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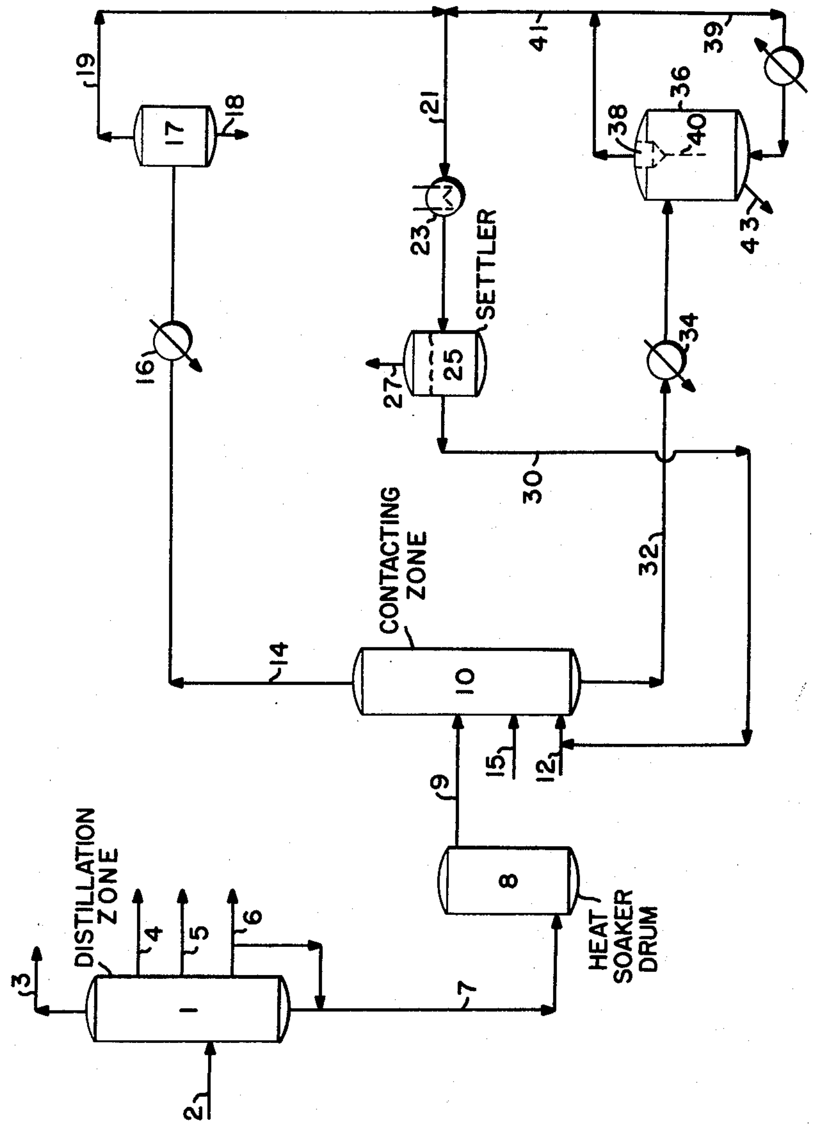

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REMOVAL OF METALLIC CONTAMINANTS FROM PETROLEUM FRACTIONS

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The present invention relates to the removal of metallic contaminants from petroleum oils and more particularly relates to an improved process for the removal of complex organo-metallic compounds of the porphyrin type, in particular those containing nickel and vanadium, from high boiling petroleum gas oils and residua.

It has long been recognized that petroleum gas oils and residua that include constituents boiling in excess of about 950° F. normally contain iron, nickel, vanadium and other metallic contaminants which have an adverse effect upon various catalysts employed in petroleum processing operations and upon combustion equipment in which such petroleum fractions are burned as fuels. In operations such as catalytic cracking, hydrofining and the like, the presence of very small concentrations of these contaminants in the feed stream leads to the rapid poisoning of the catalyst, causing a significant decrease in the product yield, an increase in coke and gas production, and a marked shortening in the life of the catalyst. In residual type fuels, such contaminants attack the refractories used to line boilers and combustion chambers; cause slagging and the build-up of deposits upon boiler tubes, combustion chamber walls and the blades of gas turbines; and severely corrode high temperature metallic surfaces with which they come into contact.

Although there have been numerous methods proposed in the past for removing these contaminants from high boiling petroleum fractions, it has been found that such methods are largely ineffective, generally result in the loss of substantial quantities of the oil, and in most cases are prohibitively expensive. As a result, it has generally been necessary to restrict the streams fed to catalytic petroleum processing units to those fractions which boil below the range in which the contaminants are found and to avoid as much as possible the use in fuels of fractions which contain the contaminants in high concentrations.

The present invention provides a new and improved process for the removal of iron, nickel, vanadium, and other metallic contaminants of the porphyrin type from high boiling petroleum oils, and in particular residual oils.

It is known that such contaminants may be removed by subjecting the contaminated oil to a pretreatment, such as heat soaking, and solvent precipitating the pretreated oil with a light hydrocarbon in the presence of an acidic gas. In accordance with the present invention, it has been found that this process can be greatly improved by the addition of an asphalt solutizer to the light hydrocarbon in the solvent precipitation step.

The drawing further illustrates the invention by means of a schematic diagram. Reference numeral **1** designates a crude oil distillation zone which may constitute, for example, an atmospheric pipe still or a combination of atmospheric and vacuum distillation towers. Crude oil may be introduced into distillation zone **1** through line **2** and separated into a variety of fractions of different boiling ranges. Light hydrocarbons in the C_1 to C_4 range may be taken off through overhead line **3**. A naphtha fraction may be drawn off through line **4** and in one embodiment of the present invention, this naphtha stream, boiling in the range of 55° to 300° F. and comprising hydrocarbons having from 4 to 10 carbon atoms, provides the solvent employed in the demetalizing step.

Middle distillates may be withdrawn through line **5**. These materials, kerosene and light gas oils, may boil up to 900° F. and are substantially metal free. A heavy gas oil fraction boiling in the range of between 950° F. and 1300° F. is withdrawn through line **6** and the residual fraction, boiling above the heavy gas oil is taken off as bottoms product through line **7**. Both of these latter streams contain substantial amounts of metallic constituents and may be subjected separately to the treating process of the present invention.

The thermal treating zone **8** to which the metal contaminated heavy oil is passed via line **7**, is preferably a coil, although a closed, agitated vessel or drum may be used. The pressure during the heat soaking step is preferably maintained between 200 and 1500 p.s.i.g As indicated previously, it is advantageous to maintain a temperature of from about 650° to 950° F. in this zone under conditions such that cracking is limited to the specified severity. A residence period of ½ minute to 50 hours is desirable, the shorter times correponding naturally to the higher temperatures and vice versa. The thermal treatment serves to increase the susceptibility of the metallic constituents to later coagulation by the acidic gas treatment, possibly by changing either the character of the metals, the asphaltenes, or the oil, or all of these materials.

The solvent precipitation step is carried out on the heat-soaked residua directly, and the latter is passed for this purpose through line **9** to contacting tower **10**. This may comprise one or more towers or other vessels adapted to permit the saturation of the oil with gaseous HCl admitted through line **15** under the desired conditions of temperature and pressure. Suitable coils, jacketing, or other temperature control means are provided, as are means for agitation.

Solvent, which is preferably an aliphatic or naphthenic hydrocarbon or mixture having 4 to 10 carbon atoms, and which may advantageously be the naphtha fraction withdrawn through line **4** from still **1**, is introduced into vessel **10** through line **12**, in amounts of from 0.1 to 10 volumes per volume of oil, preferably 0.3 to 3 volumes per volume of oil. 1–15% of asphalt solutizer, preferably 5–10%, is also introduced through line **12**.

Reaction conditions within tower **10**, which is preferably maintained as a countercurrent reaction zone, are temperatures of 30° to 300° F. and pressures of 25 to 500 p.s.i.g. The residence time of the oil may range from 5 to 100 minutes or more. The deashed oil-solvent mixture, along with gaseous HCl or other acidic metal coagulating gas, is passed overhead via line **14** and passed through heater **16** to flash tower **17**, where the hydrocarbon solvent along with HCl and any asphalt solutizer is flashed off overhead through line **19**, while oil of exceptionally low metal content is recovered from flash zone **17** through line **18**. The flashed solvents and gas are passed to cooler **23** via lines **19** and **21**, and thence to settler **25**.

Returning now to tower **10**, the semi-fluid sludge is withdrawn downwardly through line **32** and is, in a preferred embodiment of the present invention, further processed to recover the hydrocarbon solvent and the asphalt solutizer. This may be done by passing it through heating zone **34** into a fluidized solids flash zone **36**. Here a bed of finely divided solids, preferably of the same composition as the asphaltene, is maintained as a dense, fluidized bed of solids maintained by an upward flowing gas stream admitted through line **39**. This bed of solids may be at a temperature of about 100° to 1000° F., and the sludge is deposited thereon, whereby it is decomposed to a solid carbonaceous material and asphalt solutizer and hydrocarbon. The latter two gaseous materials are withdrawn through cyclone **38** equipped with dipleg **40** for return of fines to the fluidized bed, and are passed via lines **41** and **21** to settler **25**. A portion is recycled via line **39** to reactor **36** to maintain the bed in fluidized condition. Solid carbonaceous residue may be withdrawn through line **43** and be used as solid fuel.

In the settling zone, HCl may be withdrawn overhead as uncondensed gas via line **27** for recycle to the system or may be recycled dissolved in liquid streams. Similarly, the hydrocarbon solvent and asphalt solutizer (which may separate from layers) are passed, in whole or in part, via line **30** to tower **10**.

The process of the present invention may be subjected to many variations without departing from its spirit. Thus, instead of separately heat treating the oil prior to addition of solvent, it may be desirable, under certain circumstances, to thermally treat the oil-solvent mixture preferably after saturation with the coagulating gas. In still another modification, total crude, from which fixed gases have been stripped, may be fed to the heat soaking vessel **8** and then to the countercurrent contacting tower **10**. Naphtha recycle is fed to the top of the tower equivalent to about 0.1 to 10 volumes on feed. The naphtha cut may be various boiling ranges or the total fraction boiling up to about 400° F. The naphtha-deashed oil solution is taken overhead from the contacting tower to a distillation tower where the naphtha recycle stream is cut out and excess naphtha from the crude taken off as make naphtha. The residue stream is taken from the bottom of the tower and decomposed as described hitherto. The HCl fraction is taken overhead from the still and compressed for recycling. Operating in this manner integrates the distillation step after the solvent precipitation process, and produces both the precipitant for the demetalizing process as well as any other cut desired in the crude distillation step.

The concentration of metallic contaminants and the ratio of volatile to non-volatile contaminants in crude oils vary considerably. The metals content of any distillate fraction will therefore depend upon the type and concentration of contaminants in the crude oil from which the fraction was distilled, the boiling range of the fraction, and the amount of entrainment which took place during the distillation. Heavy gas oil distilled from typical crudes may contain from about 1 to about 20 pounds of metallic contaminants per 1000 barrels. Residual fractions and gas oils derived from crudes that are particularly high in contaminants may contain as much as 300 pounds of metal per 1000 barrels. Similarly, in some fractions these contaminants may be predominantly of the volatile type and in others they may be essentially of the non-volatile type, depending upon the crude source and the conditions under which the fraction was obtained.

The heat soaking step of the present invention is carried out preferably under conditions of mild thermal cracking so that undue amounts of lighter components are not formed. The conditions required will depend upon a combination of time and temperature, the nature of the feed stock, and the like. The temperature of thermal treatment, however, is below 1000° F. and preferably below about 900° F. On the other hand, temperatures above about 600° F. are needed for sufficient reaction rate to maintain times within reasonable limits. The degree of heat soaking is conventionally measured by percent conversion, i.e. the percent of treated material that is thermally cracked to form components boiling at less than a certain temperature. Five to 8% 430° F. conversion (i.e. conversion to 430° F. end boiling) is a sufficient pretreatment for the purpose of the present invention, but other refinery considerations (i.e. viscosity reduction desired, etc.) may well dictate higher conversions. These do not harm the present process but rather improve its effectiveness.

The solvent precipitation step is carried out on the pretreated feed stock. Preferred are light hydrocarbons boiling in the range of about 55° to 400° F. As a result of the solvent addition, there is precipitated as a light, flocculent precipitate the so-called asphaltene fraction. A portion of the nickel and vanadium is precipitated with these asphaltenes, while a portion remains in solution.

Accordingly, there is also employed as a metal coagulating reagent an acidic material soluble in the petroleum fractions, but not particularly reactive with the oil. Hydrogen halides, particularly dry hydrogen chloride, are suitable. The treating temperature, the volume of hydrogen halide employed and the pressure at which the treatment is carried out may be varied considerably. It is preferred to treat the solvent-residual oil mixture at temperatures between about 70° and 400° F., although higher temperatures may be employed and at pressures ranging from atmospheric to about 300 p.s.i.g., higher pressures being also permissible. The reaction time too may be varied from a few minutes to as much as a few hours, depending upon the treating conditions.

Where residual material is used for the production of #6 fuel oil, i.e. bunker C, it is undesirable to severely heat soak. In the conventional production of #6 fuel oil from residua, a mild heat soak is utilized to visbreak the material to required specifications, i.e. 175 SSF at 122° F. This is readily accomplished by passing the residua through a hot coil at about 800° F. for several minutes. A more severe heat soak would increase the amount of naphtha, a product of little importance in many markets, and cause coking and hot filtration sediment. The latter solids are harmful in that they cause clogging of consumers' fuel filters.

In conventional visbreaking the metals content is not decreased. In fact the metals content of the visbroken fuel is generally higher than in the feed because of the concentrating effect of the topping operation. This topping of the naphtha made during visbreaking is required so that the finished fuel oil will meet flash specifications.

Where it is desirable to remove metal contamination from these visbroken fuel oils, or any residua mildly heat soaked, i.e. no more than 8 to 10%. 430° F. conversion, the conventional solvent precipitation described above, gave poor yields of deasphalted oil (DAO) at satisfactory demetallization. This is because the metals removed in such sequence is very strongly dependent on the severity of the heat treating.

In accordance with this invention, it has been found that the addition of a small percentage of certain polar solvents which act as asphalt solutizers to the conventional hydrocarbon solvents increases the deasphalted oil yield while satisfactorily reducing the metal concentration.

A solvent, to be an effective asphalt solutizer, must have the ability to dissolve or peptize the asphalt. A wide variety of chemical compounds are suitable: classification may be made by virtue of their surface tension and ability to dissolve in the bulk oil. It has been found that organic solvents having surface tensions from about 24 to about 45 dynes per cm. at 25° C. are effective asphalt solutizers. Compounds such as pentane, hexane, acetone and ethanol, which have surface tensions of 15.3, 20.1, 23.1 and 21.8 dynes/cm., respectively, coagulate the asphalt and are thereby ineffective solutizers. Oxygenated solvents, such as methyl ethyl ketone and secondary butyl acetate, are also inoperative since they are essentially immiscible with the maltene matrix. Accordingly the asphalt solutizers must be non-oxygenated. Examples of such suitable solvents are carbon disulfide, carbon tetrachloride and toluene.

From 1 to 15% of asphalt solutizer is utilized in accordance with the invention, preferably from 5–10%.

This addition avoids the necessity of a second heat soak step and permits the use of the single conventional solvent precipitation step. In addition, if a low boiling point asphalt solutizer is used, no additional cost is involved because the solutizer is recovered with the HCl and light solvent in the stripping step following the filtration of the metal-containing sludge.

A further advantage obtained by the invention is that much less solvent is needed in the solvent precipitation step. This is because the asphalt solutizer improves the selectivity of the solvent.

The mechanism of the process may be more clearly understood by realizing that in the virgin residuum the metals are largely associated with asphaltene colloids. These asphaltenes are known to have paraffinic side chains which are from 4–7 carbons long. These side chains serve to solutize the colloids in the maltenes (paraffinic or "oil" matrix) and prevent them from precipitating out on standing. The visbreaking step is believed to result in dealkylation or cracking off of the side chains and thus makes the colloids much less soluble in the oil. However, because of the viscous nature of the oil, the colloids are still largely in suspension. Very little coke-like materials are formed during visbreaking.

In a subsequent deasphalting step these colloids are much less soluble than for the base case and the viscosity is, of course, very low due to the addition of diluent during deasphalting. Consequently, the cracked colloids are very easily precipitated. Since paraffinic materials have been cracked off the colloids, the yield (weight) of colloids is less in the heat soaked case than in the virgin case and also they are richer in metals since the metals are largely in the nucleus of the colloidal asphaltenes. This explains the desirability of heat soaking as a pretreatment to a metals removal precipitation.

The light hydrocarbons used in the precipitation step are not selective enough normally, in that they remove many other non-hydrocarbon materials aside from the asphaltene colloids. Another way of saying this would be that not all the asphalt precipitated by light hydrocarbons contains the same concentration of metals. Consequently, by increasing the solubility of the deasphalting solvent it is possible to still precipitate most of the metals and yet improve the yields. This is because most of the metals are in the higher molecular weight, more insoluble asphaltenes rather than in the lower molecular weight asphaltenes and heterocyclic materials. This explains the effectiveness of adding small amounts of asphaltene solutizers such as CS_2 and CCl_4.

The following data more clearly show the advantages of the invention.

A Lake Medium residuum, containing chiefly Bachaquero crude and therefore large amounts of vanadium and nickel components, was visbroken in a refinery at 820° F. for two minutes to obtain an 8% 430° F. conversion.

The sample used essentially met viscosity specifications after visbreaking but still contained 430 p.p.m. vanadium and 45 p.p.m. nickel. This material was used for all the experiments described below and summarized in attached Tables I and II. Only vanadium is reported, but nickel results were similar on a percentage removal basis.

In accordance with this invention, the visbroken oil was deasphalted in an agitated flask by adding 2 volumes of heptane containing the solutizer specified. Anhydrous HCl at 1 atm. was simultaneously bubbled into the flask, which was at room temperature. After a few minutes, HCl addition and agitation were stopped and the precipitated asphaltenes were allowed to settle. After paper filtration, the cake was washed with a little fresh heptane. The washings were added to the filtrate and the solvents were stripped off via atmospheric distillation. DAO yields are reported based on visbroken material charged to the solvent precipitation step. Metals in DAO and feed were analyzed by routine X-ray fluorescence and chemical wet-ashing techniques. For comparison, result with HCl only, heptane only, and heptane+HCl are also shown.

TABLE I

Selective demetalization with modified solvents

Treat		DAO Yield	p.p.m. V in DAO	Percent V Removal	Selectivity [1]	Surface Tension in Dynes/cm. at 25° C. of asphalt solutizer
Atm. HCl only	Base cases	88.0	232	46	4.3	----------
200% C_7 only		81.5	133	69	4.0	----------
200% C_7+Atm. HCl		70.5	30	93	3.2	----------
200% C_7+Atm. HCl:						
+5% CCl_4		84.4	74	83	5.5	26.1
+10% CCl_4		85.0	81	81	5.6	26.1
+5% CS_2		87.3	77	82	6.6	32.3
+10% CS_2		88.0	81	81	7.0	32.3
+5% Toluene		87.1	72	83	6.6	28.4

[1] Ratio of V in asphalt reject to V in feed.

These examples clearly show that the HCl deasphalting treatment was of low selectivity, i.e. when high oil yields were obtained, the metal removal fell short of the target 100 p.p.m. of vanadium, or conversely when good metal removal was obtained the deasphalted oil yield was less than 80%. The addition of the asphalt solutizer yielded high percentages of deasphalted oil and satisfactorily demetalized the oil. The surface tensions of all of these solvents are within the critical range of 24 to 45 dynes/cm.

The addition of an asphalt solutizer avoids the necessity of an additional heat soaking operation and thereby reduces the cost of demetalization operation and increases the yield of deasphalted oil.

Table II shows some negative data which further define the limits of this invention. The feed is the same visbroken oil referred to above.

Runs A and B show that over 25% solvent modifier, while it may be selective, cannot usually precipitate enough asphalt to achieve the desired low metals (less than 100 p.p.m.) DAO. The examples are for aromatic modifiers but hold also for CS_2 and CCl_4. It is well known that asphalts are completely soluble in solutions composed primarily of these solvents.

Run C shows that ketone is undesirable because of limited solubility in oil-heptane and undesirable side reactions with HCl.

Runs D, E, F and G show that HCl is needed, as well as C_7+solutizer for good metals ppt. (compare with A and Table I).

TABLE II

Run	Solvent Modifier	HCl Used	Vanadium Content, p.p.m.		Wt. Percent DAO Yield	V asphalt/V fuel
			Feed	DAO		
A	25% Benzene	Yes	430	114	84	4.8
B	50% Benzene	Yes	430	201	92	7.1
C	50% Acetone	Yes	(sludges with HCl)		(not fully miscible)	
D	20% Benzene	No	430	311	93	4.5
E	5% CS_2	No	430	263	93	6.1
F	5% CCl_4	No	430	242	90	4.9
G	5% Toluene	No	430	247	92	5.7
H	200% tripropylene [1]	Yes	430	164	82	3.7
I	200% methylcyclo hexane[1]	Yes	430	121	87	5.6
J	200% benzene	Yes	430	430	100	0
K	None	Yes	430	30	71	3.2

[1] No heptane in these runs.

Runs H, I, J and K show that light hydrocarbons are the preferred major solvents over aromatics, olefins, naphthenes.

The necessity for heat soaking is shown in Table III where the above procedures (200% C_7+solutizer+HCl) were used on the unvisbroken atmospheric residuum containing 420 p.p.m. V.

TABLE III

Solutizer	DAO Virgin	V content, p. p. m. visbroken [1]
5% CS_2	159	77
10% CS_2	195	81
5% CCl_4	147	74
10% CCl_4	164	81

[1] Data same as Table I.

When HCl was not used during these virgin residuum treatments, it was impossible to separate any asphalt at all. This clearly demonstrates the solubility of the oil for the metal-bearing asphaltenes.

The invention is not to be limited to the specific embodiments shown or to the specific examples given, nor to the theories advanced as to the operation of the invention.

What is claimed is:

1. An improved process for upgrading a metallic contaminated petroleum fraction including constituents boiling above 950° F. which comprises subjecting said fraction to an initial thermal treatment at a temperature between about 650 to 950° F. for a period of ½ minute to 50 hours, thereafter contacting said fraction in a solvent precipitation zone with a solvent composed of from about 1 to about 25% non-oxygenated asphalt solutizer having a surface tension between about 24 and 45 dynes/cm. at 25° C. and from about 99 to about 75% light hydrocarbon in a ratio of 0.1 to 10 volumes of said solvent per volume of said fraction and with hydrogen halide and precipitating and coagulating metallic contaminants and recovering a heavy oil of reduced metallic contamination.

2. The process of claim 1 wherein said hydrogen halide is hydrogen chloride.

3. The process of claim 1 wherein said thermal treatment comprises heat soaking by passing through a heated coil.

4. The process of claim 1 wherein said asphalt solutizer is carbon disulphide.

5. The process of claim 1 wherein said asphalt solutizer is carbon tetrachloride.

6. The process of claim 1 wherein said asphalt solutizer is toluene.

7. A process for upgrading a metallic contaminated visbroken heavy fuel oil which has been visbroken or heat soaked to less than 10% 430° F. conversion which comprises contacting said oil in a solvent precipitation zone with a solvent composed of from about 1 to 25% non-oxygenated asphalt solutizer having a surface tension between about 24 to 45 dynes/cm. at 25° C. and about 99 to 75% of a light hydrocarbon, about 0.1 to 10 volumes of said solvent per volume of said oil and with an acid gas, and precipitating and coagulating metallic contaminants and recovering an oil with reduced metallic contaminants.

8. The process of claim 7 wherein the said solvent is composed of from about 5 to 15% of asphalt solutizer and from about 95 to 85% of a light hydrocarbon.

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