed in this invention effects a substantial decrease in the concentration of vanadium, nickel and iron which are the principal metal contaminants present in petroleum. Of the three, vanadium is the major offender because it is normally in higher concentration than nickel and iron and because it has a particularly harmful effect on the life and selectivity of cracking catalysts.

A major advantage of the process of this invention for removing metal contaminants from petroleum is that the process effect a decrease in concentration of the metals rather than concentrating the metal contaminants in a particular fraction.

Another major advantage of the process of the invention is that there is substantially no loss of valuable hydrocarbon. The hydrocarbon-insoluble metal-containing compounds are removed from the treated petroleum fraction by filtration. There is no measurable loss of hydrocarbon other than handling losses which are insignificant in commercial installations.

Iodine alone or iodine in a suitable solvent such as acetic acid is employed as the treating agent in the process of the invention. Solvents that may be employed are aliphatic acids such as acetic and propionic acids, aliphatic alcohols such as propyl and ethyl alcohol and halogenated aliphatic compounds such as carbon tetrachloride, tetracholroethane, etc. Acetic acid is one of the preferred solvents because it can be simply removed from the treated hydrocarbon by water washing. In commercial operation, it is expected that iodine alone will be used as the treating agent.

The iodine treating agent should be employed in an amount equivalent to 0.5 to 15 weight per cent of the hydrocarbon to be treated. The preferred concentration of treating agents falls in the lower part of the prescribed range, that is, between 0.5 and 5 weight per cent of the hydrocarbon.

The process of the invention is normally effected in the liquid phase. Vapor phase operation wherein the hydrocarbon fraction in vapor form is contacted with iodine vapors is very effective in converting the hydrocarbon-soluble metal-containing organo nitrogen complexes to hydrocarbon-insoluble metal-containing compounds, but such excellent results are obtained by liquid phase operation, it is normally not necessary to resort to vapor phase operation.

Contact of iodine with the petroleum fraction can be effected during distillation of the crude petroleum. In such type of contact, there would be a mixed vapor-liquid phase contact of the hydrocarbon with iodine with the resulting conversion of the soluble metal-containing complexes into hydrocarbon-insoluble metal-containing compounds. The hydrocarbon-insoluble metal-containing compounds concentrate in the residual fractions from which they are removed by filtration.

Liquid phase contact of iodine with the hydrocarbon fraction is generally effected at a temperature between 100 and 350° F. The process is not critical to the 100 to 350° F. range, but excellent results are obtained within this range. Temperatures above 350° F. are usually not employed in liquid phase operation when the process of the invention is employed as a separate treating operation; the shorter contact times resulting from high temperature contact do not justifiy the the equipment and energy required for maintaining these temperatures.

Atmospheric pressure is normally used for the process of the invention since pressure does not appear to be a critical factor. Sub-atmospheric and super-atmospheric pressures can be employed for the process of the invention so that removal of metal contaminants by iodine treatment can be integrated with other processing operations such as vacuum distillation.

The process of the invention can be applied to crude petroleum or to selected fractions thereof obtained by distillation, solvent refining, propane deasphalting or other

means of petroleum refining. The invention will be illustrated by the treatment of a crude, but selected fractions are similarly treated for the removal of metal contaminants therefrom. Bunker C., lube oil fractions and gas oil cracking stock are examples of selected fractions most widely used in the process of the invention.

The mechanism by which the soluble metal-containing complexes are converted to hydrocarbon-insoluble metal-containing compounds by treatment with iodine is not understood. It is postulated that metals present in petroleum are tied up in complex organic porphyrin compounds in similar fashion to the manner in which iron is part of the hemoglobin molecule and magnesium is part of the chlorophyll molecule. Whatever be the mechanism, contact with iodine converts the soluble metal-containing complex nitrogen compounds into hydrocarbon-insoluble metal- and iodine-containing compounds. The process is specific to iodine inasmuch as chlorine and iodide salts such as potassium iodide, sodium iodide and cuprous iodide are ineffective in removing metal contaminants from hydrocarbon fractions.

The process of the invention is illustrated in the following examples which clearly demonstrate how metal contaminants are simply and effectively removed from petroleum by contact with iodine.

Example I

174 g. of Mara crude, which contained 220 parts per million of vanadium, 15 parts per million of nickel and 5 parts per million of iron, was mixed with 20 g. of iodine and heated to a temperature of 272° F. The mixture of iodine and Mara crude was heated with stirring at this temperature for 30 minutes. After cooling the mixture to room temperature, it was filtered. The treated oil, whose recovery was theoretical, analyzed 17 parts per million of vanadium, 1 part per million of nickel and 0.5 part per million of iron.

Example II

20 g. of iodine was added to 100 cc. of acetic acid and the resulting mixture heated in a steam bath until the iodine was partially dissolved. 217 g. of Mara crude of the same metal content as the crude employed in Example I was combined with the acetic acid-iodine mixture and the resulting composite agitated in a Waring Blendor for 30 minutes. The composite was then filtered and the filtrate water washed to remove acetic acid. The treated crude whose recovery was substantially theoretical contained 9 parts per million of vanadium, 1 part per million of nickel and 1 part per million of iron.

The foregoing examples demonstrate the effectiveness of the process of the invention in removing vanadium, iron and nickel from petroleum. It is noteworthy that single contact of the petroleum with the treating agent results in more than a twenty-fold decrease in vanadium content, more than a fifteen-fold decrease in nickel content and more than a five-fold decrease in iron content in Mara crude which has a particularly high concentration of metal contaminants. The more than twenty-fold decrease in vanadium concentration is particularly significant.

The specificity of the invention was demonstrated by treatment of Mara crude with a mixture of acetic acid and chlorine under conditions similar to those described in Example II; no significant decrease in the vanadium, nickel and iron contents of the Mara crude was effected by contact with the chlorine-acetic acid mixture. In similar fashion, treatment of Mara crude with potassium iodide, sodium iodide and cuprous iodide was ineffective in reducing the concentration of vanadium, nickel and iron in Mara crude.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for treating a heavy petroleum oil selected from the group consisting of crude petroleum, residual fractions thereof, heavy fuel oil fractions, lubricating oil fractions and gas oil fractions, said heavy petroleum oil containing a contaminating amount of oil-soluble metal compounds selected from the group consisting of compounds of vanadium, nickel, iron and mixtures thereof, which comprises contacting said heavy petroleum oil with a treating agent consisting essentially of elemental iodine in non-aqueous form under conditions to convert said oil-soluble metal compounds to oil-insoluble solid metal- and iodine-containing compounds, and separating said oil-insoluble solid compounds from the heavy oil to thereby obtain a treated heavy petroleum oil from which at least the major proportion of said contaminating metal content has been removed.

2. A process according to claim 1 in which an acetic acid solution of iodine is employed as the treating agent.

3. A process according to claim 1 in which contact of said iodine with said hydrocarbon oil is effected between 100 and 350° F.

4. A process according to claim 1 in which separation of said insoluble metal-containing compounds is effected by filtration.

5. A process according to claim 1 in which the hydrocarbon oil is contacted with 0.5 to 15 weight per cent iodine.

6. A process according to claim 1 in which contact of iodine with a hydrocarbon oil is effected in the liquid phase.

7. A process according to claim 1 in which contact of said hydrocarbon oil with iodine is effected during distillation of a crude petroleum fraction with the resulting concentration of hydrocarbon-insoluble metal-containing compounds in the distillation residue.

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