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SOLVENT DECARBONIZING PROCESS

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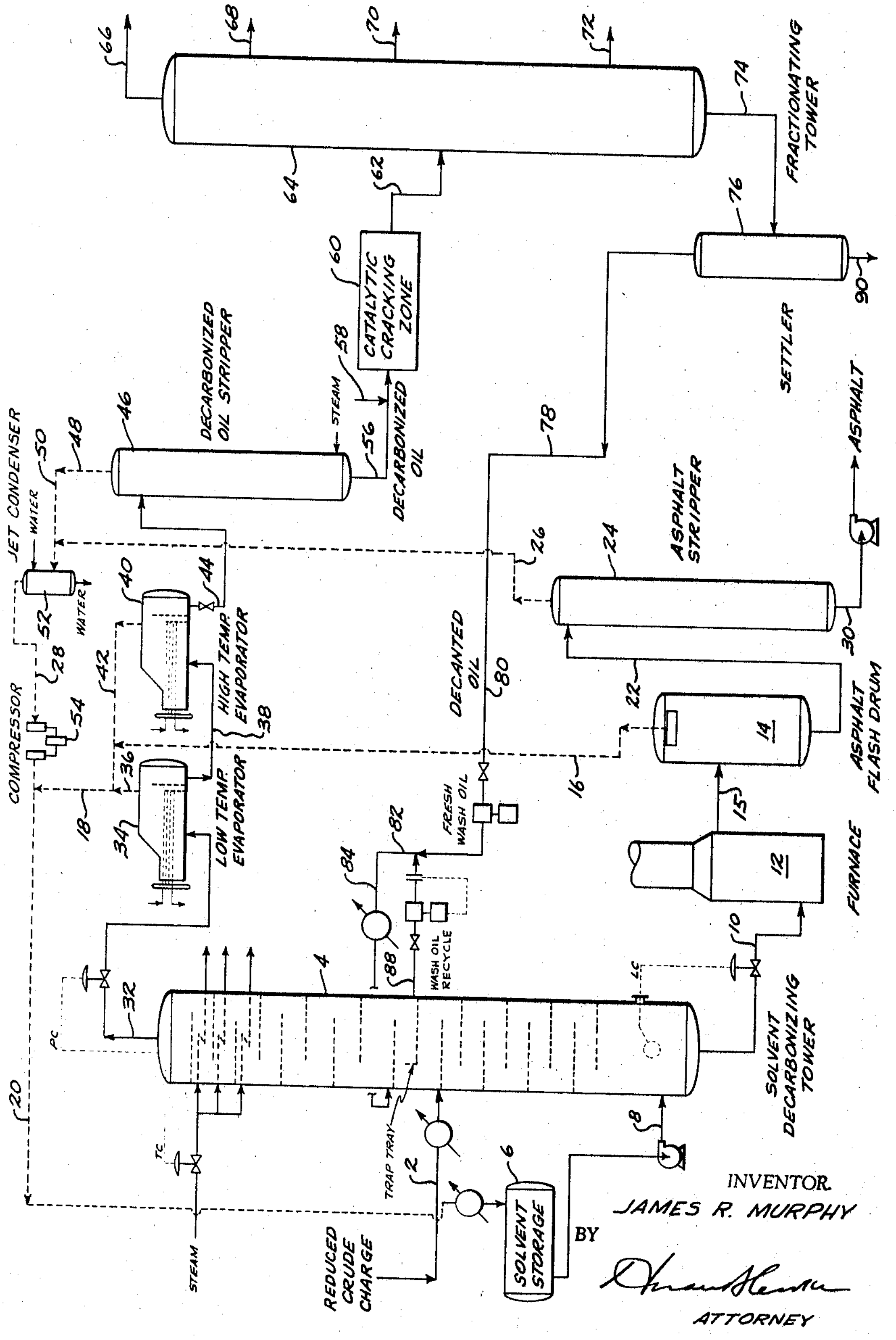

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SOLVENT DECARBONIZING PROCESS

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ABSTRACT OF THE DISCLOSURE

A high boiling feed such as a reduced crude is decarbonized with a light hydrocarbon solvent. A tar containing gas oil is added as a wash oil to the decarbonizing zone above the point of feed introduction.

This application is a continuation of Ser. No. 301,733, filed Aug. 13, 1963, and now abandoned.

This invention relates to a method for providing increased quantities of low metal content oils suitable for catalytic cracking, and more particularly, to a method for recovering increased quantities of low metal content catalytic cracking charge stock from the high boiling or residual fractions of crude petroleum oils.

Many of the crude petroleum oils that are presently subjected to commercial processing contain objectionable amounts of metallic contaminants, such as vanadium and nickel. These metallic contaminants are especially troublesome in catalytic cracking charge stocks, those portions of petroleum crude oils that are suitable for catalytic cracking to lower boiling distillates, as such metals, even in amounts as small as a few parts per million, can adversely affect cracking catalyst selectivity. Thus, other things being equal, cracking catalyst that has been contaminated by deposition of metals such as nickel and vanadium tends to form relatively lower proportions of hydrocarbons boiling in the gasoline range and relatively greater proportions of gas and coke. Although reduced gasoline production is of itself objectionable, the problem is compounded by the fact that increased coke production in turn restricts the capacity of a given cracking installation.

The metal contaminants found in crude oils normally tend to be concentrated in the heavy ends or residual fractions. As a result, it has been possbile to prepare low metal content catalytic cracking stocks simply by distillation of crude oils to form low metal content distillate cracking stocks and residues of higher metal content, which residues can be disposed of as such in the form of heavy fuel oil. However, preparation of low metal content catalytic cracking stocks by distillation alone may result in the loss to products of low market-value of unduly large amounts of low metal content oils that are also suitable as catalytic cracking stocks.

Accordingly, it has been proposed to treat in various ways the high metal content, vacuum distillation bottoms resulting from the fractional distillation overhead of low metal content cracking stocks, so as to produce additional quantities of low metal content cracking charge stock and at the same time reduce production of residual fuel. For example, it has been proposed to subject such vacuum distillation residues to a solvent decarbonizing, that is, solvent deasphalting, treatment to separate the more paraffinic, low metals content components from the more asphaltic, high metals content components. It has also been proposed further to improve the separation obtained in the solvent decarbonizing procedure by the use of a low metals content wash oil that is rich in aromatic, and that is immiscible with the decarbonized oil and decarbonizing solvent solution, to selectively extract additional metal-containing hydrocarbons from the decarbonized oil-solvent solution, the wash oil, enriched in metal-containing hydrocarbons, being removed from the system together with the precipitated asphalt phase obtained during the decarbonizing operation. The heavier fractions of catalytic cycle stocks, obtained by distillation or solvent deasphalting of full range cycle stocks, and the residual fractions obtained by distillation or solvent deasphalting of clarified or decanted oils, are examples of oils that have been proposed for use as wash oils in decarbonizing operations. By "decanted oil" is meant the oil that is obtained as a bottoms fraction during the fractional distillation of catalytically cracked oils, after separation, by gravity settling or other means of entrained catalyst particles. However, none of these previously proposed wash oils has been entirely satisfactory for this purpose, either for the reason that a portion of a stock that ordinarily would be recycled to the catalytic cracking operation is diverted to a lower quality product, as is the case when catalytic cycle stock fractions are used as wash oils, or for the reason that significant capital and operating costs are incurred in the special, preparatory treatments, i.e., distillation and/or solvent deasphalting, required in preparing such wash oils. Moreover, previous wash oil treating procedures are also subject to the objection that on occasion, not enough of a given wash oil may be available in a given refinery installation for once-through treating at the desired wash oil:charge stock ratio.

In accordance with the present invention, improved yields of low metals content oils suitable for use as catalytic cracking charge stock are obtained by the use of a wash oil during solvent decarbonizing of high boiling petroleum oils containing metal contaminants, while at the same time avoiding difficulties arising from wash oil deficiencies as well as the costs incurred in preparing previously used wash oils. In a broad sense, the present invention involves a procedure wherein a high boiling petroleum oil fraction, such as a residual oil obtained in the vacuum distillation of a petroleum crude oil, containing objectionable amounts of metallic contaminants is solvent decarbonized in a solvent decarbonizing zone with a liquefied, normally gaseous hydrocarbon, for example, propane or propane-containing mixtures, or other C_{1-4} hydrocarbons, under conditions effective to form a solution of decarbonized oil, i.e., deasphalted oil of relatively low metals content in said solvent, and a relatively high metals content asphaltic fraction that is relatively immiscible therewith. A wash oil comprising a low metals content, tar-containing gas oil is introduced into the solvent decarbonizing zone whereby a partial separation of the gas oil and tar components of the wash oil is effected. The decarbonized oil solution and the partly separated gas oil components are then contacted in a portion of the decarbonizing zone under conditions and for a time effective to permit the asphaltic components in the decarbonized oil solution to come to equilibrium with respect to the asphaltic components of the gas oil portion of the wash oil, while the decarbonized oil and the partly separated tar components of the wash oil are separately contacted in another portion of the decarbonizing zone for a time and under conditions effective to permit the metals in the decarbonizing oil solution to come to equilibrium with respect to the metals in the tar components of the wash oil. The portion of the decarbonizing zone in which the decarbonized oil solution and the partly separated gas oil components of the wash oil are contacted must contain a sufficient number of stages to permit equilibrium to be reached with single pass contacting. This requirement being satisfied, the contacting of decarbonized oil solution and the partly separated tar components of the wash oil can also be separated with single pass contacting, provided that sufficient additional stages are available in the contacting zone to permit the metals in the decarbonized oil solution to come to equilibrium with the metals in the tar components of the wash oil. However, when insufficient stages are available in the decarbonizing zone to permit equilibrium to be reached with respect to metals in a single pass, as will be the case when decarbonizing tower height or oil quality are limiting factors, equilibrium with respect to metals can be achieved by separating a portion of the partly metals-contaminated tar components of the wash oil from the decarbonized oil solution after contact therewith, admixing the same with fresh, low metals content, tar-containing gas oil, and recycling the thus-obtained mixture as the wash oil to the decarbonizing oil zone. It is preferred to employ the recycle wash oil to fresh wash oil in ratios in the range of about 0.33:1 to 1:1, but other ratios, both lower and higher, can be used. Tar-containing gas oils having an oil:asphalt ratio in the range of about 1:1 to 5:1 are the preferred wash oils for purposes of this invention, but oils having other oil:asphalt ratios can be used. For example, gas oils can be used having an oil:asphalt ratio in the range of about 0.5:1 to 9:1. Excellent results have been obtained with a full range decanted oil having an oil:asphalt ratio of about 3:1. The novel wash oils referred to herein are most useful when employed in a ratio with the oil charge to the solvent decarbonizing operation of at least 0.2:1, but smaller and greater ratios, for example, as low as 0.1:1 or as high as 5:1, can be used.

In accordance with an advantageous embodiment of the invention, a decarbonized oil-decarbonizing solvent solution, containing augmented quantities of oil suitable as catalytic cracking stock that has been demetallized by contact with wash oil, is separately removed from the processing zone and the solvent is removed and recovered therefrom, for example, by evaporation and stripping. The resulting oil of low metals content, low carbon residue (low asphalt) oil is blended with other cracking stock, such as the low metals, heavy gas oil obtained from the same vacuum reducing operation in which the charge to the decarbonizing operation is obtained, and/or regular catalytic cycle stock, and introduced into a catalytic cracking zone to produce cracked hydrocarbons of lower molecular weight. In an especially advantageous embodiment, cracked products are subjected to fractional distillation to separate distillate fractions having various boiling ranges, and a bottoms fraction containing entrained catalyst particles. Oil from this bottoms fraction is separated from catalyst and introduced into the wash zone as fresh, make-up wash oil.

Referring briefly to the attached figure of drawing, there is shown the simplified flow diagram of a preferred solvent decarbonizing operation utilizing one of the novel wash oils of the present invention, wherein a portion of the partially spent wash oil is collected after contact with decarbonized oil-decarbonizing solvent solution, withdrawn from the solvent decarbonizing operation, and recycled through the decarbonizing zone in admixture with fresh oil.

The invention is readily understood in detail by more particular reference to the attached drawing. In accordance with the process flow scheme illustrated, the charge stock to a solvent decarbonizing operation, comprising in the instance illustrated a vacuum reduced crude oil obtained as the bottoms fraction from a vacuum distillation tower, not shown, and containing substantial proportions of metallic contaminants such as vanadium and nickel, is introduced by way of line **2** into solvent decarbonizing tower **4** at about the mid-point thereof. While the feed in the present instance is described as a vacuum reduced crude oil, other metals-containing residual oils of petroleum origin, that is, oils having a major portion of constitutents that boil above about 900° F., can be used. For example, visbroken residual oils can be used.

Tower **4** is equipped internally with suitable baffles, not numbered, or other equivalent means to insure thorough inter-contact between decarbonizing solvent, described below, and the oil feed stock, and between the wash oil, described below, and the decarbonized oil-decarbonizing solvent solution. Within tower **4** the oil feed stock is countercurrently contacted with a decarbonizing or deasphalting solvent introduced into the bottom section of tower **4** from solvent storage vessel **6** by way of line **8**. That is, as the oil feed stock descends through the tower below the point of introduction, it is intimately contacted with a rising flow of decarbonizing solvent. The oily components of the feed stock tend to be dissolved in the decarbonizing solvent and to be carried upwardly therewith, and the asphaltic components, with which the bulk of the metallic contaminants are included, tend to be precipitated and to descend to the bottom section of the decarbonizing tower.

The deasphalting or decarbonizing solvents, and pressures employed in the solvent:oil ratios and treating temperatures of the process are conventional, as such. The solvent comprises a low molecular weight, liquefied, normally gaseous hydrocarbon such as methane, ethane, propane, butane or mixtures thereof. Pentane and hexane can also be used, but with less effective results. The decarbonizing solvent may contain straight and branched-chain hydrocarbons as well as unsaturates such as propylenes and butylenes. Contact between the metal-containing oil feed stock and the decarbonizing solvent can be effected in any convenient way, in a single stage or in multiple countercurrent stages, but is preferably achieved by the use of counterflow towers of the kind illustrated in FIGURE 1. The decarbonizing solvent:oil ratio is preferably maintained in the range of about 2.5:1 to 5:1 by volume, but in some instances, for example, when stage contacting is utilized, solvent:oil ratios as high as 9:1 may be desirable. The lowest solvent:oil ratio consistent with the desired separation is preferred for economic reasons, as the operating costs of the process are directly related to the volume of solvent handled. Solvent decarbonizing temperatures, like the solvent:oil ratio, are selected in accordance with the nature of the oil feed stock and in accordance with the separation desired. Average decarbonizing temperatures of 120° to 130° F. are not uncommon but may reach as much as 200° F. or higher. Temperatures less than 70° F. are undesirable as wax is precipitated at such temperatures. When counterflow towers of the kind illustrated in the drawing are employed, a temperature gradient of up to 60° F. can be used to improve the separation between oily and asphaltic components. The pressures maintained in the decarbonizing zone should always be sufficient to maintain the solvent in the liquid phase at the highest temperature in the decarbonizing zone. Such pressures may reach several hundred p.s.i.g.

Precipitated asphalt containing some decarbonizing solvent, and containing the bulk of the metal contaminants in the oil feed stock together with the metals-contaminated, asphaltic components of the wash oil, are withdrawn from the bottom of tower **4** by way of line **10** and heated in furnace **12** prior to passage into asphalt flash drum **14** by way of line **15**. A portion of the decarbonizing solvent is flashed off from the asphalt in drum **14** and recycled to solvent storage vessel **6** by way of lines **16**, **18** and **20**. Precipitated asphalt containing only traces of decarbonizing solvent is removed from the bottom of flash drum **14** by way of line **22** and introduced into the top of asphalt stripper **24**, where any remaining decarbonizing solvent is removed from the asphalt by steam stripping and recycled to solvent storage vessel **6** by way of lines **26**, **28** and **20**. Solvent-free asphalt is removed from stripper **24** by way of line **30**.

A solution of substantially metals-free decarbonized oil in decarbonizing solvent is withdrawn from the top of tower **4** through line **32**. This solution is passed into a first evaporator **34**, where a portion of the decarbonizing solvent is removed by evaporation through indirect heat exchange with low pressure steam. Decarbonizing solvent evaporated in evaporator **34** is removed by way of line **36** and is returned to storage vessel **6** by way of lines **18** and **20**. The decarbonizing oil-solvent distillation residue from evaporator **34** is withdrawn by way of line **38** and conducted to a second evaporator **40**, where additional decarbonizing solvent is removed by evaporation through indirect heat exchange with high pressure steam. This solvent is removed from evaporator **40** by way of line **42** and recycled to storage vessel **6** by way of lines **18** and **20**. The decarbonized oil residue from evaporator **40** is withdrawn from line **44** and introduced into the top of decarbonized oil stripper **46**, where the last traces of decarbonizing solvent are removed from steam stripping. Stripped solvent passes overhead from tower **46** through lines **48** and **50**, into jet condenser **52**, where stripping steam is condensed and separated. Decarbonizing solvent from jet condenser **52** is then passed through line **28** through compressor **54** for reliquefication and recycling to solvent storage vessel **6** by way of line **20**. Solvent-free decarbonized oil is removed from stripper **46** by way of line **56**. The decarbonized oil in line **56** is then admixed with an oil stream from line **58** comprising a low metals content, heavy gas oil catalytic cracking charge stock obtained as a distillate from the same vacuum distillation tower (not shown) in which there was produced the vacuum reduced crude oil feed to tower **4**. If desired, the thus-obtained oil may also have admixed therewith catalytic cycle stock obtained from tower **64**.

The mixture of decarbonized oil from line **56** and low metals content, heavy gas oil from line **58** is introduced into catalytic cracking zone **60**, which is illustrated purely schematically, where this oil is subjected to catalytic cracking, preferably fluidized catalytic cracking, with a cracking catalyst in conventional manner. The conditions employed in catalytic cracking zone **60** and the details of the structure thereof have not been illustrated or set forth in detail since such conditions and details are entirely conventional and, as such, form no part of the present invention. Very briefly, it may be mentioned that general descriptions of both upflow and downflow catalyst cracking, including cracking catalyst, operating temperatures, space velocities, regeneration temperatures, etc., can be found in Nelson's Petroleum Refinery Engineering, third edition, pages 667–702. In addition, simplified flow diagrams and brief descriptions of commercially available upflow and downflow catalytic cracking processes can be found in the 1962 Refining Process Handbook of the Petroleum Refiner, pages 155–160.

Cracked products are withdrawn from cracking zone **60** by way of line **62** and introduced into fractionating tower **64** for separation into products of various boiling range and removal by way of lines **66**, **68**, **70** and **72**. The bottoms product obtained in tower **64**, containing entrained catalyst from catalytic cracking zone **60**, sometimes referred to as "slurry oil," is withdrawn from the bottom of tower **64** by way of line **74** and introduced into settling vessel **76**, or other equivalent means for separating oil from entrained catalyst. A full range decanted oil is withdrawn from settler **76** by way of line **78**. A slurry of settled catalyst and oil is withdrawn from the bottom of settling vessel **76** by way of line **90** from which such slurry can be recycled to catalytic cracking zone **60**, by means not shown. The full range decanted oil obtained from vessel **76** by way of line **78**, comprising a substantially metals-free oil boiling in the gas oil range and containing tars formed during cracking, is pumped through lines **80**, **82** and **84** into the upper section of solvent decarbonizing tower **4** to act as a wash oil, whereby a partial separation of the gas oil and tar components in the wash oil is effected. If desired, suitable distributing means such as spiders, sparges, or other equivalent means may be utilized to introduce the wash oil into the tower **4**. The elevation in decarbonizing tower **4** at which the wash oil is introduced is sufficiently far below the top of the tower that the number of stages above the point of wash oil introduction are adequate to permit the decarbonized oil solution to come to equilibrium with respect to the asphaltic components of the partly separated gas oil components of the wash oil. As a practical matter, the maximum, permissible elevation for wash oil introduction will vary according to the oil quality, the decarbonizing conditions, decarbonizing tower structure, etc., and can be determined in any given case by trial and error. Equilibrium will have been reached when no further change in decarbonized oil quality is observed for lower wash oil inlet elevations.

The wash oil is introduced into the tower in a volume ratio of at least about 0.1:1 and preferably at least 0.2:1 with the oil feed. Higher wash oil:oil feed ratios can be used, but no additional advantages with respect to demetallization will be obtained at volume ratios in excess of about 5:1.

Inside tower **4** the partly separated gas oil components of the wash oil flow upwardly through the decarbonizing zone wherein the degree of contacting efficiency is such as to permit the decarbonized oil solution to come to equilibrium with the asphaltic constituents of the gas oil components of the wash oil. The partly separated tar components of the wash oil, being heavier than the decarbonized oil-solvent solution and immiscible therewith, flow downwardly in countercurrent contact with the upwardly flowing decarbonized oil-solvent solution. During such intercontact, metal-containing hydrocarbons contained in the decarbonized oil are preferentially extracted from the decarbonized oil and dissolved in the tar components of the wash oil, and the decarbonized oil solution is permitted to come to equilibrium with respect to the metals in the tar components of the wash oil, either after a single pass or with recycle of tar components. Again, the numbers of stages required to reach equilibrium will vary according to the nature of the oil, the decarbonizing conditions, the tower structure, etc., and can be determined for a given case by trial and error.

The nature of the oil employed as a wash oil is important for purposes of the present invention, since not every oil capable of extracting metals from the decarbonized oil-solvent solutions aids in producing improved yields of decarbonized oil. Nevertheless, any low metals content, tar-containing gas oil having an oil:asphalt volume ratio in the range indicated can be used with good results. A specific example of a preferred wash oil is a full range decanted oil, but other oils within the indicated class can be used with good results. For example, there can be used tar-containing gas oils obtained from thermal cracking of gas oils, tar-containing gas oils obtained from thermal cracking of catalytic cracking cycle stocks, tar-containing gas oils obtained from thermal cracking of decanted oils, and tar-containing virgin gas oils from crude oils that are substantially free from metallic contaminants, e.g., Anaco crude oil.

The tar-containing gas oils useful in the present invention are characterized, inter alia, by a low metals content, normally less than 1 p.p.m., so that such oils will possess a strong solvent capacity for the metallic contaminants in the decarbonized oil. The tar-containing gas oils of the present invention are also characterized by a significant oil:asphalt volume ratio (as determined by solvent deasphalting to effect separation of oil and asphaltic components) of at least 0.5:1 and preferably at least 1:1. Normally, the oil-asphalt ratio will not exceed about 5:1, but oil:asphalt ratios up to about 9:1 can be used with the wash oil:oil feed ratios disclosed herein. Wash oils having oil:asphalt ratios in the range indicated are markedly superior to wash oils having lower oil:asphalt ratios from the standpoint of decarbonized oil yields and benefits attributable to recycling, and they are superior to oils of greater oil:asphalt ratios from the standpoint of demetallization.

Referring again to the drawing, the downflowing tar components of the wash oil in tower **4**, partly enriched with respect to metal contaminants extracted from the decarbonized oil, are collected in trap tray **86** positioned at a lower elevation in solvent decarbonizing tower **4** than wash oil inlet line **84**.

In the instance illustrated, insufficient stages are present between the wash oil inlet and the charge inlet for equilibrium to be reached by the decarbonized oil solution with respect to the metals content of the tar components of the wash oil in a single pass contacting. Accordingly, provision for recycle has been made. A portion of the partly contaminated wash oil is permitted to overflow the weir of trap tray **86** and pass downwardly through the tower and out of the system along with the precipitated asphalt. Another portion of the partly contaminated wash oil collected in trap tray **86** is withdrawn through line **88** and admixed with fresh wash oil in line **82** for recycling to the solvent decarbonizing tower through line **84**. Appreciable benefits attributable to recycling are obtainable when the wash oil is recycled in a volume ratio of at least about 0.2:1 with respect to the oil feed to the decarbonizing operation, but volume ratios of at least about 0.025:1 and up to about 2.5:1 are preferred. However, greater proportions of recycle wash oil with respect to oil feed, for example, up to about 3.33:1, can be used. The above-indicated wash oil:feed stock proportions will be obtained when the recycle wash oil:make-up wash oil volume ratios are in the range of about 0.25:1 to about 2:1, and preferably within the range of about 0.33:1 to 1:1, that is, when the recycle wash oil is employed in proportions of about 25 percent to about 200 percent, and preferably about 33 percent to about 100 percent, by volume, of the fresh, make-up wash oil.

The beneficial results of the process of the present invention have been demonstrated by a series of comparable experimental runs wherein a vacuum distillation bottoms fraction obtained by vacuum distillation of a crude petroleum oil was solvent decarbonized with an approximately 40:60 mol ratio mixture of propane and butane, using a solvent:oil ratio of approximately 5:1 in a solvent decarbonizing tower at temperatures ranging from 170° F. at the solvent inlet at the bottom of the tower to 200° F. at the top of the tower, at a tower pressure of 500 p.s.i.g. The tower was 30 feet in height and was baffled at 2 inch intervals over 26 feet 8 inches of height. The tower contained five theoretical stages, or one stage per 5.35 feet of height. The wash oil utilized in the runs was a full range decanted oil having a vanadium content of 0.3 p.p.m. and a nickel content of 0.1 p.p.m., an oil:asphalt ratio, as determined by vacuum flashing at a temperature of 840° F. corrected to 760 mm. Hg, of about 3:1, a viscosity of 49.4 SUS/210° F., a carbon residue of 4.87 percent, and a pentane-insolubles content of 1.76 percent. The overhead and bottoms material derived from the aforesaid vacuum flashing and propane solvent treating, respectively, of the decanted oil had the following inspections:

	Vacuum Flashing	Solvent Treating
Overhead (74.4%):		
Gravity, ° API	10.1	15.6
Viscosity, SUV, sec. at—		
150° F	60.0	--------
210° F	40.2	40.03
Sulfur, percent	2.0	--------
Carbon Residue, percent	0.52	0.49
Aniline Point, ° F	138	--------
Metals, p.p.m.:		
Nickel	0.1	0.1
Vanadium	0.2	0.1
Bottoms (25.6%):		
Specific Gravity	1.15	1.236
Viscosity, SUV: sec. at—		
210° F	1,102	55.5
300° F	87.3	2.59
Pentane Insolubles, percent	94.5	--------
Carbon Residue, percent		13.76
Metals, p.p.m.:		
Nickel		0.1
Vanadium		0.2

In a first test run no wash oil was employed; in a second test run wash oil was passed through the decarbonizing tower in a single pass or once-through operation. In this run, wash oil was introduced 3.5 feet—approximately 0.65 stage—below the top of the tower, and the charge oil inlet was 10.2 feet—approximately 1.9 stage—below the wash oil inlet and the tower height above the wash oil inlet was insufficient to permit the decarbonized oil solution to come to equilibrium with respect to the asphaltic constituents of the gas oil components of the wash oil. However, the tower height between the wash oil inlet and the charge inlet was sufficient to permit the decarbonized oil solution to come to equilibrium with respect to the metal components of the tar components of the wash oil.

In a third test run the wash oil inlet and the charge inlet were both 17.8 feet—approximately 3.3 stages—below the top of the tower. The tower height above the wash oil inlet was sufficient for the decarbonized oil to reach equilibrium with respect to the asphaltic components of the gas oil portion of the wash oil, but the tower height between the wash oil inlet and the charge inlet was insufficient for the decarbonized oil to reach equilibrium with respect to the metals in the tar components of the wash oil.

In a fourth, composite test run the wash oil inlet is 13.4 feet—approximately 2.5 stages—below the top of the tower, a wash oil recycle trap tray is about 2.7 feet—approximately 0.5 stage—below the wash oil inlet and about 2.7 feet—about 0.5 stage—above the charge inlet, and wash oil is recycled to the wash oil inlet. In this run, there is sufficient tower height above the wash oil inlet for the decarbonized oil to reach equilibrium with respect to the asphaltic constituents of the gas oil portion of the wash oil, and with recycling of a portion of the wash oil there is also sufficient tower height between the charge inlet and the wash oil inlet to permit the decarbonized wash oil to reach equilibrium with respect to the metals in the tar components of the wash oil.

	Oil Charge to Decarbonizer	(1) Solvent Decarbonizing, No Wash Oil	(2) Solvent Decarbonizing, Wash Oil, No Recycle	(3) Solvent Decarbonizing, Wash Oil, No Recycle	(4) Solvent Decarbonizing, Wash Oil With Recycle
Description:					
Total Wash Oil to Charge Ratio; vol./vol			0.232	0.25	0.487
Make-up Wash Oil to Charge Ratio; vol./vol			0.232	0.25	0.254
Recycle Wash Oil to Charge Ratio; vol./vol					0.233
Yields:					
Decarbonized Oil, Percent by vol. of Oil Charge		54.12	76.53	70.5	76.21
Asphalt, Percent by vol. of Oil Charge		45.88	46.67	54.5	49.19
Inspections:					
Decarbonized Oil:					
Gravity, °API	8.5	18.4	14.6	16.4	16.4
Viscosity, SUS, sec. at—					
150° F		1,802	698		
210° F		292	163	393	393
Carbon Residue, wt. Percent	17.5	3.38	2.88	3.06	2.5
Metals, p.p.m.:					
Nickel	56	2.0	1.8	4.4	0.7
Vanadium	215	6.4	1.8	9.5	1.3
Asphalt:					
Viscosity, SUS, at 300° F	567	27,535	21,292		20,330
Specific Gravity			1.0320		1.0654

A comparison of the results obtained for the various test runs shows that the use of a wash oil of the class and in the manner disclosed herein results in both a significant reduction in the metals content and improved bulk quality of decarbonized oil, as determined by carbon residue, API gravity, and viscosity. The yields of decarbonized oil are also markedly improved when a wash oil is used.

More particularly, from a comparison of the results presented in the numbered columns, it will be seen that the use of a wash oil of the kind disclosed herein, together with recycle of a portion of the partly contaminated oil, effects a marked reduction in the metal contaminants of the overhead decarbonized oil stream and also results in a considerable increase in the yield of decarbonized oil that is available as low metal content catalytic cracking stock. It is significant with respect to the improvement in yield of decarbonized oil that the percent increase obtained (>21 percent by volume of the reduced crude charge stock) is larger than the entire gas oil content (18.6 percent by volume of the reduced decarbonized charge stock) of the decanted oil. Moreover, the decarbonized oil that is obtained as extra yield is of good quality for use as a cracking stock. This is somewhat surprising as decanted oil, as such, was previously considered poor quality cracking stock. This seeming inconsistency is probably explainable on the ground that the decarbonizing solvent treatment removed from the decanted oil the components chiefly responsible for the poor reputation of the decanted oil as cracking stock.

In a specific embodiment of the herein-disclosed process, 15,700 barrels per day of a vacuum distillation tower bottoms, obtained from the vacuum reduction of a crude petroleum oil, said bottoms having an API gravity of 8.5°, a Ramsbottom carbon residue of 17.45 and a Saybolt viscosity of 567 seconds at 300° F., a vanadium content of 215 p.p.m. and a nickel content of 56 p.p.m., is introduced into a solvent decarbonizing tower 52 feet in height and equipped with baffles at 2 foot intervals over 42 feet, equivalent to seven stages, for contact with 78,450 barrels per day of decarbonizing solvent. The charge inlet is 4.5 stages or 27 feet below the top baffles in the tower. The oil is countercurrently contacted in the tower with decarbonizing solvent comprising an approximately 1:1 by volume ratio mixture of propane and n-butane, using a solvent:oil ratio of approximately 5:1. Decarbonizing temperatures employed are 200° F. at the top of the tower, 185° F. at the oil inlet and 170° F. at the solvent inlet. Tower pressure is 500 p.s.i.g. Decarbonized oil-solvent mixture is contacted in the upper section of the tower with approximately 7,520 barrels per day of a wash oil introduced four stages or 24.0 feet between the top baffle in the tower. The wash oil consisting of 3,900 barrels per day of a fresh, full range decanted oil and 3,620 barrels per day of recycled wash oil withdrawn from a trap tray positioned in the solvent decarbonizing tower below the wash oil-oil inlet and above the asphalt phase. The fresh wash oil, that is, the full range decanted oil, has an oil:asphalt ratio of about 3:1, a gravity of 5.0° API, a viscosity of 49.6 SUS at 210° F., a carbon residue of 4.87, a vanadium content of 0.3 p.p.m., and a nickel content of 0.1 p.p.m. A mixture of 8,824 barrels per day of precipitated asphalt and contaminated wash oil and 8,820 barrels per day of decarbonizing solvent are withdrawn from the solvent decarbonizing tower for recovery of solvent by solvent flash and stripping. Decarbonized oil solution is removed overhead from the decarbonizing tower for recovery of solvent by solvent flash and stripping at the rate of 10,776 barrels per day of decarbonized oil and at the rate of 69,630 barrels per day of decarbonizing solvent. Approximately 10,776 barrels per day of a decarbonized oil having an API gravity of about 16.4°, a viscosity of 393 SUS at 210° F., a carbon residue of 2.5, a vanadium content of 1.3 p.p.m., and a nickel content of 0.7 p.p.m. is produced. This oil, together with additional low metals, distillate catalytic cracking stock obtained in the production of the vacuum distillation tower bottoms, is then contacted with a silica-alumina cracking catalyst in a fluidized catalytic cracking zone at a temperature of 950° F., and the cracked products are fractionally distilled to separate various overhead fractions, and a bottoms fraction, capable of yielding 3,900 barrels per day of a full range decanted oil.

In another embodiment the same processing operations are carried out without recycle of wash oil, using a similarly constructed decarbonizing tower 58 feet in height, of which 45 feet of height is equipped with baffles. The wash oil inlet is 18 feet below the uppermost baffle in the tower and the charge inlet is 12 feet below the wash oil inlet.

The herein-disclosed process is quite flexible and can be varied in many ways to suit the desired end. For example, by increasing the severity of the solvent decarbonizing operation to obtain a more complete separation of oil and asphaltic components, one can obtain still lower metals content oils than demonstrated in the specific experimental runs described herein. On the other hand, when it appears that a higher metals content than that obtained in the decarbonized oil under given conditions can be tolerated, the process can advantageously be modified by reducing the decarbonizing solvent:feed stock ratio. Under such circumstances, the wash oil and recycle achieves part of the demetallization that normally would be achieved by the decarbonizing solvent, and the use of the disclosed wash oils and recycle makes it possible to utilize less decarbonizing solvent. This feature is important from an economic standpoint in that the operating costs for solvent decarbonizing depend directly on the volume of solvent utilized in the process.

It will be understood that the herein-disclosed embodiments of the invention are illustrative only, and that good results also will be obtained with still other decarbonizing solvents, other decarbonizing conditions and other substantially metals-free, tar-containing gas oils and wash oils of the kind disclosed herein, and with other recycle wash oil to charge stock ratios within the range disclosed.

The term "gas oil" is defined by the 1962 "ASTM Standards on Petroleum Products and Lubricants" D–288 specification as a liquid petroleum distillate having a viscosity intermediate between that of kerosene and lubricating oils. Nelson, in Petroleum Refinery Engineering, 1949, page 183, indicates "gas oil" to be the material boiling between kerosene and residual oil in a topping operation.

The term "tar" is used herein to mean petroleum tar. The ASTM D–288 specification referred to above defines petroleum tar as viscous black or dark-brown product obtained in petroleum refining, which will yield a substantial quantity of solid residue when partially evaporated or fractionally distilled.

The term "stage" is used herein in its usual sense in countercurrent liquid-liquid contacting to mean a contacting zone affording a contacting efficiency such that the liquid leaving the end of the stage is at equilibrium with the liquid leaving the other end of the stage, at the temperature of the stage.

Numerous other modifications and variations of the invention as described herein will suggest themselves to those skilled in the art, and such modifications and variations can be resorted to without departing from the spirit or scope of the herein-described invention. Accordingly, the invention is not to be limited by the embodiments disclosed herein but only by the scope of the claims appended hereto.

I claim:

1. A method for refining a high boiling petroleum fraction containing both oil and asphaltic components and also containing substantial amounts of metallic contaminants, comprising contacting said fraction with a liquefied normally gaseous hydrocarbon decarbonizing solvent in a decarbonizing zone under conditions effective to form a solution of decarbonized oil of relatively low metals-content in said solvent, and a relatively high metals-content asphaltic fraction that is relatively immiscible with said solution of decarbonized oil, introducing directly into the decarbonized oil solution a wash oil in a volume ratio in the range of about 0.2:1 to 5:1 with respect to said petroleum fraction, said wash oil comprising a relatively low metals-content, tar-containing oil boiling in the gas oil range and having and oil:asphalt ratio in the range of about 1:1 to 5:1, whereby a partial separation of the gas oil and tar components of the wash oil is effected, contacting the decarbonized oil solution and the partly separated gas oil components in a first portion of the decarbonizing zone under conditions and for a time effective to permit the decarbonized oil solution to come to equilibrium with respect to the asphaltic components of the gas oil portion of the wash oil, while contacting the decarbonized oil and the partly separated tar components of the wash oil in a second portion of the decarbonizing zone under conditions and for a time

effective to permit the decarbonized oil solution to come to equilibrium with respect to the metals in the tar components of the wash oil, separating partly contaminated tar components of the wash oil from decarbonized oil solution that has been contacted therewith, recycling for use as said wash oil the thus-separated material in admixture with fresh, low metals-content, tar-containing gas oil in a proportion of about 25 percent to 200 percent by volume of said fresh oil, and separately withdrawing decarbonized oil solution of low metals-content and said asphaltic fraction of high metals-content from said decarbonizing zone.

2. A method for refining a high boiling petroleum fraction containing both oil and asphaltic components and also containing substantial amounts of metallic contaminants, comprising contacting said fraction with a liquefied normally gaseous hydrocarbon decarbonizing solvent in a decarbonizing zone under conditions effective to form a solution of decarbonized oil of relatively low metals-content in said solvent, and a relatively high metals-content miscible with said solution of decarbonized oil, introducing directly into the decarbonized oil solution a wash oil in a volume ratio in the range of about 0.2:1 to 5:1 with respect to said petroleum fraction, said wash oil comprising a relatively low metals-content, tar-containing oil boiling in the gas oil range and having an oil:asphalt ratio in the range of about 1:1 to 5:1, whereby a partial separation of the gas oil and tar components of the wash oil is effected, contacting the decarbonized oil solution and the partly separated gas oil components in a first portion of the decarbonizing zone under conditions and for a time effective to permit the decarbonized oil solution to come to equilibrium with respect to the asphaltic components of the gas oil portion of the wash oil while contacting the decarbonized oil and the partly separated tar components of the wash oil in a second portion of the decarbonizing zone under conditions and for a time effective to permit the decarbonized oil solution to come to equilibrium with respect to the metals in the tar components of the wash oil, separating partly contaminated tar components of the wash oil from decarbonized oil solution that has been contacted therewith, recycling for use as said wash oil the thus-separated material in admixture with fresh, low metals-content, tar-containing gas oil in a proportion of about 33 percent to 100 percent by volume of said fresh oil, and separately withdrawing decarbonized oil solution of low metals-content and said asphaltic fraction of high metals-content from said decarbonizing zone.

References Cited

UNITED STATES PATENTS

2,853,426	9/1958	Peet	208—309
2,882,219	4/1959	Johnson	208—86

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U.S. Cl. X.R.

208—86, 251

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,423,308 January 21, 1969

James R. Murphy

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 75, "fresh oil" should read -- fresh wash oil --. Column 8, in the table, third column, line 9 thereof, "1.236" should read -- 1.136 --. Column 12, line 21, cancel "miscible" and insert -- asphaltic fraction that is relatively immiscible --.

Signed and sealed this 24th day of March 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents