

[54] REMOVING METAL CONTAMINANTS FROM PETROLEUM RESIDUAL OIL

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[22] Filed: Nov. 2, 1972

[21] Appl. No.: 303,152

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 144,161, May 17, 1971, abandoned, which is a continuation-in-part of Ser. No. 67,085, Aug. 26, 1970, abandoned.

[52] U.S. Cl. 208/214, 208/209, 208/210, 208/211, 208/213, 208/251 H, 208/253, 208/307

[51] Int. Cl. C10g 23/12

[58] Field of Search 208/214, 213, 307, 251 H, 208/253, 209-211

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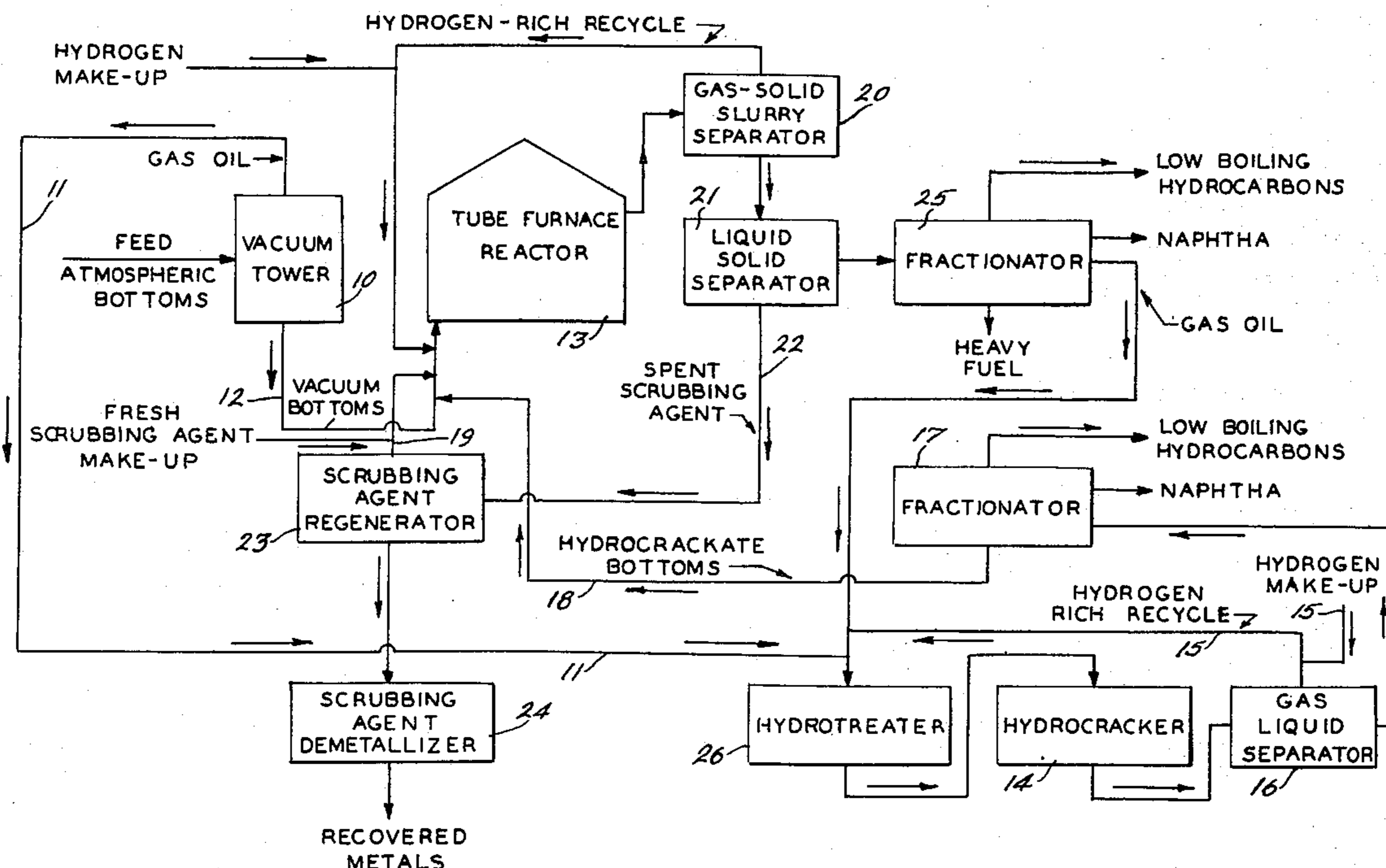
[57] ABSTRACT

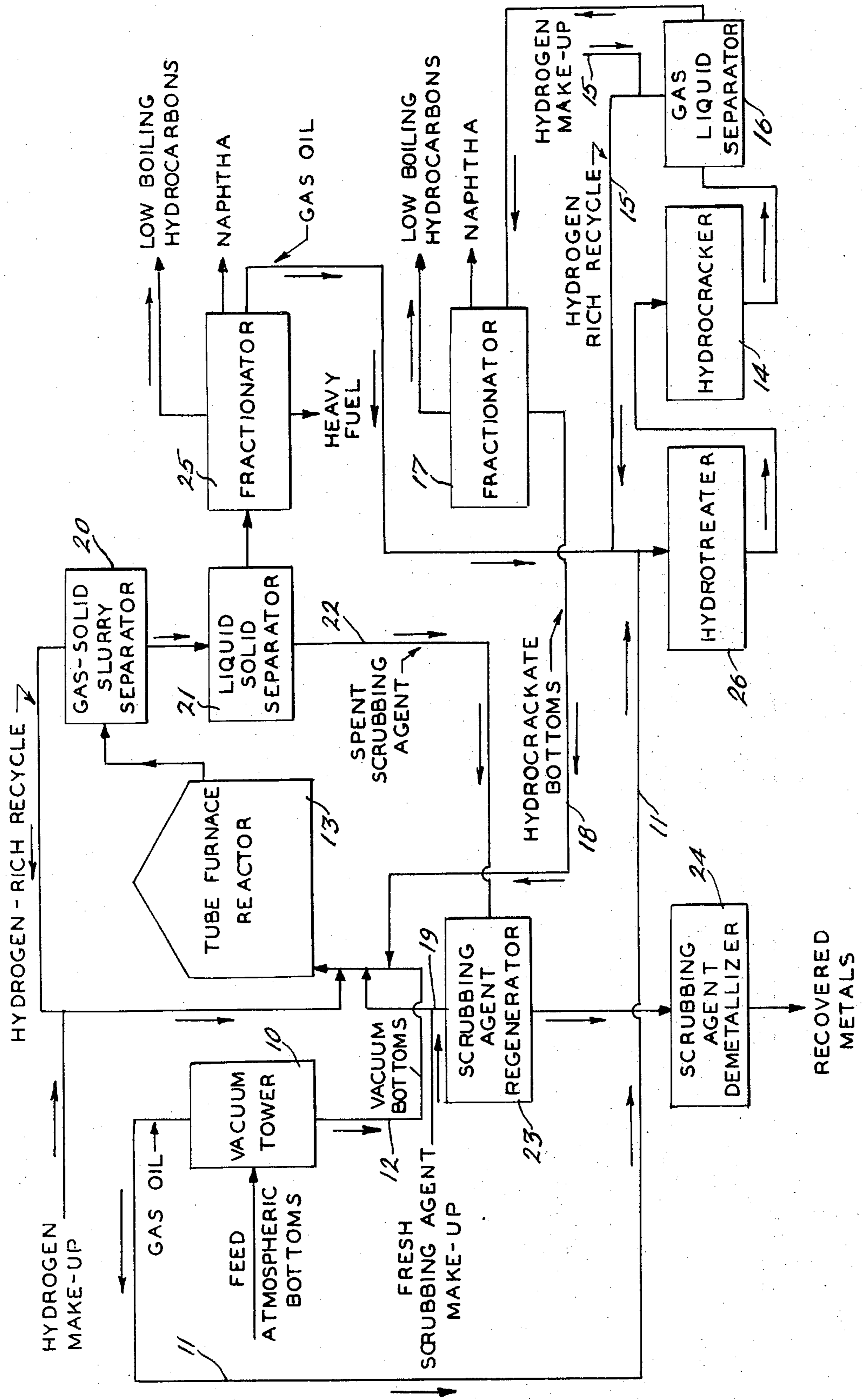
A process for removing metal contaminants from a petroleum residual oil without significant coking and loss of hydrocarbons by treating such oils with a hydrogen donor solvent in the presence of a highly porous inorganic scrubbing agent and recycling the regenerated metal-containing scrubbing agent.

[56] References Cited
 UNITED STATES PATENTS

2,253,308 8/1941 Rosen 208/214

7 Claims, 1 Drawing Figure





REMOVING METAL CONTAMINANTS FROM PETROLEUM RESIDUAL OIL

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my co-pending application Ser. No. 144,161, filed May 17, 1971 now abandoned, which was a continuation-in-part of my copending application Ser. No. 67,085, filed Aug. 26, 1970, now abandoned.

As is well known in the petroleum industry the most valuable products obtained from a crude petroleum stream are those hydrocarbons which boil below approximately 800°F. Since a substantial proportion of the crude petroleum boils above this temperature, a great deal of effort has been expended by the petroleum industry to convert these higher boiling streams to valuable feedstocks. Included in such efforts has been the refining of the residual stream, generally boiling above 1,000°F., to increase the recovery of naphtha for subsequent catalytic cracking processes.

The residual stock itself cannot be economically directly cracked due to the presence of substantial portions of metal contaminants, particularly nickel and vanadium components. These metals, which may be present in quantities of from about 10 to 50 pounds of metal per 1,000 barrels of crude, deposit on the catalyst during the conversion in such a fashion that regeneration of the catalyst is extremely difficult. Further, the cracking operation of the stream itself is adversely affected since the contaminants deposited decrease the catalyst activity, and cause excessive coke to be formed during the catalytic cracking, with a resulting loss in hydrocarbon product.

As an alternative means of upgrading a residual stream, a refining method referred to as "hydrogen donor diluent" processing has been developed. By this method, a hydrogen donor, such as hydrocrackate bottoms containing at least in part partially hydrogenated polycyclic aromatic compounds, is blended with a crude residual oil during thermal cracking, generally in the temperature range of 700°-1,000°F. to yield naphtha with only a small amount of coke. No catalyst is used in the hydrogen donor process and hence, the problem of catalyst fouling is at least initially alleviated. This process and the use of hydrocrackate bottoms is best exemplified by U.S. Pat. No. 3,238,118 of William Floyd Arey, Jr. and Ralph Burgess Mason, Issued Mar. 1, 1966.

Although the hydrogen donor process has been successful in upgrading the residual stream, the problem of metal contamination has not been fully remedied. That is, the process does not inherently tend to remove the contaminating metals from the stream and hence, when the upgraded stream is ultimately subjected to a catalytic cracking process, the aforementioned fouling problems will still be present. Also, if, as in U.S. Pat. No. 3,238,118, the improved stream is recycled to the fractionator then a build-up of the metals will occur. Some relief from this problem may be obtained by purging the residual feed to remove the contaminants and return the purged stream to the conversion zone, but this has proved both inefficient and costly. It should be noted that the term "metal" as herein employed refers to those metals which are chemically bound to the high boiling molecular structures that make up the residual

portion of a crude oil e.g., Ni or V bound in a porphyrin structure. Another problem inherent in prior art processes is the coking that occurs during treatment of the residual oils and such coking both degrades the oil and makes further processing difficult. Associated with the coking phenomenon is the consumption of hydrogen with formation of increased quantities of methane and this, too, is undesirable in that it reflects loss of hydrocarbon and makes for an inefficient process.

It is therefore the overall object of this invention to provide a process for upgrading a petroleum residual stream by removing a substantial portion of the metal contaminants present in the residual stream without incurring any significant amount of coking. It is an additional object of this invention to provide a hydrotreating, hydrocracking process sequence on the demetalized liquid product to remove sulfur and nitrogen contaminants and to provide a hydrogen donor solvent for recycle to the demetallizer. The distillate materials produced by this system are highly purified and are therefore quite suitable for conversion into petroleum products.

In accordance with the foregoing objects, it has been found that a metals-contaminated petroleum residual stream can be upgraded without significant coking, by subjecting the residual stream to a hydrogen donor diluent process in the presence of a porous, high surface, inorganic scrubbing agent, separating the metal containing inorganic material and regenerating and recycling it for reuse.

The process is particularly suitable for those highly contaminated streams containing greater than 500 ppm. of metals, particularly where the metals are nickel and vanadium. The demetallization step of this process may be carried out in a slurry type of operation or in an ebullated bed but preferably in a slurry operation. As a further embodiment of the invention, the residual streams can first be subjected to the hydrogen donor diluent process and then contacted with a scrubbing agent, but the preferred operation and that which secures superior results is when the processes are carried out together. It should be noted that satisfactory results are not obtained when the residual stream is first contacted with a scrubbing agent and then subjected to the hydrogen donor process.

The hydrogen donor, porous scrubbing agent demetallization step is carried out at temperatures of incipient coking which is usually in the range of from at least about 750°F. to 1,000°F. and at a pressure in the range of from about 500 to 5,000 psig. The hydrogen donor to residual oil ratio will generally be from about 0.1 to 10. The preferred conditions consist of a temperature in the range of from about 750° to about 875°F., a hydrogen pressure in the range of from about 1,000 to about 3,000 psig, and a hydrogen donor to residual oil weight ratio of from about 0.25 to about 2.5, and the conversion is generally carried out for a period of from 5 minutes to 3 hours. The ratio of hydrogen donor to resid is not critical with respect to metals removal, but in order to minimize carbon build-up it is preferable to operate the process at a donor to resid weight ratio of about 1. This will depend on hydrogen donor ability of the solvent and the activity of the regenerated recycled porous scrubbing agent. The hydrogen donor can be any such material well-known in the art such as hydrocrackate bottoms or other refinery stream containing partially hydrogenated polycyclic aromatics com-

pounds, with the preferred donor being hydrocrackate bottoms.

As aforementioned, the highly porous inorganic scrubbing agent can be any porous, high surface area, inorganic adsorbent material such as alumina silicates. The pore size of the material should be large enough to accept the metals as their sulfides, and generally it should have a minimum pore size of at least 30 A but preferably may possess a broad range of pore size distribution to facilitate entry and accumulation of the metallic components deposited from the contaminated residual oil. The material's surface area should generally be at least 50 sq. M/gm. measured by nitrogen adsorption but preferably will have a surface area of 100 to 250 sq. M/gm. Examples of suitable agents are montmorillonite, beidellite, kaolinite, etc. and polygorskite minerals such as attapulgus clay which is a preferred scrubbing agent. Activated alumina and activated bauxite possessing high surface area are also highly suitable as scrubbing agents for use in this invention. Once the scrubbing agent has been employed either during or after the hydrogen donor thermal conversion process, it is withdrawn from the system, regenerated, and returned thereto for additional use, since it has been found that the use of the regenerated scrubbing agent has a significant effect in minimizing any tendency to form coke. The material can be regenerated by any system well-known in the art, such as thermal treating with air or an air-inert gas mixture to burn off coke without sintering. It should be noted that the scrubbing agent serves a dual purpose. Besides its major function of removing metal contaminants, the material also functions as a site for the deposition of any coke that might be formed and also provides a scouring action on the walls of the process equipment. The amount of scrubbing agent generally used in the system will be from about 3 to about 15 weight percent based on the charge to the reactor. The quantity of scrubbing agent charged depends on the coking tendency of the residual oil, residence time, H₂ pressure, and amount of Ni and V accumulated from previous exposures to metalliferous residual oils.

A general mode of carrying out the instant invention when employing hydrocrackate bottoms as the hydrogen donor is exemplified in the drawing as follows: A whole crude petroleum oil which has been subjected to atmospheric distillation to remove light material or other feed such as heavy athabaskan tar oil is separated in a vacuum tower (10) into fractions including therein a gas oil fraction (11) boiling from about 500°F. up to about 1,000°F. and a bottoms or residual stream (12) boiling above about the end point of the gas oil stream and this residual stream is ultimately subjected to the combined hydrogen donor diluent-porous scrubbing agent process of this invention which occurs in the demetallizer (13).

The separated gas oil fraction is fed from the vacuum tower (10) to a hydrotreating reactor (26) and then to a hydrocracking reactor (14) where hydrocracking occurs in the presence of a hydrocracking catalyst under conditions well known in the art. The feed is generally subjected to temperatures in the range of from 550° to 850°F. at a pressure of from 500 to 2,500 p.s.i.g. Suitable catalysts for hydrotreating include the well known alumina supported cobalt-molybdenum and nickel-molybdenum catalysts. The hydrocracking catalyst may be any suitable hydrocracking catalyst, such as

nickel sulfide on silica-alumina, a noble metal such as platinum or palladium on a molecular sieve base having uniform pore openings between about 6 and 15 angstrom units, noble metal on silica-alumina, and various catalysts comprising Group VI and VIII metals, oxides and sulfides on suitable supports such as silica-alumina, clays, etc. A hydrogen stream (15) is also introduced into the hydrotreater.

Following the hydrocracking reaction, the products are withdrawn, cooled and passed into a separator (16) wherein hydrogen-containing gas is separated from the liquid. This gas can then be recycled into the hydrotreating zone. The liquid product then passes into a fractionator (17) where several light fractions are separated leaving a hydrocrackate bottoms (18) which will be used as the hydrogen donor in the process of the invention. In order for the bottoms to be successfully employed as such, it will have a boiling point above about 430°F. and have more than about 20 percent by volume of condensed ring naphthenes. To insure such properties, the hydrocracking reaction should be carried out at pressure greater than 800 psig and temperatures less than 800°F. Further, since the naphthene content of the bottoms varies with the conversion, the feed rate should be such as to limit conversion to less than 70 percent.

The hydrocrackate bottoms are combined with the residual or crude oil bottoms stream (12) from the vacuum tower (10) in desired proportions, heated, and passed to a thermal demetallizing zone, such as a tube furnace reactor, (13) wherein the scrubbing agent (19) is introduced. The scrubbing agent introduced is a mixture of mainly regenerated, recycled material plus some fresh make-up material. The aforementioned temperature and pressure conditions are maintained in the zone. The recycled scrubbing agent containing Ni and V previously deposited provides sufficient catalytic activity to minimize coke formation. Within the reactor (13) hydrogen exchange occurs between the residual oil and the hydrocrackate bottoms by the release of hydrogen from the donor to produce lower boiling hydrocarbons, and thermal cracking occurs within the zone. Hydrogen is also adsorbed from the gas phase due to the activity of the recycled scrubbing agent. Also, a substantial amount of metals present in the residual stream are accumulated on the scrubbing agent, as is some coke formed during the conversion, thus allowing for the easy removal and recovery of the metals. Electromicroprobe analysis of the scrubbing agent reveals that the nickel and vanadium from the contaminated oil has permeated into the porous interior of the scrubbing agent.

Following the conversion, the product is removed from the reactor and is then further processed for the recovery of petroleum fractions in a gas-solid slurry separator (20) and a liquid-solid separator (21). The liquid reactor products are separated in a fractionator (25) to yield low boiling hydrocarbons, naphtha and gas oil. The gas oil and similar products from the fractionator (25) are also fed to the hydrotreater (26) and then to the hydrocracker (14). The scrubbing agent used for the acculation of the metallic contaminants is separated by filtration or centrifuging in the liquid-solid separator (21) and spent scrubbing agent (22) regenerated in the regenerator (23) and recycled to the demetallizer-reactor (13). Part of the scrubbing agent may be processed to recover the deposited metals (24).

The regeneration step simply involves burning off any coke from the used agent, but leaving the metals in the pores. In accord with the invention, however, it is important that a major part of the spent scrubbing agent containing the metals removed from the resid will be returned directly to the demetallizer since the metal-containing scrubbing agent, surprisingly, results in improved metals pick-up and by means of this recycle system minimizes coke formation during the demetallizing step.

The process of the invention is extremely effective in metal removed from the resid. For example, about 90 to 95 percent of vanadium and 80 to 85 percent of nickel present in the resid is removed by treatment with the hydrogen donor-scrubbing agent system of the invention and this is accomplished without significant loss of hydrocarbons due to coking or methane formation. Since the sulfur content of the resid is also lowered by the process the resid is also upgraded in quality in this respect and this is an additional significant advantage.

In order to further illustrate the invention, the following examples are given:

Examples 1 to 3

The process details described above were followed using a Venezuelan Lagomedio resid and a hydrogen donor solvent which was a dewaxed hydrocrackate oil which was essentially a naphthenic oil and boiling above 650°F. The Lagomedio resid is a vacuum tower bottoms consisting of material boiling above 1,070°F. and contains 16.1 percent asphaltenes. The scrubbing agent used was an attapulugus clay having a 100 mesh particle size and was regenerated for recycle by burning off any deposited carbon at 875°F. The following table indicates the conditions of the various runs and gives the results obtained.

TABLE I

Operating Data	Feed	Ex. 1	Ex. 2	Ex. 3
Temp. °C.	—	425	425	425
°F.	—	797	797	797
Pressure—p.s.i.g.	—	2500	2500	2500
Time—Hrs.	—	2.5	2.5	2.5
Total H ₂ Adsorbed S.C.F./bbl	—	—	—	310
Scrubbing Agent to Resid Ratio-Gm:Gm	—	0	10:60	10:60
Solvent to Resid Ratio—Gm:Gm	60:60	60:60	60:60	60:60
Scrubbing Agent Recycled	—	—	No	Yes
Liquid Product Composition				
Wt. % of H	12.66	12.66	13.57	13.09
C	85.61	86.51	84.75	85.42
N	0.27	0.18	0.21	0.39
S	2.22	1.14	1.03	1.24
Mol. Wt.	576	333	418	422
Ppm. Nickel	27	4	5	2.4
Ppm. Vanadium	285	33	30	11
Ramsbottom Carbon	8.0	6.12	5.12	5.71
Carbon Recovered	—	4.3	4.1	0.3
Off Gas Analysis				
% H ₂	—	88.3	86.5	92.6
% CH ₄	—	7.0	8.2	4.3

It can readily be seen from the above table that the scrubbing agent was only significantly effective in reducing nickel and vanadium content of the resid when

it was used under recycle conditions (compare Example 2 without scrubbing agent with Example 3). Furthermore, the total of Ramsbottom carbon of the liquid product and recovered carbon (6.01g) in Example 3 was significantly less than Examples 1 and 2 where the process of the invention was not in effect. It is also of interest that the amount of methane in the off-gases from Example 3 were lower than in Examples 1 and 2 and the sulfur content of the processed resid was also significantly reduced.

Examples 4 and 5

In a second set of runs shown in Table II, preferred and severe conditions were used to illustrate the kind of conditions needed in a short contact time tube furnace reactor. The feed was a Venezuelan Lagomedio resid and a hydrogen donor solvent which was dewaxed hydrocrackate lube oil boiling above 650°F. The scrubbing agent used was recycled bauxite in Example 4 and fresh bauxite in Example 5.

TABLE II

Operating Data	Feed	Ex. 4	Ex. 5
Temp. °C	—	469	465
Time — Min.	—	5	5
H ₂ pressure psi	—	2925	2600
Total H ₂ Adsorbed S.C.F./bbl	—	425	—
Catalyst/Resid gm:gm.	—	10/84	10/84
Catalyst	—	Fresh Bauxite	Recycled Bauxite
Liquid Product Composition			
Wt % H	—	13.01	12.12
C	—	84.92	85.91
N	—	0.29	0.43
S	—	1.50	1.47
Mol. wt.	—	314	362
Ppm. Ni	38	4	6
Ppm. V	398	67	65
Rams Carbon of Liquid Product	—	8.6	7.59
% Metals Removed ⁽¹⁾			
Ni	—	87	84
V	—	83	83

⁽¹⁾ Based on 38 Ppm Ni and 398 Ppm V in mixed feed

It can be seen from the table that at a higher temperature and pressure, significant amounts of metal are removed at greatly reduced contact times over Example

3. Example 5, showing recycled bauxite also shows a significant decrease in Ramsbottom carbon of the liquid product over Example 4 where no recycle of the scrubbing agent was performed.

Examples 6 to 8

In another series of runs a Venezulean Boscan resid was used. This Boscan resid is a vacuum tower bottoms consisting of material boiling above 995°F. and contains 35.0 percent asphaltenes. The data is shown in Table III.

As is evident from the table, the recycle system (Example 7) resulted in the lowest nickel and vanadium content in the resid and this run also gave the smallest amount of carbon formed.

Examples 9 to 12

In another series of runs with Boscan resid, hydrocrackate bottoms as solvent and an activated bauxite scrubbing agent having a 20 mesh particle size, the regeneration and recycle step was repeated three times. The data follow in Table IV. These data indicate the beneficial effect to be obtained by the use of a recycled porous scrubbing agent for obtaining improved metals removal while at the same time repressing coke and light gas formation. Chemical analysis by x-ray fluorescence methods indicates the presence of about 0.5 weight percent nickel and 2.0 weight percent vanadium deposited in the pores of bauxite after being recycled three times.

TABLE III

Activity of Recycled Regenerated Attapulugus Clay				
Operating Data	Feed	Ex. 6	Ex. 7	Ex. 8
Temp. °C.	—	425	425	425
H ₂ Pressure, p.s.i.g.	—	2500	2500	2500
H ₂ Adsorbed Total, S.C.F./bbl	—	177	825	430
Scrubbing Agent:Resid gm:gm	—	10:60	10:60	0:60
Solvent:Resid gm:gm	60:60	60:60	60:60	60:60
Scrubbing Agent Recycled	—	No	Yes	—
Time, Hrs.	—	2.5	2.5	2.5
<u>Liquid Product Comp.</u>				
Wt. % H	12.43	14.94	14.76	14.45
C	83.52	84.10	83.63	84.84
N	0.79	0.35	0.84	0.26
S	3.08	1.65	1.44	1.52
Mol. Wt.	609	314	323	293
Ppm. Ni	86	10	5.4	9
Ppm. V	1018	48	28	40
Rams. Carbon of Liquid Product	14.29	4.20	5.72	4.32
Gms. of Carbon Recovered	—	6.7	2.07	4.58
<u>Off Gas Analysis</u>				
% H ₂	—	81.9	82.0	79.4
% CH ₄	—	9.3	9.8	11.5

TABLE IV

Operating Data	Feed	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Temp °C.	—	425	425	425	425
H ₂ Pressure P.s.i.g.	—	2500	2500	2500	2500
Total H ₂ Adsorbed, S.C.F./bbl	—	39	670	710	725
Time—Hrs.	—	2.5	2.5	2.5	2.5
Scrubbing Agent:Resid gm:gm	—	10:60	10:60	10:60	10:60
Solvent: Resid gm:gm	60:60	60:60	60:60	60:60	60:60
Cycle of Scrubbing Agent	—	Fresh	1st Recycle	2nd Recycle	3rd Recycle
<u>Liquid Product Composition</u>					
Wt. % H	12.43	12.95	12.95	13.63	13.56
C	83.52	85.16	85.46	84.40	84.60
N	0.79	0.90	0.21	0.42	0.13
S	3.08	1.58	1.53	1.82	1.51
Mol. Wt.	609	301	338	340	390
Ppm. Ni	86	7.3	8.8	10	6.9
Ppm. V	1018	41	26	14	25
Ramsbottom Carbon	14.29	4.93	4.82	4.95	5.11
Gms. Carbon Recovered	—	6.7	4.4	3.6	1.4
<u>Off Gas Analysis</u>					
% H ₂	—	80.1	82.1	85.9	86.2
% CH ₄	—	12.3	8.7	7.8	7.9

Example 13

A demetallized product residual oil obtained by the aforementioned hydrogen donor, porous scrubbing agent treating technique was further subjected to desulfurization by hydrogenation with a conventional sulfided cobalt-molybdenum on alumina catalyst. The details of the procedure are shown in Table V.

TABLE V

Operating Data	Feed	Ex. 13
Temp. °C.	—	375-408
Time—Hrs.	—	2.8
H ₂ Pressure psi	—	2500
Total H ₂ Adsorbed S.C.F./bbl	—	525
Catalyst/Resid gm/gm	—	20/100
Catalyst	—	Co-Mo on alumina
<u>Liquid Product Composition</u>		
Wt. % H	13.41	15.05
Wt. % C	84.92	84.61
Wt. % N	0.11	0.14
Wt. % S	1.27	<0.06
Mol. Wt.	348	269
ppm Ni	5	<2
ppm V	17	<20
Rams. Carbon of Liquid Product	—	0.68
Gms. Carbon Recovered	—	2.0

It is evident from the above data that the hydrogenated product is quite low in nickel, vanadium, nitrogen, and sulfur contamination and is thus quite suitable for further processing to useful petroleum products.

The invention claimed is:

1. A process for the reduction of sulfur and removal of metal contaminants from a petroleum residual oil

without significant coking which comprises the steps of contacting said oil with a hydrogen donor liquid and a highly porous, inorganic scrubbing agent at a temperature of incipient coking at a pressure of about 500 to 5,000 psig., and at a weight ratio of hydrogen donor liquid to residual oil of from about 0.1 to 10, separating the liquid hydrogen donor and demetallized products from said highly porous inorganic scrubbing agent, regenerating said highly porous inorganic scrubbing agent in an air-regeneration zone to remove carbon deposits while leaving metals in the pores of said scrubbing agent and recycling said regenerated metal-containing inorganic scrubbing agent for further contact with residual oil and hydrogen donor liquid.

2. The process of claim 1 wherein (a) the contact temperature of residual oil and hydrogen donor liquid is from about 750° to about 875°F., (b) the donor solvent to residual oil weight ratio is from about 0.25 to about 2.5, and (c) the pressure is about 1,000 to about 3,000 psig.

3. The process of claim 2 where the scrubbing agent is attapulugus clay.

4. The process of claim 2 where the scrubbing agent is activated bauxite.

5. The process of claim 2 where the scrubbing agent is activated alumina.

6. The process of claim 2 wherein a minor amount of the metal in the petroleum residual oil feed is an added nickel or vanadium compound.

7. The process of claim 2 wherein the total metals content of the petroleum residual oil is at least about 500 ppm.

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