

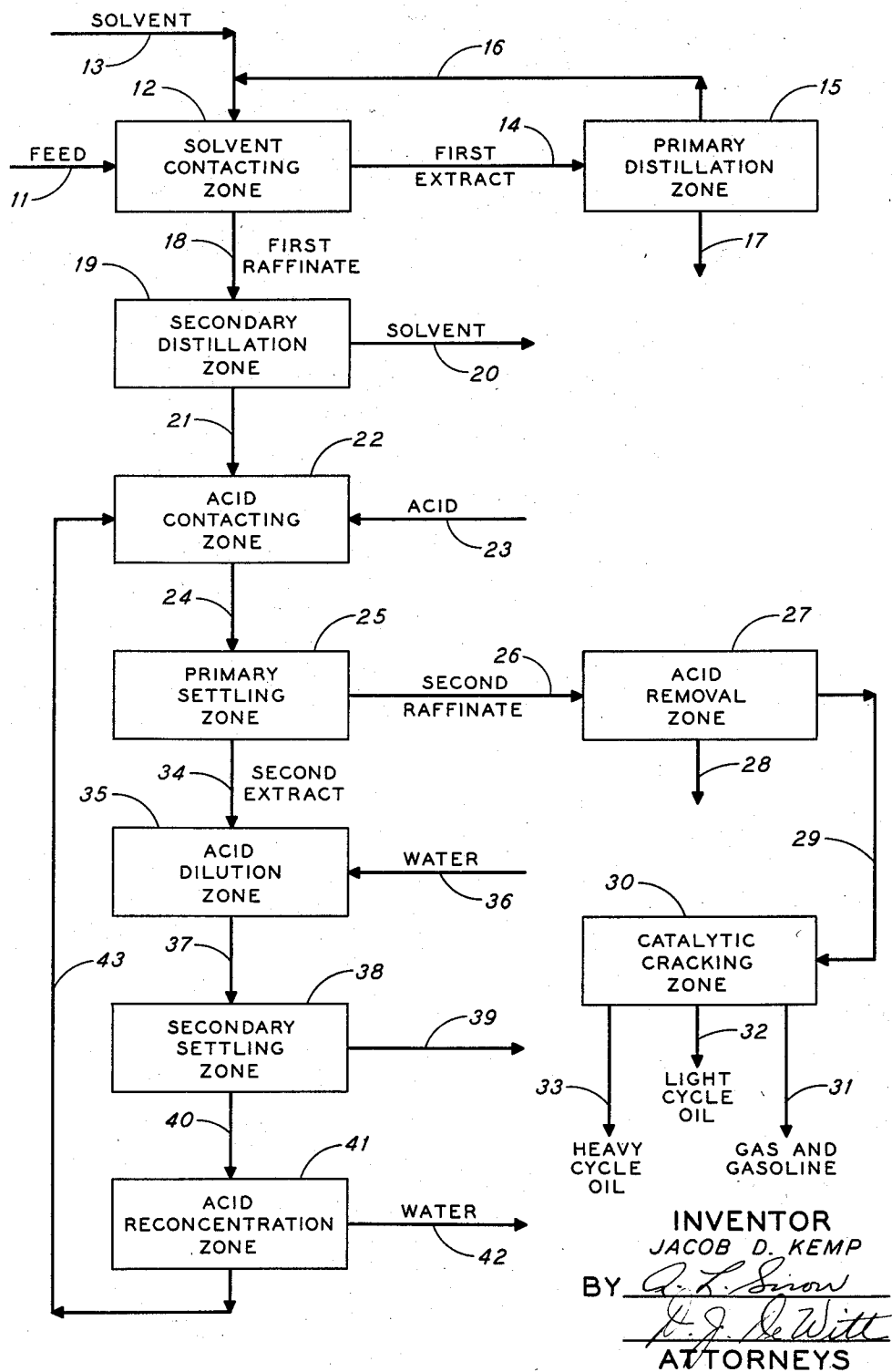
Aug. 12, 1958

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2,847,362

TWO-STAGE TREATING PROCESS

Filed Sept. 29, 1954



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TWO-STAGE TREATING PROCESS

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Application September 29, 1954, Serial No. 459,068

9 Claims. (Cl. 196—50)

This invention relates to a process for the treatment of hydrocarbon oils, and more particularly to a process for removing basic nitrogen and organo-metallic compounds from hydrocarbon oils prior to catalytically cracking the same.

