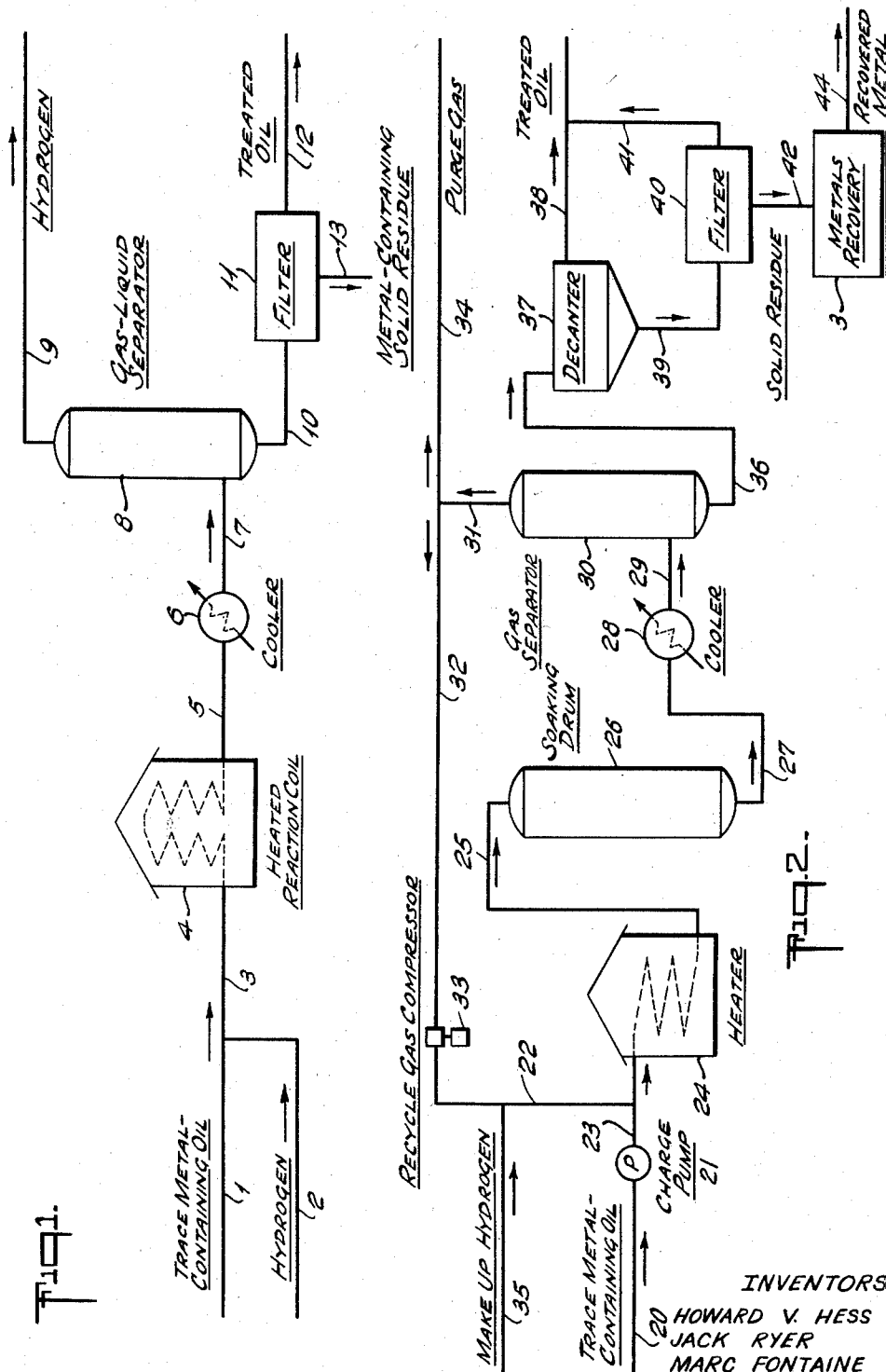


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PROCESS FOR REMOVING TRACE METALS WITH HYDROGEN
AND AN INERT PACKING MATERIAL
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PROCESS FOR REMOVING TRACE METALS WITH HYDROGEN AND AN INERT PACKING MATERIAL**Howard V. Hess, Glenham, Jack Ryer, Wappingers Falls, and Marc Fontaine, Fishkill, N.Y., assignors to Texaco Inc., a corporation of Delaware**

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8 Claims. (Cl. 208—251)

This invention is concerned with the treatment of petroleum crude oils and residual oils to effect the removal of trace metal components.

