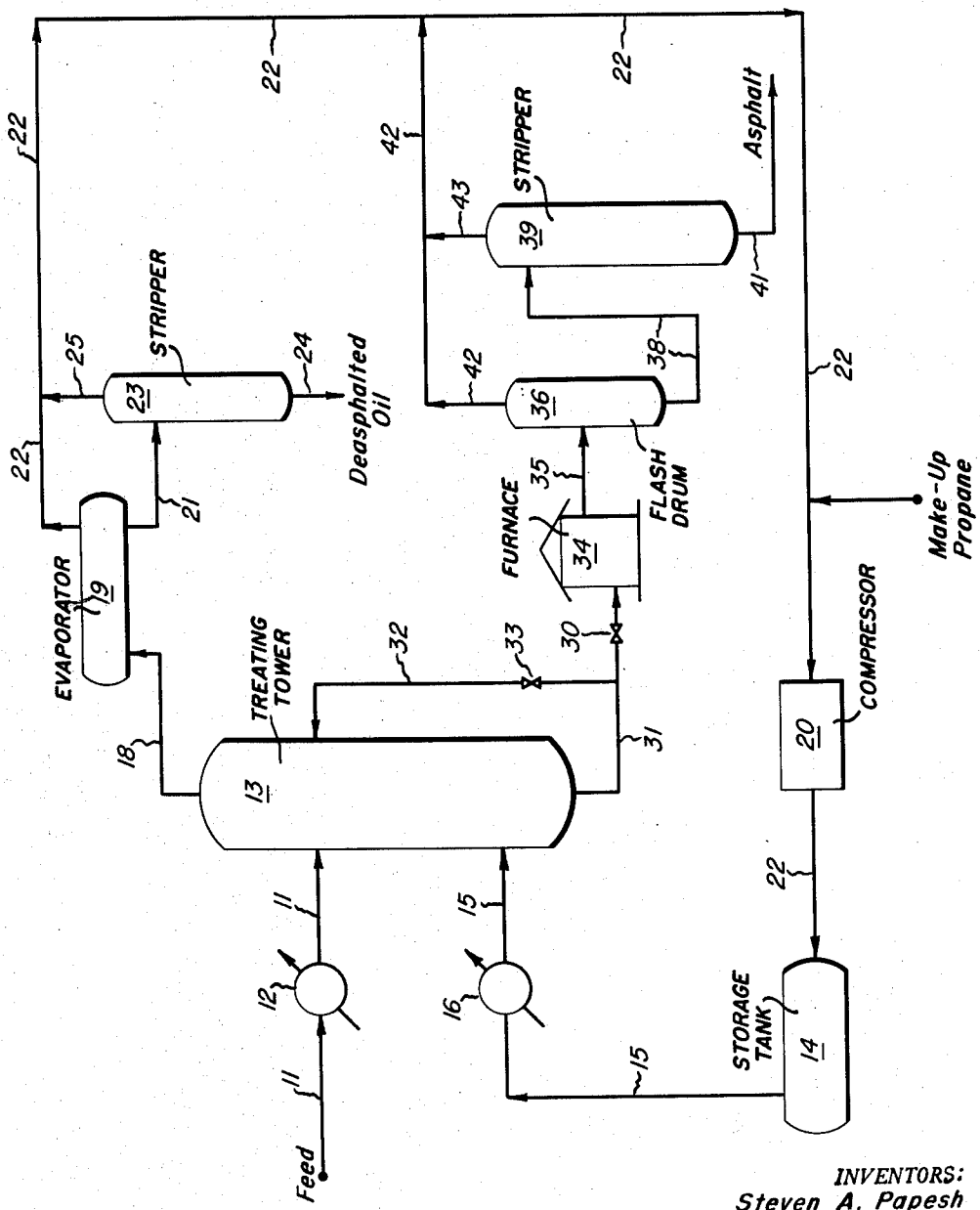
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METAL REMOVING WITH AN ASPHALTENE CONTAINING WASH OIL

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METAL REMOVING WITH AN ASPHALTENE CONTAINING WASH OIL

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This invention relates to a process for refining petroleum oil for the removal of metallic contaminants contained in such petroleum oil. More particularly, this invention relates to a method for removing metallic contaminants from a residual petroleum fraction by contacting the residual petroleum fraction with a wash solvent which removes such metallic contaminants. In the refining of crude petroleum oils for production of residual and distillate products, the petroleum oil is treated to remove metallic contaminants. One of the common commercial methods for removing metallic contaminants is by extraction of the reduced crude with an anti-solvent for asphalt containing such metallic contaminants. The anti-solvent is a solvent for the desired oil content of the reduced crude and causes the asphalt to precipitate from the reduced crude. During the treating with the solvent, it has long been known that a wash oil will increase the amount of metallic contaminants precipitated as part of the asphalt. It has been proposed that a metals-free asphalt may be used as a convenient wash oil. Such wash oils are generally described as metals-free synthetic asphalts and may be prepared by distilling heavy catalytic cycle oil.

We have now discovered an improved process for separating metallic contaminants from petroleum oils such as reduced crudes. In accordance with our invention, in the refining of the petroleum oil for removal of metallic contaminants by treating the petroleum oil with a solvent to precipitate the asphaltic phase containing metallic contaminants, the solvent and deasphalted oils phase is treated with a wash oil comprising asphaltic phase containing metallic contaminants. The asphalt phase contains carboids, carbenes, asphaltenes and resins. The asphaltenes are substances insoluble in petroleum ether, but at least slightly soluble in benzol and contain a large percentage of metallic contaminants relative to the petroleum oil feed.

More advantageously, the treating of the solvent phase is with an asphalt phase containing oxidized asphaltenes. Such oxidized asphaltenes may be formed during the treating by treating in the presence of molecular oxygen, such as in the presence of air. The temperature of the treating may conveniently be maintained in the range of from about 50 to about 250° F., although lower and higher temperatures may be used. The amount of asphalt phase used in the treating may conveniently be from about one to about 100 weight percent or more and preferably from about 5 to about 25 weight percent based on petroleum oil, e.g. residual oil, charged to the deasphalting zone.

More particularly, the combination process of this invention is a process for refining a residual oil, such as, for example, a reduced crude, comprising contacting the residual oil having an asphaltic phase containing metallic contaminants with a deasphalting solvent and treating the resulting soluble extract phase with high metals-containing asphaltenes from the asphalt phase whereby the asphaltenes remove additional metallic contaminants from the deasphalted oil of the extract phase.

The solvents, i.e., anti-solvents for asphaltic materials, which may be used in accordance herewith, are those solvents normally employed in deasphalting processes wherein the solvent dissolves deasphalted oil and precipitates an asphalt phase. For example, the solvent may be a light or low-boiling hydrocarbon such as methane, ethane, propane, butane, pentane, methylpentane, dimethylbutane, hexane, heptane, ethylhexane, isooctane, etc. Other advantageous solvents are the low molecular weight aliphatic alcohols, such as, for example, ethanol, butanol, amyl alcohol, hexanol, octanol, 3-methylbutanol, 2-methylbutanol, 1,1-dimethylpropanol, 1-methylbutanol, 1-ethylpropanol, etc. Other solvents which may advantageously be used are ethers, esters, and ketones; however, the deasphalting action of esters, ethers and ketones, in most instances, is not sufficiently strong for commercial employment. The preferred solvents are those low-boiling hydrocarbons having from about 2 to about 6 carbon atoms, and particularly preferred are propane and a mixture of propane and butane.

The process of this invention may advantageously be used to treat any petroleum oil containing metallic contaminants. The metallic contaminants with which this invention is concerned and which are herein intended are those metallic contaminants which occur naturally in a crude petroleum oil. The metallic contaminants are believed to contain porphyrins of heavy metals which are difficult to remove by normal extraction procedures. Thus, in accordance herewith, any petroleum fraction derived from a crude petroleum oil and containing natural metallic contaminants may advantageously be used as a feed to this process. Such petroleum oils or fractions include residual oils such as reduced crudes and residual stocks containing appreciable asphaltic matter. Although not normally subjected to deasphalting, distillate oils or even stocks from high paraffinic crudes may be utilized as feeds to this process if desired. The process finds particular utility where a residual oil derived from an asphaltic crude is used as the feed because of the very high metals content of such residual oil.

The FIGURE illustrates a flow diagram of an embodiment of this invention.

With reference to the figure, a 28% reduced crude obtained by fractionating a Mid-Continent crude oil to remove a gasoline distillate (275° F.), a naphtha distillate (325° F.), a kerosene distillate (450° F.), a gas oil disillate (525° F.), gas oil, and a wax distillate, is charged through line 11, heated in heater 12, and charged to treating tower 13. Liquid propane is charged to treating tower 13 through line 15 and heater 16 in an amount sufficient to provide 4 volumes of liquid propane per liquid volume of reduced crude in tower 13. The amount of propane used may vary with the charge oil but generally falls within the range of from about 2 to 1 to as high as about 10 to 1 volumes of propane to volumes of reduced crude. The treating temperature is maintained within a range of from 100 to 160° F., conveniently at about 120° F., and at a pressure of 200 p.s.i. sufficient to maintain the propane in the liquid state. Deasphalted oil solution in propane is removed from tower 13 through line 18 and is evaporated and stripped in evaporator 19 and stripper 23. Propane is recovered through lines 22 and 25 and comingled in line 22 and recycled. The deasphalted oil

product is removed from stripper 23 through line 24. Precipitated asphalt is removed from tower 13 through line 31 and may be charged through valve 30 to furnace 34 where it is heated. The heated asphalt may then be flashed in flash drum 36 to remove propane through line 42 and the flashed asphalt is then charged via line 38 to stripper 39 for further propane removal through line 43. The asphalt product may be recovered from stripper 39 through line 41. Propane in lines 42 and 43 is charged through recycle line 22 to compressor 20 where the propane is liquefied and then charged to liquid propane storage tank 14 for reuse. At least a portion of the precipitated asphalt in line 31 is charged through line 32 and valve 33 to the solvent phase in tower 13 during the contacting of the crude oil with the propane. In this embodiment, the return of precipitated asphalt recycled to tower 13 is controlled by valves 30 and 33 so as to provide 15 weight percent of recycle asphalt based on reduced crude charged to tower 13. More advantageously, where more intimate contact with asphaltenes is desired, line 32 may alternatively discharge into line 11, preferably upstream from heater 12, to provide mixing of asphaltenes with feed in the feed line prior to charging to the contacting zone or tower 13. The deasphalted oil recovered from line 24 has a very low metals content relative to the reduced crude charged.

It is obvious that other embodiments of this invention may be used. For example, two or more treating towers may be employed in lieu of the single treating tower of the illustrated embodiment. Thus, the precipitated asphalt containing high metals asphaltenes from one tower may be used to enhance metals removal from a crude oil in a second tower in contact with a deasphalting solvent by charging the precipitated asphalt to the extract phase of the second tower. In like manner, a third tower or a great plurality of towers may also be used.

EXAMPLES

The examples set out below further illustrate the process of this invention. The examples demonstrate the ability of asphaltenes highly contaminated with metals to further increase the removal of metals from a reduced crude in the presence of a deasphalting solvent. The starting materials used in the examples below were two reduced crudes and an asphaltene fraction. The two reduced crudes were a 46% reduced crude and a 12% reduced crude and both were obtained from vacuum reduction of an asphaltic crude petroleum oil. The asphaltene fraction was approximately 3.5% reduced and was obtained from the 46% reduced crude. An analysis of the reduced crudes and the asphaltene fraction with regard to vanadium and nickel content (indicative of the heavy metals content) is reported below in Table I:

Table I

Percent reduced crude	Metals content, p.p.m.	
	V	Ni
46	20	10
12	72	31
3.5 (asphaltenes)	170	100

EXAMPLES 1–3

Three runs were made using a 12% reduced crude by contacting a given amount of the reduced crude in each run with a given amount of pentane solvent at atmospheric pressure and room temperature (70° F.) The reduced crude was mixed with the amount of asphaltenes indicated in each run in Table II in a beaker. The mixtures were then treated with about 5 volumes of pentane. The precipitated solids were filtered and washed with pentane until dry and powdery. The deasphalted oil was recovered by evaporating the pentane solvent under a heat lamp. Metals content in the deasphalted oil from each run is reported in Table II. The percent improvement of each of the second two runs over the first run (wherein no asphatenes were added) was calculated and is also reported in Table II:

Table II

Percent added asphaltenes [1]	Percent residue from crude [2]	Metals content in deasphalted oil			
		Amount, p.p.m.		Percent improvement	
		V	Ni	V	Ni
0	23.5	14	8.5		
25	23.2	9.8	7.2	30	14
100	21.0	10	6.0	29	29

[1] Based on total reduced crude starting material.
[2] Computed as total percent residue at end of run less amount of added asphaltenes.

As can be seen from the data of Table II, the added asphaltenes decreased the metal content in the deasphalted oil to an appreciable extent. Further, the amount of residue obtained from the crude apparently was also slightly decreased as percent of added asphaltenes increased. Metals improvement showed somewhat scattered results in the three runs, but the data demonstrate overall improvement due to addition of asphaltenes.

EXAMPLE 4

In this example, the procedure of Examples 1–3 was repeated for runs 1 and 2 of Table III except that the 46% reduced crude was used. In run 2 the same feed was used as in run 1 and in each of runs 1 and 2 the feed was subjected to deasphalting in accordance with the same procedure used above with the amount of added asphaltenes shown in Table III. The deasphalted oil recovered from run 2 was then again subjected to deasphalting in run 3 with the amount of added asphaltenes shown in Table III. The results are reported in Table III below:

Table III

Run No.	Percent added asphaltenes	Percent residue from crude	Metals content in deasphalted oil			
			Amount, p.p.m.		Percent improvement	
			V	Ni	V	Ni
1	0	6.5	7.0	3.5		
2	33	6.9	4.6	2.8	34	20
3	40	0	3.1	2.0	56	43

The results of Example 4 reported in Table III demonstrate a definite metals improvement in the deasphalted oil with only a slight increase in percent residue from the crude by subsequent contacting with added asphaltenes.

EXAMPLE 5

In this example, three additional runs using the 46% reduced crude were made in accordance with the same procedure of Examples 1–3 except as herein stated. At the end of run 1, the residue from the reduced crude was used as the added asphaltenes of run 2, and the residue from the reduced crude of run 2 was used as the added asphaltenes of run 3. All three runs were conducted under a blanket of nitrogen and in the absence of oxygen.

The results from the three runs are reported in Table IV below:

Table IV

Run No.	Percent added asphaltenes	Percent residue from crude	Metals content in deasphalted oil			
			Amount, p.p.m.		Percent improvement	
			V	Ni	V	Ni
1	0	7.6	9.2	4.6		
2	7.6	−0.9	6.6	3.4	28	26
3	6.7	0	6.4	3.7	30	20

Although the deasphalting of the runs in Example 5 was conducted in the absence of oxygen, there was still a marked improvement in the metals content of the deasphalted oil due to added asphaltenes even in amounts recoverable from the next preceding deasphalting step. The effect of excluding oxygen from the step of contacting solid asphaltenes with the extractant mixture is somewhat inconclusive because the asphaltenes were apparently oxidized on the filter during the operation from the deasphalted oil of previous runs.

EXAMPLE 6

In this example, three additional runs were made under the same conditions as the runs in Example 5 except that the amount of added asphaltenes were varied as indicated in Table V. The results are as listed below:

Table V

Run No.	Percent added asphaltenes	Percent residue from crude	Metals content in deasphalted oil			
			Amount, p.p.m.		Percent improvement	
			V	Ni	V	Ni
1	25	8.6	6.3	4.0	32	13
2	40	1.4	4.0	2.4	57	48
3	45	0	4.9	2.9	47	37

A comparison of the results of Example 6 with those of Example 5 demonstrates that additional asphaltenes give an overall improvement with regard to metals removal from the deasphalted oil.

EXAMPLE 7

In a particularly preferred embodiment of this invention, oxidized asphaltenes were used as a wash oil in the deasphalting of the 46% reduced crude. The oxidized asphaltenes were prepared by spreading a thin layer of asphaltenes over a sintered glass filter and then heating with a heat lamp while drawing air through the filter for about 20 to 25 hours. This deasphalting example was carried out in the same manner as Example 1 with the exception, of course, that the added asphaltenes were oxidized asphaltenes. The results of the treatment with oxidized asphaltenes are reported in Table VI below:

Table VI

Percent added asphaltenes	Percent residue from crude	Metals content in deasphalted oil			
		Amount, p.p.m.		Percent improvement	
		V	Ni	V	Ni
25	10.0	3.9	2.1	58	54

It is evident from the above data of Table VI that the oxidized asphaltenes on only one contact gave an improvement similar to that of run 2 of Example 6, i.e., after two contacts with asphaltenes which were not substantially oxidized. Because of this improvement, it is preferred to use oxidized asphaltenes. The oxidized asphaltenes may be obtained by oxidation of the asphalt product; e.g., by heating in contact with oxygen, such as air. It was also found, when air blowing and filtering a solution of deasphalted oil in pentane, there was no apparent demetallation. Therefore, it is apparent that the increased yield is due to presence of oxidized asphaltenes or asphaltenes in the presence of oxygen. Apparently the oxygen does not attack the metals contaminants directly at the low deasphalting temperatures, but rather the asphaltenes are capable of transferring the effect of oxygen to the metals compounds and oxidizing them into insoluble asphaltenes or else the oxygen oxidizes the asphaltenes and thus produces sites which can absorb the metals-containing compounds and remove them from the deasphalted oil in solvent solution.

In our experimentation with the asphaltenes as wash oils in solvent deasphalting, a saturation point of the asphaltenes, i.e., a metals content beyond which the asphaltenes were ineffective, was not reached after three contacts. It is believed that the asphaltenes may be reused again and again as wash oils without loss of effectiveness. However, because the asphaltenes are readily available in the asphalt phase from solvent deasphalting, there is always an available and inexpensive wash oil for use in the deasphalting operation.

The process of this invention is applicable to any solvent deasphalting process wherein the solvent acts as an anti-solvent for asphalts containing asphaltenes. As an additional example, the asphaltene wash oil may be used in a combination deasphalting-dewaxing operation wherein a light hydrocarbon dewaxing solvent is used to precipitate both asphalt and wax. In this example, in order to insure the dewaxing function, the temperatures employed should be sufficiently low to fall within the normal dewaxing temperature for the particular hydrocarbon solvent, e.g., from about −44 to about 70° F. for propane dewaxing.

The process of this invention may also be carried out in two or more contacting zones, if desired. For example, the feed and solvent, e.g., propane, may be contacted in a first zone, the asphaltic phase may be removed from the bottom of the zone, and the extract phase containing the oil of lower metals content may be removed from the top of the zone and charged to a second zone to which the asphaltic phase containing asphaltenes from the first zone is charged. In the second zone further metals removal is accomplished by asphaltenes passing downwardly through the extract phase and the asphaltenes and additionally removed metals contaminants are taken from the bottom of the second zone and may be combined with asphaltic phase from the first zone. Other arrangements using two or more zones are within the skill of the art.

It is evident from the foregoing that we have provided a process for refining a petroleum oil for the removal of metallic contaminants using as a convenient and available wash solvent the asphalt phase from the deasphalting operation.

We claim:

1. A process for refining a petroleum oil for the removal of metals-containing contaminants which comprises treating said petroleum oil with a wash oil comprising asphaltenes which contain a large percentage of metallic contaminants from petroleum oil, whereby said asphaltenes remove metals-containing contaminants from said petroleum oil.

2. The improvement in a method of removing metallic contaminants from a residual petroleum oil by extraction with a liquid light hydrocarbon solvent whereby metallic contaminants are precipitated from the light hydrocarbon-soluble extract phase as a component of a hydrocarbon-insoluble asphaltic phase, which improvement comprises washing said extract phase in the liquid state with asphal-

tenes of said asphaltic phase containing said contaminants whereby said asphaltic phase removes additional metallic contaminants from said extract phase.

3. The improvement of claim 2 wherein said washing is at a temperature in the range of from about 50 to about 250° F.

4. The improvement of claim 2 wherein said washing is with from about 5 to about 25 weight percent of said asphaltenes based on residual petroleum oil treated with said hydrocarbon solvent.

5. The improvement of claim 2 wherein said washing is with oxidized asphaltenes.

6. A method for deasphalting a reduced crude petroleum oil, which method comprises extracting said petroleum oil with a liquid light hydrocarbon solvent whereby there are formed an extract phase containing said solvent and deasphalted oil and asphaltic phase containing asphaltenes of high metals content relative to said reduced crude petroleum oil, separating said asphaltic phase from said

extract phase, and washing said extract phase in the liquid state with said asphaltic phase containing said asphaltenes whereby said asphaltenes of said asphaltic phase remove additional metallic contaminants from said deasphalted oil.

7. The process of claim 6 wherein said light hydrocarbon solvent is a mixture of propane and butane.

8. The process of claim 6 wherein said liquid hydrocarbon solvent is propane.

9. The process of claim 6 wherein said light hydrocarbon solvent is pentane.

10. The process of claim 6 including the additional step of oxidizing said asphaltenes prior to said washing of said extract phase with said asphaltenes.

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