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## PROCESS FOR REMOVING HEAVY METALS FROM PETROLEUM WITH AN OIL-INSOLUBLE SULFONIC ACID

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This invention relates to a process for removing heavy metal contaminants from petroleum. More particularly, the invention involves a process for effectively reducing the vanadium and nickel contents of heavy hydrocarbons such as crude petroleum and its residual fractions.

Metal contaminants, particularly vanadium 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 stock 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 residual stock 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 and nickel in the cracking hydrocarbon charge stock obtained from crude or residual petroleum fractions 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 the cracking charge, metal contaminants present in residual oils cause pitting corrosion of turbine blades and fuel oil 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 charges of metal contaminants involves distillation of the fraction or its source material under conditions which prevent entrainment of the high boiling metal-containing nitrogen complexes with the result that the metal contaminants concentrate in the residual fractions and cause pitting and corrosion of burners when the latter are utilized as fuel.

It has now been found that heavy metals such as nickel and/or vanadium contaminants can be removed from petroleum crude or residual fractions thereof by treatment in the liquid phase with oil-insoluble aromatic sulfonic acids which are liquids at the treating temperature. These sulfonic acids are usually of benzenoid hydrocarbons containing one or more lower alkyl or lower cycloalkyl radicals. Representative sulfonic acids are those of mixed meta and xylenes, toluene, an aromatic reformat fraction in the C<sub>8</sub> to C<sub>10</sub> range, etc. or mixtures thereof. The aromatic hydrocarbon which is used to provide the sulfonic acid is preferably in the gasoline boiling range and is frequently composed predominantly of methyl and ethyl-substituted benzenes. Some of our metal contaminated hydrocarbon charge stocks may contain water, say up to about 5% so we prefer to employ water-soluble sulfonic acids that will

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not precipitate as solids in the presence of the contaminating water. It is also preferred to employ the anhydrous form of sulfonic acids although sulfonic acids having up to about 10% by weight of water have been successfully used. We have observed essentially no chemical reaction between the sulfonic acid and the hydrocarbon treated. Also in addition to obtaining demetalization by our process there is evidence that desalting, denitrating and possibly desulfurization of the hydrocarbon are effected and the treated material or a distillate therefrom exhibits less carbon-forming tendencies when subsequently cracked.

In accordance with the present invention a crude petroleum or residual fraction thereof containing contaminating amounts of nickel and vanadium is intimately contacted with the sulfonic acid in amounts sufficient to remove a substantial portion of the nickel and vanadium contaminants at a temperature up to about 150° F. for instance, within the range of about 50 to 150° F. Temperatures materially above about 150° are not desirable since loss of the sulfonic acids results through reaction with the feedstock. Room or ambient temperatures are normally used and produce satisfactory results. The sulfonic acid-feedstock mixture can then be allowed to settle into two immiscible phases, a feedstock raffinate layer and a precipitate layer. After settling is complete, the demetallized feedstock raffinate layer can be decanted from the precipitated sulfonic acid phase.

The amount of the sulfonic acid of the present invention contacted with the feedstock is that sufficient to remove a substantial portion of the nickel and vanadium contaminants contained in the feedstock and the amount exceeds the portion which might be compatible with the hydrocarbon treated. Generally, amounts ranging from about 1 to 30 or more, preferably about 5 to 15, weight percent based on the contaminated hydrocarbon feedstock are employed and have been found sufficient. Similarly the contact and settling times may be varied over a considerable range. A contact time of about one-half hour has been found sufficient and settling has been found substantially complete after about 24 hours.

The process of the invention can be applied to crude petroleum or to residual fractions thereof which frequently contain up to about 1000 p.p.m. of contaminating metals. Representative stocks are, for example, crude petroleum (25–100 p.p.m.), atmospheric tower bottoms (75–200 p.p.m.), vacuum tower bottoms (500–1000 p.p.m.), oil from deoiling vacuum tower bottoms or from deasphalting vacuum tower bottoms (2–400 p.p.m.), hydrocracked residuals and thermally cracked residuals. Because of difficulties presented in the handling of many of the feedstocks to which the present invention is applicable, it has been found advantageous to dilute these feedstocks with a suitable hydrocarbon solvent, for instance, an aliphatic hydrocarbon of about 3 to 7 carbon atoms. Frequently, the solvent volume is about 0.1 to 10 or more times that of the contaminated hydrocarbon. Crude petroleum on the other hand, presents no handling problems and therefore needs no dilution.

The process of the present invention will be further illustrated by the following examples but they are not to be considered limiting.

### EXAMPLE I

1500 ml. of Kuwait crude petroleum containing 20 p.p.m. of NiO and 46 p.p.m. of V<sub>2</sub>O<sub>5</sub> was charged to a 2-liter flask equipped with a stirrer. Stirring was started and 60 grams of liquid, mixed xylene and ethyl benzene sulfonic acids (11% para, 49% meta, 16% ortho, 24% C<sub>6</sub>H<sub>5</sub>·C<sub>2</sub>H<sub>5</sub>) were added. Stirring was con-



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tinued for one-half hour and the mixture was allowed to settle. Settling was substantially complete in about 24 hours and resulted in the formation of a precipitate layer and a raffinate layer. The raffinate was decanted from the precipitate layer, washed with water and analyzed for NiO and V<sub>2</sub>O<sub>5</sub> content. The approximate volume of raffinate obtained from the decanting was 1100 ml. The raffinate was again treated with the same amount of the xylene sulfonic acids and the raffinate of the second treatment similarly analyzed for NiO and V<sub>2</sub>O<sub>5</sub> content. The above experiment was repeated using toluene sulfonic acid. The results of the raffinate analyses are shown in Table I.

Table I

Raffinate Analysis	NiO (p.p.m.)	V <sub>2</sub> O <sub>5</sub> (p.p.m.)
1st Extraction:		
xylene sulfonic acid .....	2.5	12
toluene sulfonic acid .....	1	3.8
2nd Extraction:		
xylene sulfonic acid .....	1.1	1.8
toluene sulfonic acid .....	0.43	0.61
Feed .....	20	46

EXAMPLE II

An atmospheric tower bottoms having a carbon residue of 7.46 and containing 49 p.p.m. of NiO and 100 p.p.m. of V<sub>2</sub>O<sub>5</sub> was charged to each of six 2-liter flask equipped with a stirrer. Stirring was started and amounts ranging from 2 to 6.7 weight percent of mixed xylene sulfonic acids were added immediately followed by various volumes of pentane. Stirring was continued for one-half hour and the mixture was allowed to settle two days. At the end of the settling period the solvent-crude mixture was decanted from the precipitate layer. The precipitate was weighed and then the dissolved pentane was removed under vacuum at room temperature to a constant weight. The pentane-free precipitate was dissolved in benzene and the solution washed with four portions of water. The water washes were titrated with sodium hydroxide solution to determine the percent xylene sulfonic acids in the precipitate. The water washed benzene solution was evaporated down on a hot plate to a terminal temperature of 320° F. The residue was then submitted for percent pentane soluble. The crude pentane solution decanted from the sulfonic acid-precipitate layer was washed with proportions of water which were also titrated to give the acid content of the crude layer. The washed pentane solution was evaporated down on a hot plate to a terminal temperature at 320° F. The residue was then analyzed for metal and carbon residue. The results obtained from these experiments are tabulated in Table II.

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Table II

Experiment	1	2	3	4	5	6
5 Ratio by volume pentane/ATB.	.5	1.5	1.5	3	3	3
Wt. percent xylene sulfonic acid on ATB .....	4	2	6.7	2	4	6
Extract Layer:						
Wt. percent yield on ATB <sup>a</sup> ..	21.7	17.9	21.4	12.2	13.6	16.7
Wt. percent pentane <sup>b</sup> .....	13.3	40.2	26.4	44.2	30.5	34.2
Wt. percent xylene sulfonic acid <sup>b</sup> .....	5.7	1.2	11.7	3.5	8.5	11.7
Percent Pentane soluble <sup>c</sup> ..	71	73	58	50	45	51
Raffinate layer:						
Wt. percent pentane .....	27	52	53	69	69	69
Wt. percent xylene sulfonic acid .....	1.1	0.37	0.72	0.25	0.37	0.40
Wt. percent carbon residue <sup>d</sup> ..	5.66	6.12	4.06	5.14	4.43	3.88
p.p.m. NiO <sup>e</sup> .....	17.2	23	13	20	16	12
p.p.m. V <sub>2</sub> O <sub>5</sub> <sup>e</sup> .....	64	96	31	88	58	32
20						
25						
30						
35						
40						
45						
50						

<sup>a</sup> Calculated on a pentane and xylene sulfonic acid free basis.  
<sup>b</sup> Percent based on total precipitate weight.  
<sup>c</sup> Determined on xylene sulfonic acid and pentane-free residue.  
<sup>d</sup> Determined by Conradson method on xylene sulfonic acid and pentane free oil.  
<sup>e</sup> Determined on xylene sulfonic acid and pentane free oil:  
ATB—carbon residue .....

7.46  
p.p.m. NiO .....

49  
p.p.m. V<sub>2</sub>O<sub>5</sub> .....

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Examination of the data clearly demonstrates the effectiveness of the process of the present invention in removing vanadium and nickel contaminants from crude petroleum and reduced crudes.

We claim:

1. In a process for demetallizing a heavy metal containing heavy hydrocarbon, the steps comprising contacting said hydrocarbon with a liquid, oil-insoluble aromatic sulfonic acid at a temperature of up to about 150° F. in an amount sufficient to reduce the heavy metals content of said hydrocarbon and separating a hydrocarbon phase reduced in heavy metal content from a sulfonic acid phase.

2. In a process for demetallizing a petroleum hydrocarbon containing nickel and vanadium and selected from the group consisting of crude petroleum and its residual fractions, the steps comprising intimately contacting said hydrocarbon with a liquid, oil-insoluble, water-soluble benzenoid sulfonic acid at a temperature of up to about 150° F. in an amount of about 1 to 30% based on said hydrocarbon, setting the contacted mixture, and separating a hydrocarbon phase reduced in nickel and vanadium contents from a sulfonic acid phase.

3. The method of claim 2 in which the sulfonic acid is a mixture of ortho, meta, para, xylene and ethylbenzene sulfonic acids.

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