It has long been known that various metallic elements are found in naturally occurring petroleum crude oils. Among the metallic elements which have been found in crude oils are: iron, nickel, vanadium, aluminum, sodium, copper, calcium, magnesium, manganese, barium, silicon, chromium, tin, lead, molybdenum, strontium, cobalt, beryllium, lithium, rubidium, silver, bismuth, titanium, zinc, potassium, and gold.¹ In addition to naturally occurring metals, extraneous metals may be introduced in the refining of crude oils and appear in the residual oils from crude oil distillation.

Some of these metals are known to be harmful when included in charge stocks for further refining. In catalytic cracking, the presence of minute amounts of heavy metals, for example, iron, nickel, vanadium and copper in the charge stock causes greatly increased gas and coke yields and reduced gasoline production. Some of these metals, particularly nickel and vanadium, have been found to be undesirable in fuels for boilers and combustion turbines. In the case of boiler fuels, these metals accelerate the deterioration of the common refractory materials. In the case of combustion turbines, these metals accelerate corrosion, and failure of the turbine blades.

Because of the harmful effects of trace metal components of crude and residual oils, these oils have usually been considered unsatisfactory for inclusion in the charge to catalytic cracking facilities. One method of preparing catalytic cracking feed stocks from such metal-containing oils has been to use low pressure distillation to separate a distillate charge stock. However, when high yields of distillate are obtained, trace metals are frequently found in the distillates in objectionable quantities. Although some of these metals may be introduced into the distillate by mechanical entrainment, it appears that the naturally occurring metals are present in the form of metallo-organic compounds of significant vapor pressure and are distilled with the oil.

This invention provides a means by which crude oils, residual oils, and other contaminated oils may be treated to render them satisfactory for inclusion in catalytic cracking charge stock, boiler fuels, turbine fuels, or for other applications where trace metallic components are undesirable. In the method of this invention, the oil

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to be treated is contacted with hydrogen under conditions such that at least a portion of the hydrogen is reacted with a component of the oil to produce an oil of increased API gravity and reduced trace metal content, and a solid residue incorporating trace metals. The treated oil is then separated from the metal-containing solid residue. The solid residue may be further processed to recover the metals contained therein.

An advantage of this process is that it provides a method of separating trace metal components from crude petroleum oils, residual oils, and other oils containing metallic contaminants.

A further advantage of this process is that it converts oils of low quality to useful stocks suitable for inclusion in catalytic cracking charge stocks, boiler fuels, and combustion turbine fuels.

Another advantage of this process is that valuable trace metals contained in many oils may be removed in the form of a solid residue. This residue may be further processed to recover the valuable metals contained therein.

The accompanying figures diagrammatically illustrate the process of our invention. Although the drawings are illustrative of embodiments in which the process of this invention may be practiced, it is not intended to limit the invention to the particular apparatus or materials described.

Figure 1 is a flow diagram of one embodiment of the invention. Figure 2 is a flow diagram of another embodiment of the invention. Referring to Figure 1, a trace metal-containing oil to be treated is withdrawn from external storage, not shown, and admitted to the system through line 1. Hydrogen or a hydrogen-containing gas from an external source, not shown, is charged through line 2, admixed with the oil in line 1 and the combined stream is directed through line 3 to heated reaction coil 4. In heated reaction coil 4 the oil and hydrogen are raised to a temperature at which hydrogen reacts at a reasonably rapid rate with a component of the oil. Effluent from reaction coil 4 passes through line 5, cooler 6, line 7 and is discharged into gas-liquid separator 8. Unreacted hydrogen or hydrogen-containing gas is withdrawn from separator 8 through line 9 and discharged from the system. The liquid phase separated in gas-liquid separator 8 comprises a solid residue dispersed in treated oil. This dispersion or suspension is withdrawn from separator 8 through line 10 and directed to filter 11. The solid residue containing trace metals is separated from the treated oil in filter 11, the treated oil withdrawn through line 12 and discharged to external tankage, not shown. The separated metal-containing solid residue from filter 11 is withdrawn by solids handling facilities indicated as line 13 and is transferred to external storage, not shown.

Several modifications of this invention are shown in Figure 2. Referring to Figure 2, a trace metal-containing oil is withdrawn through line 20 from an external source, not shown and is fed to the system by charge pump 21. Hydrogen-containing recycle gas in line 22 is admixed with the oil discharged from pump 21 and transferred through line 23 to heater 24. Heater 24 is used to bring the oil and hydrogen to a temperature at which hydrogen will react rapidly with a component of the oil. The

¹ Milner, O. I., Glass, J. R., Kirchner, J. P., Yurick, A. N., Anal. Chem., 24, 1728 (1952).

heater effluent is then transferred through line 25 to soaking drum 26 which provides additional time for reaction between the oil and hydrogen. Soaking drum 26 may be an unobstructed vessel the function of which is to provide additional reaction time, or as described in more detail later, it may be provided with means to retain at least a part of the solid residue formed by the hydrogenation of the trace metal-containing oil. Effluent from soaking drum 26 is withdrawn through line 27, passed through cooler 28 and line 29, and is discharged into gas separator 30. Hydrogen-containing gas from separator 30 is withdrawn through line 31 and at least a portion recycled through lines 32 and 22 by means of recycle gas compressor 33. The concentration of hydrogen in the recycle hydrogen stream is maintained at the desired value by purging a portion of the recycle gas through line 34 and adding make up hydrogen to the system through line 35. The liquid phase in gas separator 30 comprises a suspension of a solid residue in the treated oil and this liquid phase is withdrawn through line 36 and charged to decanter 37. Decanter 37 is a thickener which separates a clarified oil from an oil of increased solid content and is used to facilitate subsequent filtration. Clarified oil from decanter 37 is withdrawn through line 38 and discharged to treated oil storage, not shown. Oil of increased solids content is withdrawn through line 39 and charged to filter 40. Filtered oil from filter 40 is withdrawn through line 41 combined with the clarified oil in line 38 and discharged to treated oil storage, not shown. The solid residue from filter 40 is withdrawn by means of solid handling facilities indicated diagrammatically as line 42 and is transferred to metal recovery facility 43. The metals content of the solid residue may be recovered by various means. The metals may be concentrated by calcining to remove volatile and combustible materials and leave an ash high in metals content, or the metals may be extracted from the solid residue by extraction with acid. The metal concentrate may then be processed by chemical purification and reduction for recovery of the metal as indicated diagrammatically by line 44.

As mentioned above soaking drum 26 may be provided with a means to retain at least a portion of the solid residue formed in the hydrogenation of the trace metal-containing oil. Solid residue may be separated in soaking drum 26 by packing this vessel with an inert material. A portion of the solid residue is deposited on the packing and to this extent the solids separating load of decanter 37 and filter 40 is reduced. Suitable packings to retain a part of the solid residue are porcelain chips, steel turnings, crushed petroleum coke, gravel, or other similar in-

ert material. If an inert packing is used in soaking drum 26, means for adding and removing the packing, not shown, are required. Addition and withdrawal of inert packing may be continuous during the operation of the process, or a multiple vessel system may be provided so that alternate soaking drums may be disconnected from the system to permit batch discharging and recharging of the packing. Similarly, the metals contained in the residue deposited upon the packing may be recovered by the means described in connection with metals recovery facilities 43.

The invention is further illustrated by the following examples:

EXAMPLE I

In the series of tests of this example an oil containing trace metal components is treated in the presence of hydrogen under the conditions shown. The reaction vessel used in these tests is an unpacked reactor and the treated liquid and solid residue are withdrawn as a suspension and separated by filtration.

Table I lists laboratory tests on the trace metal-containing oils employed in this and the following examples. Table II lists operating data and product quality tests when applying this invention for the removal of trace metals from Mara Crude oil. Table III presents similar data obtained with San Ardo Crude oil. Table IV presents data obtained in applying the process of this invention to a vacuum distillate which contains trace metal components.

It will be noted that the process of this invention may be employed to remove substantially all of the vanadium contained in a heavy crude oil or a heavy vacuum distillate. Essentially complete separation of vanadium is obtained with treated liquid recoveries as high as 96.0 weight percent of the feed oil.

Table I.—Feed stock quality

	Crude I	Crude II	San Ardo Crude	Heavy Paraffin Distillate
Gravity, ° API	29.0	26.1	12.1	18.5
Vis., c.s., at 130° F	11.13	17.51	748	
Vis., c.s., at 210° F	4.57	5.79	107.6	42
ASTM distillation, ° F:				
IBP	162		426	388
10% rec.	288		542	642
50% rec.	664		705	746
End point	752		730	Cracked
Vanadium, p.p.m.	220	220	100	40
Nickel, p.p.m.	15	15	64	11
Iron, p.p.m.	5	5	31	15
Carbon residue, percent	5.8			

Table II.—Tests with Mara Crude¹

Test	A	B	C	D	E	F
Operating conditions:						
Temperature, ° F	700	700	700	700	700	750
Pressure, p.s.i.g.	685	1,000	1,500	2,000	3,000	4,600
Hydrogen rate, cu. ft./bbl.	142.2	192.2	169.8	440.0	657.0	1,073.0
End point						
Yields, basis charge:						
Treated liquid, weight percent	92	91.8	95	94.0	96.0	90.0
Solid residue, weight percent	4.3	4.3	.5	5.0	3.7	1.0
Hydrogen consumption cu. ft./bbl.	4.2	86.2	76.8	293.0	290.3	417.0
Product quality: Treated oil—						
Gravity, ° API	30.4	30.9	30.9	34.6	34.6	39.8
Vis., c.s., at 130° F	3.72		4.11		3.49	1.64
Vis., c.s., at 210° F	1.86		2.0		1.69	0.98
ASTM distillation, ° F:						
IBP					160	150
10% rec.					302	230
50% rec.					556	440
End point					700	760
Vanadium, p.p.m.	32	42	32	5.6	<0.1	<1.0
Nickel, p.p.m.	4	5	3	0.2	0.1	3
Iron, p.p.m.	0.8	0.8	4	0.9	1.0	
Percent vanadium removal	86	81	86	97.4	100	100
Solid residue:						
Vanadium, p.p.m.		2,000	1,400	2,400	4,300	1,600
Nickel, p.p.m.		1,200	1,200	1,300	2,200	1,300
Iron, p.p.m.						3,200

¹ Tests A, B, C, D, and E are made with Mara Crude I and Test F with Mara Crude II.

Table III.—Tests with San Ardo Crude

Test	G	H	J
Operating conditions:			
Temperature, ° F	700	700	750
Pressure, p.s.i.g.	2,000	5,000	4,550
Hydrogen rate, cu. ft./bbl	865.0	1,585.0	1,175.0
Yields, basis charge:			
Treated liquid, weight percent	91.6	96.3	82
Solid residue, weight percent	1.5	1.5	1.2
Hydrogen consumption, cu. ft./bbl	565.0	639.0	915.0
Product quality: Treated oil—			
Gravity, ° API	26.4	22.7	29.3
Vis., c.s., at 130° F		9.35	1.93
Vis., c.s., at 210° F		3.32	1.05
ASTM distillation, ° F.:			
IBP	146	180	112
10% rec.	255	354	221
50% rec.	529	649	447
End point	760	760	760
Vanadium, p.p.m.	1.0	5	0.3
Nickel, p.p.m.	7.0	12	4
Iron, p.p.m.	0.6	1.3	0.2
Percent vanadium removal	99	95	99.7
Solid residue:			
Vanadium, p.p.m.	6,000	2,100	1,200
Nickel, p.p.m.	2,500	1,100	2,700
Iron, p.p.m.	1,800	2,100	1,700

Table IV.—Tests with a heavy paraffin distillate

Test	K	L
Operating conditions:		
Temperature, ° F	700	750
Pressure, p.s.i.g.	2,000	5,000
Hydrogen rate, cu. ft./bbl	663.0	1,105
Yields, basis charge:		
Treated liquid, weight percent	95.6	96
Solid residue, weight percent	3	2.5
Hydrogen consumption cu. ft./bbl	253	410.0
Product quality: Treated oil—		
Gravity, ° API	27.4	33.1
Vis., c.s., at 130° F		3.12
Vis., c.s., at 210° F		1.62
ASTM distillation, ° F.:		
IBP	146	128
10% rec.	365	258
50% rec.	755	581
End point	760+	760+
Vanadium, p.p.m.	0.5	0.7
Nickel, p.p.m.	0.5	<0.02
Iron, p.p.m.	3.0	0.9
Percent vanadium removal	99	98
Solid residue:		
Vanadium, p.p.m.	1,400	1,400
Nickel, p.p.m.	3,000	850

EXAMPLE II

In another series of tests, oils containing trace metal components are treated in the manner used in Example I except that hydrogen is neither admixed with nor included in the feed stock. Data for these tests are given in Table V.

It will be noted that treatment of metal-containing oils

in the absence of hydrogen may be used to separate the metallic components. However, even though the operating conditions are so severe that the treated liquid yield is only 73.6 weight percent of the feed, complete removal of the metals is not obtained although as shown in Example I essentially complete separation of vanadium is obtained in the presence of hydrogen with treated liquid yields as high as 96.0 weight percent of the feed.

Table V.—Tests in absence of added hydrogen

Test	M	N	O
Feed Stock (See Table I)	Mara Crude I	San Ardo Crude	
Operating conditions:			
Temperature, ° F	700	700	750
Pressure, p.s.i.g.	270	2,000	3,000
Yields, basis charge:			
Treated liquid, weight percent	78.5	73.6	84
Solid residue, weight percent	6.5	12.6	7
Product quality: Treated oil—			
Gravity, ° API	32.2	22.1	20.3
Vis., c.s., at 130° F	2.78		6.14
Vis., c.s., at 210° F	1.42		2.43
ASTM distillation, ° F.:			
IBP	240	195	206
10% rec.	294	284	301
50% rec.	528	516	568
End point	724	738	742
Vanadium, p.p.m.	20	6	19
Nickel, p.p.m.	2	5	19
Iron, p.p.m.	0.7	3	0.4
Percent vanadium removal	91.0	94	81

EXAMPLE III

In another series of tests Mara Crude oil is heated with hydrogen and passed through a soaking drum in which an inert packing is disposed. In this method of processing a major portion of the solid residue formed is retained by the inert packing. Only that portion of the solid residue not retained by the packing in the soaking drum appears as a suspension in the treated liquid. The solid residue remaining in the treated oil is separated by filtration and combined with the fouled packing removed from the soaking drum at the conclusion of the test for recovery of the metals contained therein. The operating conditions and results of this series of tests are given in Table VI.

Comparison of the results obtained with an inert packing as used in this example with the data of Example I where an unpacked reactor was used indicates that this method of operation is equally satisfactory as a means of removing metallic components. Furthermore, this method of operation permits the separation of a substantial amount of the metal-containing solid residue by retention with an inert packing.

Table VI.—Tests employing inert packing in a soaking drum

Test	P	Q	R	S	T	U	V	W	X
Feed Stock (See Table I)	Mara Crude I								
Inert packing	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(2)	(2)
Operating conditions:									
Temperature, ° F	750	800	830	835	845	850	850	835	850
Pressure, p.s.i.g.	3,000	2,500	2,500	2,500	2,500	2,500	2,500	2,500	2,500
Hydrogen rate, cu. ft./bbl	10.7	365.0	438.5	657.0	990.0	920.4	682.7	7	443.0
Oil residence time, min	7	7	7	7	7	7	7	7	7
Yields, basis charge:									
Treated liquid, weight percent	96	94	90.6	90.0	90.9	89.1	88.9	94.6	89.3
Solid residue, weight percent			2.3	3.4	2.3	2.0	2.6	1.3	4.1
Hydrogen consumption cu. ft./bbl			245.2	291.0	660.0	396.6	339.9	373	256.0
Product quality: Treated oil—									
Gravity, ° API	29.0	30.6	35.1	35.2	35.8	35.9	33.4	34.6	33.8
Carbon residue, percent	7.3	5.0	3.5		2.1	1.8			3.3
Vanadium, p.p.m.	190	140	27	23	6	2	35	36	41
Nickel, p.p.m.	17	12	2	2	1	0.6	2	2.4	3
Iron, p.p.m.	7	1	20.1	0.3	0.1	0.3	0.3	0.4	20.1
Percent vanadium removal	13	36	88	89	97	99	84	84	82
Solid residue:									
Vanadium, p.p.m.			4,200	3,600	4,400	4,300	4,400		3,200
Nickel, p.p.m.			940	780	2,300	720	1,200		670
Iron, p.p.m.				1,800					

¹ Berl saddles.² Steel turnings.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of treating a petroleum oil containing trace metal components for the separation of said components which comprises contacting said oil in the absence of a catalyst with hydrogen at a hydrogen feed rate of from about 438.5 cubic feet to about 1585 cubic feet per barrel of said petroleum oil and at a temperature of 700 to 850° F. and a pressure of 2000 to 5000 p.s.i.g. to react at least a portion of said hydrogen with a component of said oil to produce a treated oil of reduced metal content and a solid metal-containing residue and separating said treated oil from said residue.

2. The method of claim 1 in which said hydrogen and said oil are contacted in the presence of a contact material consisting essentially of an inert non-catalytic packing material.

3. A method for removing vanadium and other trace metal components from a petroleum oil containing same which method comprises converting said petroleum oil into a liquid phase substantially free from such metal components and a solid residue phase containing most of said metal components by non-catalytically reacting said petroleum oil with hydrogen in a reaction zone at a temperature of 70 to 850° F., a pressure of 2000 to 5000 p.s.i.g., and a hydrogen feed rate within the range of from about 438.5 cubic feet to about 1585 cubic feet per barrel of petroleum oil, withdrawing said liquid phase

and said solid phase from said reaction zone and then separating said solid phase from said liquid phase.

4. A method in accordance with claim 3, wherein said reaction is carried out in an unpacked reaction zone.

5. A method in accordance with claim 3, wherein said reaction zone is packed with an inert non-catalytic solid packing material and wherein said packing material retains part of said solid residue thereon.

6. A method in accordance with claim 5, wherein said solid packing material is selected from the group consisting of berl saddles, steel turnings, porcelain chips and crushed petroleum coke.

7. A method as claimed in claim 3, wherein the hydrogen feed rate is within the range of from about 657 cubic feet to about 1175 cubic feet per barrel of said petroleum oil.

8. A method as claimed in claim 3, wherein hydrogen is consumed in said reaction in an amount within the range of from about 290 cubic feet to about 915 cubic feet per barrel of said petroleum oil.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,910,434

October 27, 1959

Howard V. Hess et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 30, for "70 to 850° F." read -- 700 to 850° F. --.

Signed and sealed this 10th day of May 1960.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents