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2,308,001 1/1943 Forney 208/256
 1,935,162 11/1933 Morrell 208/265
 2,131,879 10/1938 Ault et al. 208/256
 2,865,838 12/1958 Mills 208/90

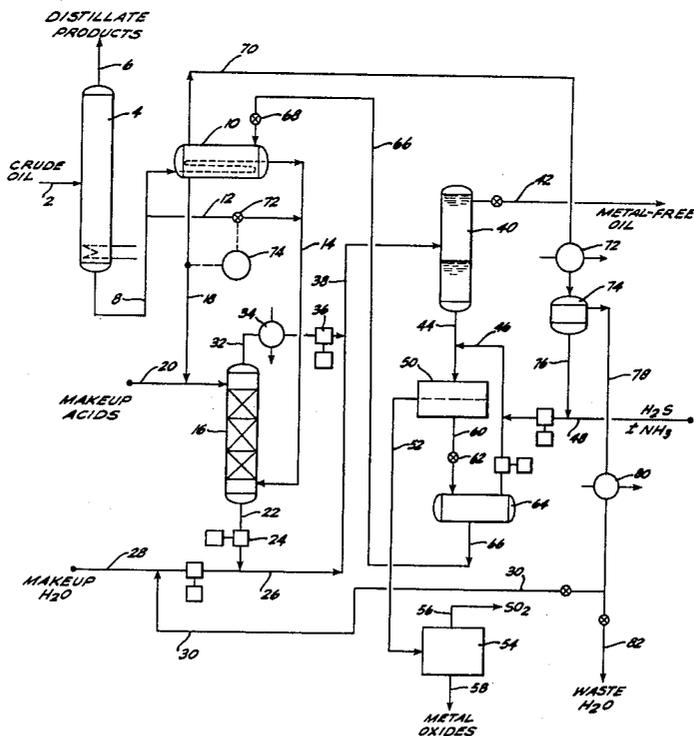
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[54] **DEMETALLIZATION OF RESIDUAL OILS WITH POLYPHOSPHORIC ACIDS**
 12 Claims, 3 Drawing Figs.

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 256, 265, 90, 98, 219

[56] **References Cited**
UNITED STATES PATENTS
 2,682,496 6/1954 Richardson et al. 208/90

ABSTRACT: Crude oil residua containing normally incident organometallic impurities, e.g., vanadium and nickel porphyrins, are subjected to extraction with anhydrous liquid polyphosphoric acid at elevated temperatures, whereby the metals in the oil are extracted into the acid phase in the form of metal chelates of the linear polyphosphoric acids. In a cyclic process, the extracted metals are recovered as sulfides by precipitation with H₂S, and the regenerated polyphosphoric acid is recycled.



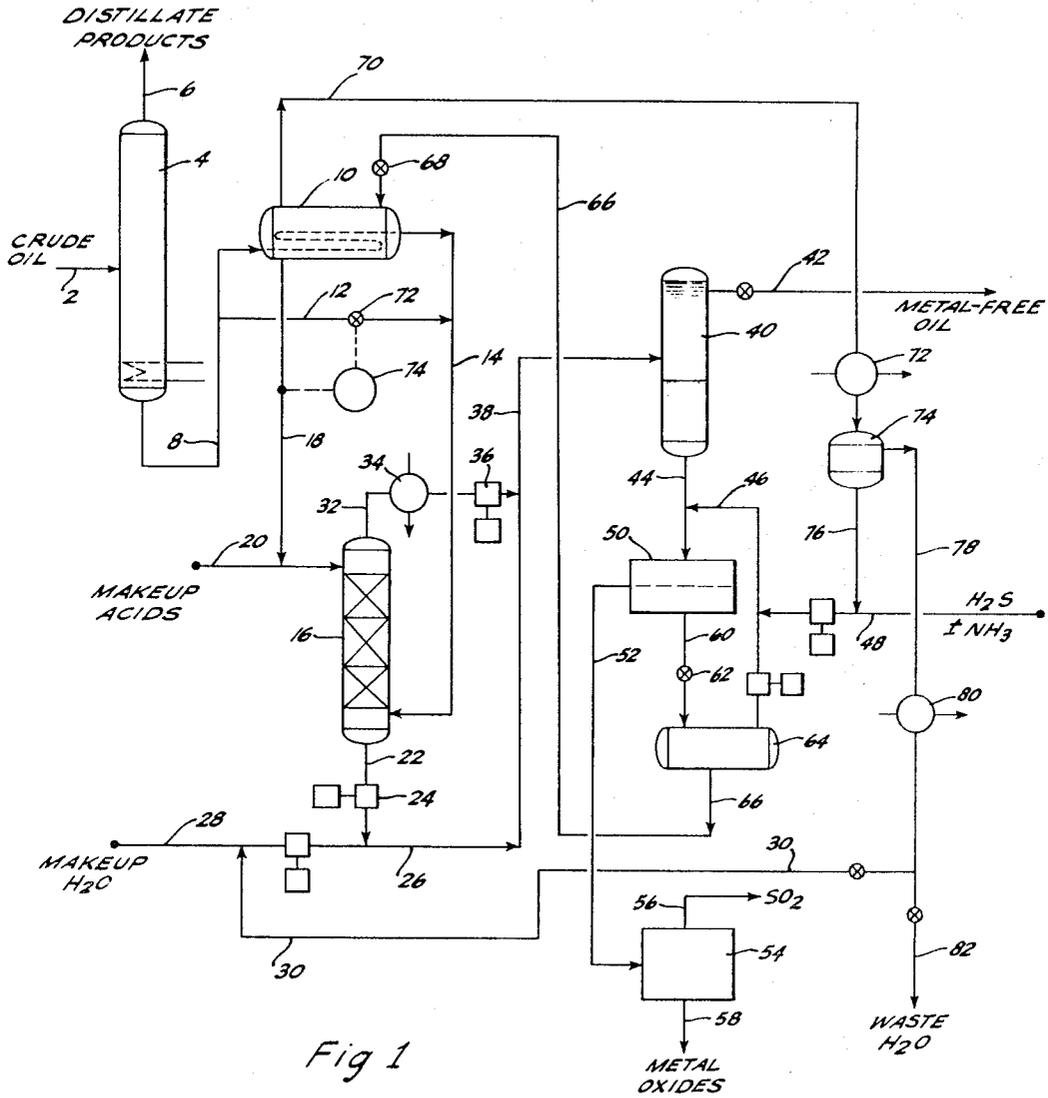


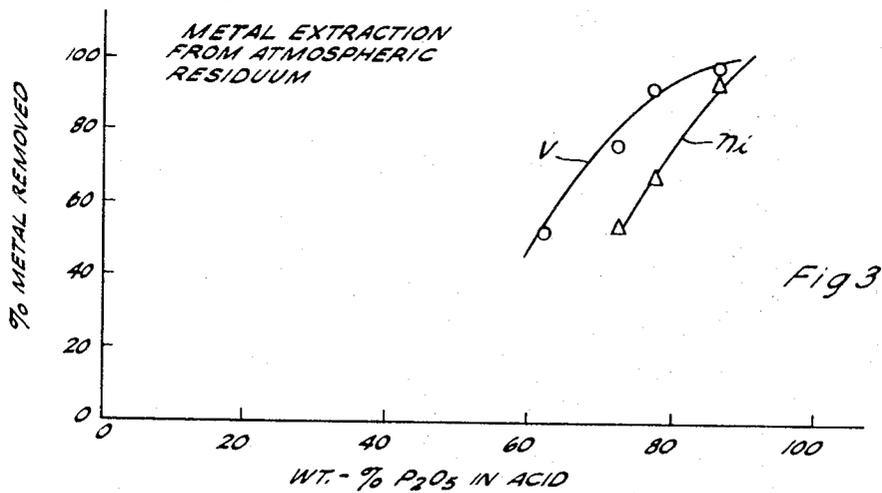
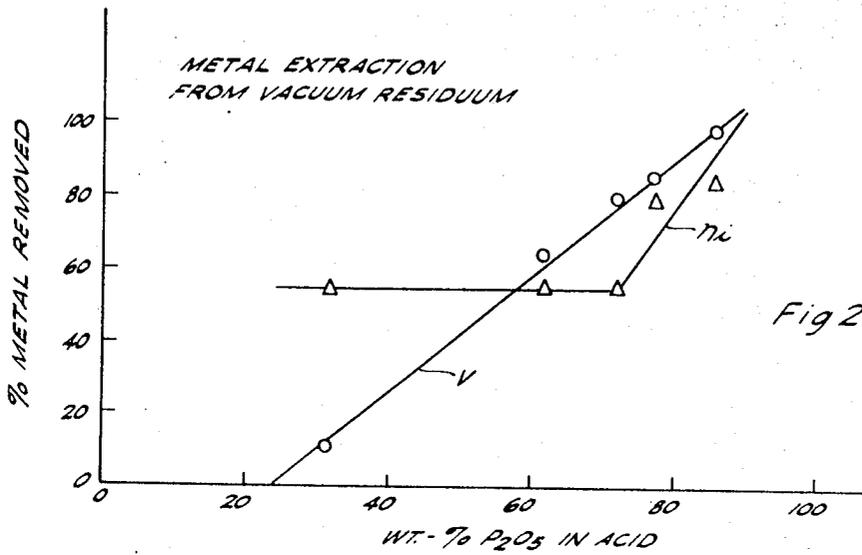
Fig 1

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DEMETALLIZATION OF RESIDUAL OILS WITH POLYPHOSPHORIC ACIDS

BACKGROUND AND SUMMARY OF THE INVENTION

The primary refining of crude oils by fractional distillation (either at atmospheric or reduced pressures) always leaves behind an undistillable residue which has been a challenge to petroleum refiners for many years. It may represent from 5 to 50 volume-percent of the original crude oil, and there is hence a considerable economic incentive in converting it to more valuable distillate products. Thermal coking can be utilized to recover some additional relatively low value distillate products, but the yield is low and a considerable portion of the residuum is converted to coke. Products such as asphalt, paraffin waxes and lube oils can be recovered from such residua but the demand for these products is insufficient to consume more than a minor proportion of the available residua. As a result of all these factors, probably the major portion of petroleum residua has in the past been diverted to low value products such as fuel oils.

A possibility which has long intrigued petroleum refiners has been to effect a substantially total conversion of petroleum residua to high value distillate products such as gasoline, turbine fuels, diesel fuels and the like. To achieve this objective requires that the asphaltic constituents thereof, instead of being converted to coke as in thermal coking, be first hydrogenated so that they can be cracked or hydrocracked without rapidly coking up the catalyst employed. A major difficulty encountered in any initial hydrogenation of such residua resides in the rapid fouling of the hydrogenation catalyst brought about by the metallic constituents in the residua. Metals commonly found in crude oils include vanadium, arsenic, nickel, copper and iron, and they evidently occur mainly in the form of soluble chelates with various organic compounds such as porphyrins. Vanadium and arsenic are particularly potent poisons for most of the conventionally used hydrogenation catalysts. Much effort has been devoted in the past to the development of methods for demetallizing petroleum residua so as to render them amenable to catalytic hydrogenation, but for various reasons none of these methods have proven to be economically satisfactory.

In addition to the economic incentive of upgrading residua into distillate products, air pollution problems have in recent years made it more difficult to dispose of residua even as fuel oils, primarily because of the high sulfur content thereof. The most practical means of removing sulfur is by catalytic hydrodesulfurization, but here again the problem of catalyst poisoning by the metallic constituents is a major deterrent.

One of the most commonly suggested methods of removing metals from oils is by extraction with strong acids. Acids which have been suggested include the hydrogen halides, sulfuric acid alkyl and aryl sulfonic acids, fluorophosphoric acid, and orthophosphoric acid (see U.S. Pat. No. 2,682,496). Although these acids can effect nearly complete demetallization, their use presents serious problems. At the high temperatures required to reduce the viscosity of the undiluted residual oils sufficiently for convenient processing, the sulfonic acids decompose, and the hydrogen halides require high pressure vessels. Moreover, all of the above acids except orthophosphoric will, at the temperatures required herein, chemically attack olefins, resulting in reduced yields and loss of acid. Orthophosphoric acid also requires a high-pressure extraction vessel at the temperatures here required, in order to prevent the evolution of water vapor (which would disrupt the efficiency of a countercurrent extraction column).

We have now discovered that all of the foregoing acid extraction problems can be avoided by the use of a specific class of polyphosphoric acids wherein the mole ratio of H_2O/P_2O_5 is less than 3.0 but greater than about 1.2, which corresponds to a P_2O_5 content of about 72.5 to 86.5 weight-percent, on an impurity free basis. Acids of this character are found to present several unique advantages. Firstly, as compared to orthophosphoric acid, they extract metals, particularly

vanadium, much more efficiently and completely, and can be used at temperatures above 500° F. and at atmospheric pressure without generating a vapor phase which would upset the contacting efficiency of a countercurrent extraction column. Secondly, as compared to the sulfonic acids, they are completely stable at the required temperatures. Thirdly, as compared to any of the above enumerated acids except orthophosphoric, they do not attack olefins. Finally, their specific gravity is such that they can be readily separated from the demetallized oil.

The unique efficiency of the polyphosphoric acids as metal extractants is believed to stem from their chelating properties. To form chelates it is necessary that a substantial proportion of the phosphorus in the acid be present in the form of linear poly acids, e.g., pyrophosphoric acid, tri-, tetra-, and pentapolyphosphoric acids. The acid having an H_2O/P_2O_5 mole ratio of 3.0 contains 72.5 weight-percent P_2O_5 , and about 11.5 percent of the total phosphorus is present as linear polyacids. The acid having an H_2O/P_2O_5 mole ratio of 1.2 contains 86.5 weight-percent P_2O_5 , and about 97 percent of the total phosphorus is present as linear polyacids.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a simplified flow diagram illustrating a specific adaptation of the invention utilizing continuous countercurrent extraction with regeneration and recycle of the acid.

FIG. 2 is a graph illustrating the data hereinafter set forth in example II.

FIG. 3 is a graph depicting the data set forth hereinafter in example III.

DETAILED DESCRIPTION

A. Description of Acids

The polyphosphoric acids utilized herein can be derived from commercial wet process phosphoric acid, but preferably they are produced by concentrating furnace grade white phosphoric acid. The wet process acid normally contains about 25-55 weight-percent of P_2O_5 , and is contaminated with metal salts and fluorine, while the white acid is substantially free of metallic impurities and fluorine. In either case, the commercial acid is subjected to conventional concentration procedures involving essentially the boiling off of water until the desired P_2O_5 concentration is attained. Operative and preferred acids may be characterized as follows, on an impurity free basis:

Table 1

	Operative	Preferred
Wt.-% P_2O_5	72.5-86.5	75-83
H_2O/P_2O_5 Mole-Ratio	3.0-1.2	2.6-1.6
Wt.-% of total P as Polyphosphoric Acids	11.5-97	44-93

The acid of minimum strength above, i.e., containing 72.5 weight-percent P_2O_5 , corresponds to nominally 100 percent H_3PO_4 . However, as is well known, this material actually contains a small amount of polymer acid as well as free water. The presence of free water appears to be undesirable in our process, and hence acids of at least about 75 weight-percent P_2O_5 are preferred, since they contain substantially no free water. The acids containing from 83 to 86.5 percent P_2O_5 are very efficient extraction agents, but they are not preferred because of their extremely high boiling points, ranging above 1,000° F. Since, as will be noted hereinafter, it is preferred to add water to the extract acid and raffinate oil phases in order to promote better phase resolution, it becomes necessary in a cyclic process to evaporate off the excess water to obtain a concentrated acid for recycle. This becomes a difficult and expensive operation when it is desired to maintain acids of greater than about 83 percent P_2O_5 in the extraction zone. But

from the standpoint of simple operability, the acids containing up to 86.5 percent or more of P_2O_5 are very effective. The boiling points of several of the preferred acids for use herein are as follows:

Table 2

Wt.-% P_2O_5	Boiling Point, °F.
72.4	491
75.3	575
76.3	617
78.2	720
79.7	801
81.5	928

B. Feedstocks

The residual oils employed herein as feedstocks comprise the bottoms fraction from conventional fractional distillation or vacuum distillation of substantially any petroleum crude oil. They are dark, viscous materials rich as asphaltenes, sulfur and nitrogen compounds; their pour point may range between about 50° and 300° F. The solvent extraction of such oils has in the past presented serious handling difficulties due to the viscosity problem. In the past, when strong acids such as sulfuric were utilized (which chemically attack the oils at high temperatures), it was necessary to employ a light hydrocarbon diluent in order to reduce viscosity sufficiently for low temperature operations. The use of a diluent is undesirable because of the required increase in equipment capacity and the increased expense involved in the heating, cooling and product recovery operations. One of the unique advantages of the polyphosphoric acids is that they can be employed at sufficiently high temperatures to reduce the viscosity of the oil to a level such that inert diluents are not required. However the optional use of a diluent is not excluded.

In other respects, the residual oil feedstocks employed herein may be characterized as comprising at least about 50 volume percent of components boiling above about 1,000° F., and having an API gravity below about 20°.

C. Process Conditions

The extraction may be carried out employing conventional contacting procedures generally used in solvent extractions; either single stage batch operations with suitable agitation to obtain intimate contacting of the two phases, or multistage, continuous countercurrent extractions may be utilized. The latter form of contacting is generally preferred, and may consist in passing the hot oil upwardly through a column packed with glass beads, Raschig rings or the like, countercurrently to a descending stream of polyphosphoric acid. Although it is possible to remove more than 90 percent of the metal content of the oil in a single stage of contacting, it is generally preferable from the standpoint of reducing contact time and increasing metals removal to substantially 100 percent, to employ at least two, and preferably three to about 10 theoretical contacting stages. The principal operative and preferred conditions for the contacting are summarized as follows:

TABLE 3

	Broad Range	Preferred Range
Temp., °F.	350-750	450-700
Pressure, p.s.i.g.	0-2,000	0-50
Contact Time, Minutes	2-100	10-45
Solvent/Oil Ratio, V/V	0.01-0.5	0.02-0.1

Those skilled in the art will understand that the more extended contact times in the above ranges will be utilized in

conjunction with relatively low temperatures and/or inefficient contacting techniques, while the shorter contact times will ordinarily be utilized in conjunction with higher temperatures and efficient contacting procedures. Also, for an equivalent degree of metals removal, longer contact times will be required for a single stage operation than for multistage operations. It is preferred to adjust the extraction conditions so as to remove at least about 99 percent of the vanadium content of the oil, and at least about 75 percent of the nickel content.

During the contacting, particularly if substantial agitation there will be some emulsification of oil in the acid phase, and of acid in the oil phase, thus creating a separation problem. One effective method for improving phase resolution consists in adding sufficient ammonia to the aqueous phase to raise the pH to about 6-8, whereby a clear, colorless aqueous phase is obtained. However, the resulting ammonium phosphate solution must then either be diverted to other uses, or subjected to high temperature regeneration procedures for recovering the ammonia and acid. A more desirable method consists simply in adding water, either to the two-phase system, or to each phase separately, with suitable agitation as could occur for example in a transfer line, followed by a simple gravity separation. Large amounts of water are not required; generally we add only sufficient water to provide an aqueous phase containing about 20-50 weight-percent P_2O_5 , preferably about 25-35 weight-percent.

When water is added to the system to promote phase separation, high temperatures, above about 400° F. must still be maintained in order to keep the oil phase in a sufficiently nonviscous state. This entails a pressure separation system from which the aqueous acid phase may be recovered, treated for metals recovery by any desired method (one of which will be described hereinafter), and then flashed into a low pressure heating zone to evaporate off water and recover the polyphosphoric acid for recycle. In some cases it may be desirable to subject the raffinate oil phase to a final water wash in order to remove traces of remaining acid.

D. Description of FIG. 1

FIG. 1 illustrates a specific adaptation of the process embodying continuous countercurrent contacting, and recovery of the extracted metals from the acid extract by precipitation with hydrogen sulfide. The initial crude oil is brought in via line 2 and fractionated in distillation column 4, from which distillate products are withdrawn via line 6. The remaining residual oil is withdrawn as bottoms via line 8 and passed in part through flash evaporator 10 in heat exchange relationship to recycle acid as will be described hereinafter, and in part via bypass line 12 and line 14 to the bottom of countercurrent extraction column 16, in which it flows upwardly, countercurrently to descending recycle and makeup polyphosphoric acid admitted to the top of the column via lines 18 and 20. Contacting in column 16 occurs under the conditions above described, preferably at atmospheric pressure.

From extraction column 16, the acid extract is withdrawn via line 22 and pressured via pump 24 into water line 26 containing makeup and recycle water from lines 28 and 30. The temperature of the water in line 28 is preferably adjusted so that upon mixing with the acid extract in line 26, the resulting temperature will be in the range of about 400° to 600° F., preferably 400° to 500° F., whereby the autogeneous pressure in line 26 to maintain the water in liquid phase will range between about 250 and 650 p.s.i.g. The dilute acid in line 26 is then mixed with the demetalized raffinate oil which is withdrawn from extraction column 16 via line 32, precooled to the desired temperature in heat exchanger 34 and pressured via pump 36 into line 26. The combined mixture of acid extract and raffinate oil in line 26 is then transferred to a separating vessel 40, from which the upper phase of demetalized oil is withdrawn via line 42.

The lower phase of acid extract in separator 40 is withdrawn via line 44 and mixed therein with recycle and makeup hydrogen sulfide brought in via lines 46 and 48. Sufficient

hydrogen sulfide is added at this point to saturate the aqueous acid, thereby effecting maximum precipitation of the metals as sulfides. Due to the high acidity of the extract in line 44, complete metals precipitation ordinarily cannot be obtained, but this is not a critical factor; it is necessary to precipitate only enough of the metals as sulfides to provide an acid for recycle which has sufficient capacity to economically chelate and extract additional metals from the oil. If the metals concentration in the extract in line 44 is high, satisfactory precipitation of e.g., 50 to 90 percent of the metals can be obtained by merely saturating the acid with H₂S. However, if the metals concentration in the extract is low, it may be desirable to raise the pH of the acid stream somewhat in order to drive the metal sulfide precipitation further toward completion. For this purpose, sufficient ammonia may be introduced with the hydrogen sulfide in line 48 to raise the pH of the acid extract in line 44 to e.g., about 4 to 8.

The resulting slurry of precipitated metal sulfides and aqueous acid in line 44 is then passed through a suitable filter 50 (or other suitable separating means such as a centrifuge) from which the solid metal sulfides are withdrawn via line 52 and sent to a suitable roaster 54 which converts the sulfides to metal oxides withdrawn via line 58. Sulfur dioxide taken off via line 56 may be sent to suitable sulfur recovery facilities not shown. The demetallized acid from filter 50 is then passed via line 60 and pressure-reducing valve 62 into flash separator 64, from which excess H₂S is withdrawn via line 46 and recycled as previously described. If no ammonia was added to the system via line 48, a substantially complete flashoff of H₂S is obtained in vessel 64 by simply reducing the pressure by about 50–100 p.s.i.g., giving a substantial steam stripping effect.

The stripped acid in separator 64 is then transferred via line 66 and pressure reducing valve 68 to flash evaporator 10 in which water vapor and any remaining H₂S and ammonia are flashed off at substantially atmospheric pressure and withdrawn via line 70. Evaporator 10 thus acts as a concentrator to remove the water which was added to the system via line 28 and return the acid to the desired strength for use in extraction column 16. The degree of concentration in evaporator 10 is controlled automatically by means of motor valve 72 in bypass line 12 which is operated by temperature recorder controller 74 in response to temperature detected in line 18. Temperature recorder controller 74 is calibrated so as to maintain a temperature in line 18 corresponding to the atmospheric boiling point of the desired concentration of acid by opening or closing valve 72, thus forcing a smaller or larger proportion of hot residual oil through flash evaporator 10.

The steam in line 70 may, if it is free of hydrogen sulfide and ammonia, be recycled directly to line 28, but in cases where ammonia was added via line 48, both ammonia and H₂S will be dissociated and driven off from the acid being concentrated in evaporator 16. To recover such ammonia and H₂S, the steam in line 70 may be passed through a cooler 72 to condense out, e.g., about 5 to 10 percent of the water content and thereby absorb the bulk of the H₂S and ammonia. The resulting steam and aqueous ammonium sulfide condensate is passed into separating vessel 74, from which the condensate is withdrawn via line 76 and recycled via line 48. The remaining steam is taken off via line 78, treated for heat recovery and condensation in heat exchanger 80 and then either exhausted as waste water via line 82 or recycled to line 28 via line 30 as previously described.

EXAMPLE I

As a specific illustration of our process carried out with countercurrent contacting as described in connection with FIG. 1, a 17 percent vacuum residuum feedstock derived from a California crude oil is utilized, having the following principal characteristics:

Gravity, °API	6.5
Pour Point, °F.	>200
Sulfur, wt-%	2.37
Nitrogen, wt-%	1.1

Fe, p.p.m.	97
Ni, p.p.m.	150
V, p.p.m.	190

To achieve 99+ percent removal of vanadium and 90+ percent removal of nickel from this oil, while achieving at least 95 percent recovery of demetallized oil, the following operative conditions are found to be suitable:

Wt-% P ₂ O ₅ in Acid	76
Number of Extraction Stages	3
Acid/Oil Ratio, V/V	1/10
Extraction Temp., °F.	650
Contact Time in Extraction Column, Minutes	15

The metals are precipitated from the extract acid by saturating the same with H₂S at a temperature of 500° F. and 650 p.s.i.g. Under these conditions about 60–70 percent of the total metal content of the extract (diluted with water to 35 weight-percent P₂O₅) is precipitated as sulfides. The remaining extract with its equilibrium metal content can be reconcentrated and recycled indefinitely.

EXAMPLE II

The vacuum residuum feed described in example I was subjected to several single stage batch extractions with polyphosphoric acids of various P₂O₅ concentrations. In each case a constant 6.6/1 weight-ratio of oil/P₂O₅ was maintained, with the acid and oil being placed in a quartz lined bomb under nitrogen and rocked at 650° F. for 2 hours. After cooling, sufficient water was added to give an acid phase containing 30 weight-percent P₂O₅, and the contents were then heated to 500° F. and rocked for 1 hour, allowed to settle for 1 hour and then cooled. Analyses of the resulting oil phases gave the following data:

Table 4

Run No.	1	2	3	4	5
Wt-% P ₂ O ₅ in Acid	31	61	72	76	85
Product Analysis					
Feed					
Ni, p.p.m.	150	71	70	33	28
V, p.p.m.	190	73	43	31	7
Metal Removal, %					
Ni	53	53	53	78	81
V	10	62	77	84	96

The above data, which is plotted in FIG. 2, shows that the efficiency of extraction of vanadium increases substantially linearly with the degree of polymerization (and hence chelating capacity) of the acid. Nickel, on the other hand, appears to be present in two different forms: one which is easily extracted by nonchelating acids (Runs 1–3), and another which requires a chelating acid (Runs 4,5).

It should be noted that the foregoing runs do not represent optimum commercial extraction conditions. They were designed merely to assure the attainment of equilibrium in each case, so that the relative efficiency of the acids could be compared.

EXAMPLE III

A 35 percent atmospheric residuum derived from a California crude oil and having a pour point of 85° F., and an API gravity of 10.7° was subjected to a series of extractions similar to those of example II except that the contact time in each case was 4–5 hours and the bomb temperature was 450° F. The demetallized oils were recovered by centrifugation instead of water dilution and settling as in example II. Analysis of the resulting oils gave the following data:

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Table 5

Run No.	6	7	8	9
Wt. % P ₂ O ₅ in Acid Product Analysis	61	72	76	85
	Feed			
Ni, p.p.m.	83	76	39	28
V, p.p.m.	92	63	23	9
Metal Removal, %				
Ni	8	53	66	81
V	31	75	90	95

The foregoing data is plotted in FIG. 3, and shows in general the same increased extraction efficiency with increasing acid polymerization as was shown in example II.

EXAMPLE IV

One of the most efficient previously known acids for demetallizing residual oils is methane sulfonic acid (U.S. Pat. No. 3,190,829). The data of this example shows that polyphosphoric acids are superior. Samples of the atmospheric residuum employed in example III were stirred with the respective acids at 250° F. for 30 minutes and then allowed to settle. These mild conditions were not designed to give commercially acceptable degrees of demetallization, but for comparison purposes are acceptable. Analysis of the extracted oils gave the following data:

TABLE 6

Run No.	Acid used	Oil/acid ratio, v./v.	Percent demetallization	
			Ni	V
10.....	Polyphosphoric (76% P ₂ O ₅)---	2/1	70	76
11.....	Methane sulfonic.....	2/1	22	21
13.....	Polyphosphoric (76% P ₂ O ₅)---	10/1	51	72
14.....	Methane sulfonic.....	10/1	20	23

It is clearly evident that the polyphosphoric acids are much more efficient demetallizing agents than is methane sulfonic acid.

Additional modifications and improvements utilizing the discoveries of the present invention can readily be anticipated by those skilled in the art from the foregoing disclosure, and such modifications and improvements are intended to be included within the scope and purview of the invention as defined in the following claims.

We claim:

1. A process for demetallizing a crude oil residuum contaminated with at least one of the metals, nickel, vanadium and iron or compounds thereof, which comprises intimately contacting said residuum with an extraction solvent consisting essentially of liquid polyphosphoric acid concentrated to a P₂O₅ equivalent above about 72.5 but below about 86.5 weight-percent, said contacting being carried out at a temperature between about 350° and 750° F. to thereby effect a substantial extraction of metals from said residuum, and recovering from said contacting a substantially demetallized

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product oil.

2. A process as defined in claim 1 wherein said polyphosphoric acid contains a P₂O₅ equivalent between about 75 and 83 weight-percent.

3. A process as defined in claim 1 wherein said extraction is carried out at a temperature between about 450° and 700° F.

4. A process as defined in claim 1 wherein said contacting is carried out in the absence of a hydrocarbon diluent for said residuum.

5. A process as defined in claim 1 wherein said polyphosphoric acid contains a P₂O₅ equivalent between about 75 and 83 weight-percent, and wherein said contacting is carried out at a temperature between about 450° and 700° F. in the absence of a hydrocarbon diluent for said residuum.

6. A cyclic process for demetallizing a crude oil residuum contaminated with at least one compound of a metal from the class consisting of vanadium and nickel which comprises:

1. intimately contacting said residuum with an extraction solvent consisting essentially of a liquid polyphosphoric acid concentrated to a P₂O₅ equivalent above about 72.5 but below about 86.5 weight-percent, said contacting being effected at a temperature between about 350° and 750° F;

2. separating from said contacting an acid extract phase containing extracted metals and a substantially demetallized raffinate oil phase;

3. adding sufficient water to said acid extract phase to reduce the P₂O₅ concentration thereof to between about 20 and 50 weight-percent, thereby releasing additional emulsified oil from said acid extract and forming a secondary raffinate phase and a substantially hydrocarbon-free aqueous acid phase;

4. separating said secondary raffinate from said aqueous acid phase;

5. removing at least a substantial portion of the metal content from said aqueous acid phase;

6. evaporating sufficient water from the aqueous acid phase from step (5) to concentrate the same to a P₂O₅ content above about 72.5 but below about 86.5 weight-percent; and (7) recycling the concentrated acid from step (6) to step (1).

7. A process as defined in claim 6 wherein the P₂O₅ concentration of said polyphosphoric acid recited in steps (1) and (6) is between about 75 percent and 83 percent.

8. A process as defined in claim 6 wherein said extraction step (1) is carried out at a temperature between about 450° and 700° F.

9. A process as defined in claim 6 wherein said extraction step (1) is carried out in the absence of a hydrocarbon diluent for said residuum.

10. A process as defined in claim 6 wherein said contacting step (1) is carried out in continuous countercurrent fashion.

11. A process as defined in claim 6 wherein said removal of metals in step (5) is effected by the addition thereto of hydrogen sulfide to precipitate the metals as sulfides.

12. A process as defined in claim 6 wherein said contacting step (1) is carried out in continuous countercurrent fashion in the absence of a hydrocarbon diluent for said residuum, at a temperature between about 450° and 700° F., and wherein said polyphosphoric acid has a P₂O₅ equivalent between about 75 and 83 weight-percent.

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