

[72] Inventors **Robert W. Rieve**
Springfield;
Harold Shalit, Drexel Hill; John J.
Rothrock, Ambler, all of Pa.
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[73] Assignee **Atlantic Richfield Company**
New York, N.Y.

[54] **METALS REMOVAL FROM HEAVY**
HYDROCARBON FRACTIONS
19 Claims, No Drawings

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Primary Examiner—Delbert E. Gantz
Assistant Examiner—J. M. Nelson
Attorneys—Robert R. Cochran and Charles R. Wetter

ABSTRACT: The use of alkali or alkaline earth metals with amines or ammonia to reduce the level of metal contamination of heavy hydrocarbon fractions boiling above about 900° F. such as, tars, residua, and asphaltenes.

METALS REMOVAL FROM HEAVY HYDROCARBON FRACTIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates broadly to the removal of metal-comprising contaminants from hydrocarbons. The invention is applicable to the treatment of heavy hydrocarbon fractions derived from crude petroleum oil, oil shale, coal tar, and tar sands so as to improve substantially the characteristics of the hydrocarbon fraction. The invention is particularly directed to the addition of alkali or alkaline earth metals to a solution or stirrable mixture of heavy hydrocarbon fractions, i.e. those boiling above about 900° F. and amines or ammonia to facilitate removal of nickel, vanadium, iron, an other metal contaminants which are naturally occurring in the hydrocarbons.

2. Description of the Prior Art

Metallic contaminants naturally occur in hydrocarbons and it is known that these contaminants are concentrated in the heavy fractions of the oils in the form of metal complexes including nickel, iron and vanadium porphyrins. These contaminants are difficult to remove by ordinary distillation procedures as they tend to vaporize at temperatures of the order of 1,050° F. Various methods of removing these metal contaminants have been tried including, (1) the contacting of the heavy fractions with a quantity of pulverized contact clay; (2) washing the contaminated hydrocarbons in either hydantoin or alkyl substituted hydantoin; (3) the use of butyrolactone as a washing agent; and (4) subjecting of the hydrocarbons to a direct current electrical field of high voltage. Additionally various wash oils, comprising deasphalting solvents which are described as metal-free synthetic asphalts, have also been used for treating metal-contaminated heavy hydrocarbon fractions. While all of the above-listed methods have had some limited success in removal of the metal contaminants from asphalts, residua and tars, they have been found impractical for economical large-scale commercial operation, mainly because of large yield losses owing to recovery of treated products and reagents.

SUMMARY OF THE INVENTION

In view of the above discussion, it is an object of this invention to provide an economical method of removing metallic contaminants from heavy hydrocarbon fractions, such as those found in petroleum oils, oil shale, coal tar and tar sands, suitable for large-scale operations wherein a high yield of treated product can be obtained.

It is a further object to remove metals from heavy hydrocarbon fractions that tend to react with and deactivate catalytic cracking catalysts.

Another objective is to upgrade the value of heavy hydrocarbon fractions for use as a fuel.

These and other objectives may be achieved through practice of the present invention.

We have discovered that the heavy fraction of petroleum oils and other carbonaceous materials (those having a boiling point of above 900° F.) can be upgraded by removal of the metal contaminants naturally found therein by mixing said fraction with sufficient amine or ammonia to form a solution or stirrable slurry and then adding an alkali or alkaline earth metal to the solution or slurry. This tends to release the contaminant metals in the heavy fraction so that water washing will remove substantial amounts of these contaminants with little or no loss of the hydrocarbon fraction.

All of the alkali or alkaline earth metals are suitable for the practice of this invention. They may be used alone or in combination with each other. The metals preferred for use in our invention include lithium, sodium, calcium, and magnesium, while sodium is the most preferred.

The amines suitable for use in our invention include all of the primary and secondary aliphatic mono- and di-amines including ethylamine, isomylamine, n-hexylamine, cetylamine,

dimethylamine, diisobutylamine, methylethylamine, ethylenediamine, putrescine, and hexamethylenediamine. Those mono- and di-amines having more than 16 carbon atoms are not readily available in the pure form, therefore, their use is not considered practical at this time. The tertiary amines are not suitable for this invention as they do not have an available hydrogen on the amine nitrogen to react with the active alkali or alkaline earth metals. Ammonia with its readily available hydrogen is quite satisfactory when used in suitable equipment such that it can be maintained in a liquid state up to its critical temperature and pressure.

The diamines having two amine nitrogens with their available hydrogen are preferred. Additionally the higher boiling point of the diamines with respect to their corresponding monoamines allows operation in liquid phase at higher temperatures. We prefer using ethylenediamine as its availability and boiling point are advantageous in practicing the invention.

The heavy hydrocarbon fraction and amine can be mixed in any proportion that will produce a stirrable slurry or a solution at reaction temperature. Stirrability is necessary to ensure contacting between the mixture and the active metal to be added later. Larger amounts of the amine are not harmful as it can be easily recovered from the reaction zone and recycled as will be explained later. It is only necessary that there be a molar excess of the amine group with respect to the alkali or alkaline earth metal to be added to the solution or slurry.

Into the heavy hydrocarbon fraction-amine solution or slurry can be added the active alkaline or alkali earth metal. Contacting can be insured by any suitable means such as constant stirring within the reaction vessel. The alkali or alkaline earth metal can be added to the solution in such amounts that 0.05 to 75 parts by weight of the metal are present per 100 parts by weight of the heavy fraction in the solution. It is preferred that the active metal to solution weight ratio be between 0.1 and 25 parts metal per 100 parts heavy fraction.

While not wishing to be bound by any theories of operation, it is believed the active metal reacts with the amine in such a way as to release hydrogen and electrons. The additional amine in the solution serves as the solvent and provides an improved contacting medium in which the active ingredients may contact the heavy hydrocarbon fraction. The freed hydrogen and electrons attack the metal-organic bonds of the heavy hydrocarbon fraction releasing the metal contaminants from suspension therein and the metals tend to become suspended or dissolved in the amine-hydrocarbon mixture in a water-soluble form. Additionally, some of the hydrogen released in the reaction between the metal and amine tend to combine with the heavy fraction and upgrade it by decreasing the carbon percentage therein as a result of hydrogen addition.

Treatment of the heavy fraction can take place over a wide range of temperatures, however, the temperature should preferably be at or below the boiling point of the amine. Solvent vapors may be contained by refluxing or superatmospheric pressures. When ethylenediamine is used we have found that satisfactory results can be obtained when the temperature is maintained between 80° and 100° C. Using this amine we prefer to maintain the temperature between 90° and 105° C. Although treatment may take place at any pressure, we prefer to practice the invention at below 10 atmosphere pressure in order to simplify the equipment needed. Very good results have been obtained when practicing this invention at atmospheric pressure.

Separation of the modified contaminants from the treated oil can be carried out by quenching the reaction with water and then filtering, centrifuging, or settling or by any combination of these methods. A combination of settling and water washing has been found to be particularly effective and is therefore preferred.

In order to better understand the teachings of this invention, the following specific example is offered as one embodiment. It is not intended to limit the scope of the disclosure in any way.

A 2-gram portion of a 7-percent bottoms fraction of asphaltene was placed in a reaction chamber. The asphaltene was obtained by washing the tar residue of petroleum refining with isopentane until only 7 percent of the residue remained. This entire residue had an initial boiling point of over 1,000° F. and the asphaltene had a boiling range above 1,050° F. Analysis of the asphaltene indicated that it contained 796 p.p.m. iron, 73 p.p.m. nickel and 40 p.p.m. vanadium. Ten cubic centimeters of ethylenediamine were added and the mixture was heated to 100° C. and stirred to obtain a solution. Then 0.2 gram of sodium ribbon was added to the reaction chamber and stirring was continued for 2 hours while maintaining the temperature at 100° C. The product was water washed with five volumes of water with respect to the solution volume to remove the metal contaminants and the heavy petroleum fraction was dried using moderate heat and vacuum removal of moisture and then analyzed. It was found that 77 percent of the iron, 49 percent of the nickel and 85 percent of the vanadium had been removed using this process. Essentially no loss of the hydrocarbon was incurred.

Other active metals including calcium, magnesium, and lithium were used in the above process and considerable amounts of metal contaminants were removed. By varying the weight ratio of the active metal to the heavy hydrocarbon fraction to be upgraded it was found that some selectivity in the metals removed could be obtained. Essentially all of the hydrocarbon was recovered under all conditions. One could select the active metal and the metal to solution ratio depending upon the further use intended for the upgraded heavy hydrocarbon fraction.

Table 1 gives some results obtained using the above-described procedure on asphaltenes. It can be seen that when using sodium and allowing the reaction to continue for 66 hours, 100 percent of the vanadium and about 96 percent of the iron can be removed from a heavy fraction thereby upgrading the fraction for further processing. It may also be seen that considerable amounts of the metals can be removed by allowing the reaction to continue for as little as 2 hours.

A 2-gram sample of 7-percent bottoms fraction of asphaltene was used in each run at atmospheric pressure. Sufficient ethylenediamine to form a solution at reaction temperature was added. Preliminary analysis of the asphaltene indicated the presence of 796 p.p.m. Fe, 73 p.p.m. Ni, and 40 p.p.m. V. All runs were maintained at 100° C. except No. 6 which was maintained at 80° C.

TABLE 1

CONTAMINANT METALS REMOVAL FROM ASPHALTENES

Run	Metal Used	Grams Metal	Reaction Time, hrs.	Metals Removed		
				%Fe	%Ni	%V
1	Na	1.0	66	96	47	100
2	Na	0.93	2	86	40	90
3	Na	0.38	2	76	72	85
4	Na	0.2	2	77	49	85
5	Na	0.036	50	93.5	91	72
6	Li	0.1	2	57	30	12
7	Ca	1.5	23	58	9	36
8	Mg	0.2	10	66	27	82

Table 2 depicts results obtained when sodium was added to a solution of vacuum flashed tars in ethylenediamine. The tar had an initial boiling point of 1,000° F. The procedures were the same as described above. Preliminary analysis of the tar indicated the presence of 356 p.p.m. Fe, 50 p.p.m. Ni, and 56 p.p.m. V. It can be seen from the percent of the contaminants removed that the tars can be considerably upgraded by practicing this invention. A 2-gram sample of tar was used in each run. Reaction temperature was maintained at 100° C.

TABLE 2

METAL CONTAMINANTS REMOVAL FROM TARS

Run	Grams Na	Reaction Time, hrs.	Metals Removed		
			%Ni	%Fe	%V
21	0.047	67	60	74	41
22	0.233	40	65	61	53
23	0.461	65	85	100	71

We claim:

1. A process for removing nickel, vanadium and iron contaminants from a hydrocarbon fraction having a boiling point above 900° F., which consists essentially of the steps of:

placing said fraction into a reaction zone;

adding a solvent selected from the group consisting of liquified ammonia, primary and secondary aliphatic mono amines, and primary and secondary aliphatic diamines, said amines having up to 16 carbon atoms therein, in an amount to produce a stirrable slurry or solution;

adding a metal selected from the group consisting of alkali or alkaline earth metals in an amount ranging from 0.05 -75 parts metal per 100 parts per hydrocarbon on a weight basis; and

removing the metal contaminants by water washing.

2. The process of claim 1 wherein the amount of alkali or alkaline earth metal added ranges between 0.1 to 25 parts metal per 100 parts hydrocarbon on a weight basis.

3. The process of claim 1 wherein the solvent is added in an amount to produce a solution.

4. The process of claim 3 wherein the solvent is liquified ammonia.

5. The process of claim 3 wherein the solvent is a primary or secondary aliphatic diamine.

6. The process of claim 5 wherein the diamine added to the petroleum fraction is ethylenediamine and the reaction zone is maintained at 80° to 110° C.

7. The process of claim 3 wherein the metal additive is selected from the group consisting of lithium, calcium, sodium and magnesium.

8. The process of claim 7 wherein the metal additive is sodium.

9. The process of claim 3 wherein the solvent is ethylenediamine and the metal is sodium and the reaction is allowed to take place at atmospheric pressure at 100° C.

10. The process of claim 1 wherein the solvent is added in an amount to produce a stirrable slurry.

11. The process of claim 10 wherein the solvent is liquefied ammonia.

12. The process of claim 10 wherein the solvent is a primary or secondary aliphatic diamine.

13. The process of claim 12 wherein the diamine added to the petroleum oil fraction is ethylenediamine and the reaction zone is maintained at 80° to 110° C.

14. The process of claim 10 wherein the metal additive is selected from the group consisting of lithium, calcium, sodium and magnesium.

15. The process of claim 14 wherein the metal additive is sodium.

16. The process of claim 10 wherein the solvent is ethylenediamine and the metal is sodium and the reaction is allowed to take place at atmospheric pressure at 100° C.

17. The process of claim 1 including the step of drying the product to remove all water used in the water washing.

18. The process of claim 1 wherein the solvent is removed by fractional distillation.

19. The process of claim 1 using ethylenediamine as the solvent, sodium as the metal, and wherein the reaction zone is maintained at atmospheric pressure and between 95° to 105° C. including the steps of:

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removing the solvent by fractional distillation, and
drying the product to remove all water used in the water
washing.

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