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REMOVAL OF METALS FROM PETROLEUM FRACTIONS

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This invention relates to the removal of metals, particularly vanadium and/or nickel, from petroleum fractions.

It is well known that many crude oils contain compounds of metals, for example iron, nickel and vanadium. The compounds occur in the fractions of crude oils boiling above 250° C. and, in the fractions recoverable by distillation at normal or reduced pressure, it is believed that the compounds are largely metalloporphyrins.

It is also well known that the presence of these metal compounds may be disadvantageous. When heavy fuels containing metal compounds are used as turbine fuels, fouling of the turbine blades occurs for example, and in the catalytic cracking or hydrocatalytic treatment of heavy fractions, deposition of the metal compounds on the catalysts contributes to loss of catalytic activity when the catalysts are regenerated. Various proposals have been made, therefore, for the removal of these metal compounds, for example by hydrocatalytic treatment or solvent extraction.

According to the present invention a process for reducing the metal content of petroleum fractions boiling above 250° C. comprises contacting a petroleum feedstock having at least a proportion of metal-containing material boiling above 250° C. with active Raney nickel, active Raney iron or active Raney cobalt and recovering a product of reduced metal content.

Raney metals are well known and are generally prepared by forming an alloy of the metal with aluminium and dissolving out the aluminium with sodium hydroxide with the simultaneous formation of nascent hydrogen. After washing to remove the hydroxide the resultant active metal is porous and contains a considerable amount of occluded hydrogen.

The present process is suitable for the removal of metal compounds, particularly metalloporphyrins, from petroleum fractions boiling above 250° C., including both distillate petroleum fractions and residues. Examples of metal compounds which can be removed are vanadium and nickel compounds, particularly vanadyl and nickel porphyrins.

The preferred Raney metal is Raney nickel which is particularly suitable for the removal of vanadium compounds, for example vanadyl porphyrins, from petroleum fractions.

Reduction in the metal content of the petroleum fraction by contact with a Raney metal occurs readily at ambient temperatures of 0–25° C. although elevated temperatures of up to 250° C. may be used if desired. The pressure is conveniently atmospheric and the petroleum feedstock is preferably in the liquid phase.

The ratio of Raney metal to the petroleum fraction and the contact time will depend on the amount of metal compounds in the fraction, their nature and the degree of

removal required, and may be determined by simple experiment.

Generally, suitable ratios of Raney metal to petroleum fraction will be from 1:1 to 100:1 with contact times of 10 minutes to 100 hours. Substantial removal of metalloporphyrins has been obtained with ratios of petroleum fraction to Raney metal of from 5:1 to 60:1 and contact times of 24 to 64 hours.

The method of contacting may be any of those normally used for liquid-solid contacting. For example the metal may be added and mixed with the feedstock or the feedstock may be passed through a bed of the metal. The metal is conveniently in particulate form.

The petroleum fraction may if desired be dissolved in a lower boiling hydrocarbon solvent, for example benzene.

The contacting may also be carried out in the presence of other metal-free lower-boiling petroleum fractions. Thus, for example, a total crude oil may be contacted including the lower-boiling fraction.

In addition to the removal of metal compounds, the process of the present invention may also substantially reduce the sulphur and nitrogen contents of petroleum feedstocks.

The metal compounds may be recovered from the Raney metal by deactivating it. One suitable method of doing this is to contact the metal, preferably at elevated temperature, with a solvent for the metal compounds. Examples of suitable solvents are hydrocarbons, e.g. petroleum hydrocarbons boiling below 250° C. Compounds known to be solvents for extracting metal compounds from heavy petroleum fractions may also be used, for example phenol, furfural, pyridine or butyrolactone. Another suitable method is to deactivate the Raney metal by the addition of a deactivating compound, for example an unsaturated or sulphur-containing organic compound or an alkyl hydroperoxide, such as tertiary butyl hydroperoxide. The Raney metal can also be dissolved in acid and the metal compounds recovered from the solution by extraction with a suitable solvent. Metalloporphyrins can be recovered unchanged in these ways.

The invention is illustrated by the following examples.

EXAMPLE 1

3 mg. of vanadyl etioporphyrin I were dissolved in 133 ml. of benzene and 67 ml. of ethyl alcohol at room temperature. The solution had the characteristic dark red colouration shown by dissolved vanadyl porphyrins. 78 g. of granular active Raney nickel was added and the mixture was shaken by hand. The red colouration disappeared rapidly indicating that the vanadyl porphyrin had been totally adsorbed.

The mixture was then heated under reflux for an extended period. After 8 hours the liquid had a pink colouration indicating that the vanadyl prophyrin was beginning to be desorbed and redissolved in the solvent. After 480 hours the colouration had returned to dark red. The solution was then separated from the Raney nickel and examined spectroscopically. 1.27 mg. of the vanadyl etioporphyrin I were present in the solution, a recovery of 42.3% wt.

EXAMPLE 2

A vanadium containing crude oil was distilled to remove material boiling below 260° C. Portions of this stabilised crude oil were dissolved in 115 ml. of benzene.

Active Raney nickel was separated from the ethyl alcohol in which it was stored by centrifuging and rinsed into the crude oil-benzene solutions with ethyl alcohol. The mixtures were heated under reflux on steam baths. After the heating the mixtures were filtered. The separated Raney nickel was washed with benzene and chloroform till the washings were colourless. The washings were added to the separated solutions and the solvents removed by distillation at 100° C. and 20 mm. pressure. The ratio of Raney nickel to stabilised crude oil and the metalloporphyrin and sulphur contents of the treated stabilised crude oil are given in Table 1 below.

Table 1

		Sulphur, percent wt.	Metallo-porphyrins (p.p.m.)
Stabilised crude oil		5.5	3,420
Ratio of Raney nickel to oil	Time of heating (hours)		
5:1	24	2.58	2,680
28:1	24	3.06	1,257
25:1	64	1.06	1,490
60:1	64	0.98	1,465

Example 3

0.375 g. of the stabilised crude oil used in Example 2 were dissolved in 250 ml. benzene and 78 g. of active Raney nickel were added. The mixture was shaken by hand and within a few minutes the solution had turned from a very dark brown to a pale straw colour. The straw coloured solution was shown by spectroscopic analysis to contain only 0.07 mg./l. of metalloporphyrins (measured as vanadyl etioporphyrin I) compared with 6.38 mg./l. for the original dark brown solution. The Raney nickel was separated from the solution by filtration and dissolved in concentrated hydrochloric acid. This solution was then extracted with benzene until the last extract was colourless. The extracts were bulked and examined spectroscopically. The examination showed the presence of 0.5 mg. of metalloporphyrins (39% of original).

EXAMPLE 4

Vanadyl etioporphyrin I (12.6 mg.) was dissolved in benzene and shaken with Raney nickel (52 g.), when all the colour rapidly disappeared from the supernatant liquor. Four successive portions of thiacyclopentane (4 x 100 ml.) were added and the total liquid phase was separated, all solvent removed by vacuum distillation and the residual solid dissolved in fresh benzene. Spectroscopic examination showed the presence of 6.85 mg. of vanadyl etioporphyrin I (54.3% wt. recovery).

On the fourth addition of thiacyclopentane above, red colour was still being released in the solvent phase, and it was therefore considered that there was still some vanadyl porphyrin on the nickel.

EXAMPLE 5

Vanadyl etioporphyrin I (5.7 mg.) was dissolved in benzene and adsorbed onto Raney nickel. The nickel was separated, and dissolved in concentrated hydrochloric acid. Four successive extractions of this acid solution with benzene were then employed to extract the vanadyl porphyrin, and the total benzene was examined spectroscopically. 3.8 mg. of vanadyl etioporphyrin I were present in the solution, a recovery of 66.7% wt.

EXAMPLE 6

Vanadyl etioporphyrin I (0.5 mg.) was dissolved in benzene and adsorbed onto Raney nickel.

The nickel was separated, and the metalloporphyrin was desorbed by a benzene solution of tert-butyl hydroperoxide. (1.4 g. of a 60% wt. solution.) Spectroscopic examination showed the presence of 0.49 mg. of vanadyl etioporphyrin I in the solution, a recovery of 98%.

We claim:

1. A process for reducing the metal content of petroleum fractions boiling above 250° C., consisting of directly contacting a petroleum feedstock having at least a proportion of metal-containing material boiling above 250° C. with an active Raney metal selected from the class consisting of active Raney nickel, active Raney iron and active Raney cobalt, and recovering a product of reduced metal content.

2. A process as claimed in claim 1 wherein the metal in the feedstock is vanadium.

3. A process as claimed in claim 1 wherein the metal in the feedstock is nickel.

4. A process as claimed in claim 1 wherein the metal in the feedstock is present as metalloporphyrins.

5. A process as claimed in claim 4 wherein the metalloporphyrins are vanadyl porphyrins and the Raney metal is active Raney nickel.

6. A process as claimed in claim 1 wherein the contacting temperature is from 0 to 250° C.

7. A process as claimed in claim 1 wherein the contacting temperature is from 0 to 25° C. and the pressure is atmospheric.

8. A process as claimed in claim 1 wherein the ratio of Raney metal to petroleum fraction is from 1:1 to 100:1 and the contact time is from 10 minutes to 100 hours.

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