With the advent of catalytic cracking in the petroleum refining industry, it has been found that various charging stocks are more susceptible to catalytic cracking than others. Thus, paraffins and olefins are more readily cracked than are aromatic hydrocarbons. However, while certain of these differences in susceptibility to cracking are attributable to the nature of the hydrocarbon feed stock, another important factor relates to the presence or absence in the stock of various materials such as basic nitrogen and organo-metallic compounds which act as deterrents to cracking efficiencies and susceptibilities and are termed "catalyst poisons." These poisons have the effect of promoting coke formation and generally reducing the activity of the cracking catalyst, thus lowering the conversion to the desired lower boiling products. Pyridine and quinoline are examples of these undesirable nitrogen bases while the organo-metallic compounds are generally of extremely complicated structure, with compounds containing vanadium, nickel, copper and/or iron predominating.

The method heretofore employed to remove these basic nitrogen and organo-metallic compounds has been to treat the oil with a mineral acid such as concentrated H_2SO_4 , HF, or H_3PO_4 . However, the use of each acid entails numerous disadvantages. For example, upon treating the oil with concentrated H_2SO_4 , there separates out not only an oil phase and an acid phase, but also a substantial amount of an interfacial phase which not only is difficult to handle due to its tendency to plug equipment and lines, but which also contains considerable quantities of acid that cannot be recovered and are, therefore, lost from the system. A further disadvantage is that stock losses are unduly high (often amounting to 15% or more of the total feed) since H_2SO_4 not only removes nitrogen compounds, but also many other hydrocarbon components of the feed.

When employing concentrated HF, stock losses are also high. Furthermore, the use of HF is extremely hazardous and requires costly equipment as well as the practice of elaborate safety precautions due to its highly corrosive nature, particularly if any water is present in the system.

While treatment with concentrated H_3PO_4 alone does not impose the difficulties mentioned above, this acid is relatively expensive and, since large quantities thereof must be used, this method is commercially unattractive due to the fact that the spent acid cannot be recovered with any degree of completeness by a practice of conventional distillation methods.

Accordingly, it would be desirable if a method could be found for treating hydrocarbon oils to remove nitrogen bases and organo-metallic compounds contained therein without encountering the foregoing or other difficulties.

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It is, therefore, a primary object of this invention to provide an improved method for treating hydrocarbon fractions to remove any basic nitrogen compounds and organo-metallic compounds present therein.

5 A more particular object is to provide a removal method of this character which is well adapted to be practiced with respect to catalytic charging stocks and thus increase the yield of high-quality motor fuels which can be obtained therefrom as a result of the cracking step.

10 A further object is to provide a method for removing these catalyst poisons which utilizes a minimum amount of the treating agent and which also keeps stock losses at a relatively low value.

15 A still further object is to provide a method whereby the materials employed to remove these undesirable catalyst poisons may readily be recovered for further use with other hydrocarbon stocks. The nature of other objects of the invention will be apparent from a consideration of the descriptive portion to follow.

20 According to the present invention, the hydrocarbon stock to be freed of its basic nitrogen and organo-metallic compound content is first extracted with a lower aliphatic alcohol, said alcohols having been found to selectively dissolve any highly basic nitrogen compounds present in the stock being treated. The alcohol-hydrocarbon mixture is then separated into a first extract and a solvent-free first raffinate. The first raffinate is then contacted with concentrated phosphoric acid (H_3PO_4) to extract the less basic nitrogen compounds as well as any organo-metallic compounds which are present after which the mixture is separated into a second extract and an acid-free, second raffinate which is substantially free of nitrogen bases and organo-metallic compounds.

25 As indicated above, I have found that the more highly basic nitrogen compounds can be selectively removed from the hydrocarbon stock by treating the same with a lower aliphatic alcohol or mixture of such alcohols, representative agents of this character being methanol, ethanol, and the various propyl and butyl alcohols. This treating step, in addition to removing a portion of the undesired impurities, also has the advantage that it greatly reduces the amount of phosphoric acid required to remove the remaining (less basic) nitrogen compounds and organo-metallic compounds as compared to a process wherein H_3PO_4 is the sole treating agent employed. Furthermore, these alcohols have a relatively low boiling point and are easily recovered for reuse by simple distillation procedures. Methanol has been found to be a particularly good solvent for these more basic nitrogen compounds and thus is preferred for use in the present invention.

30 Following the alcohol treating step, the resulting raffinate, on being freed of its alcohol content, is then contacted with phosphoric acid having a concentration (in terms of the H_3PO_4 content thereof) of from 90 to 116%, this concentration having been found to be optimum for more completely removing the less basic nitrogen and organo-metallic compounds. The acid is employed in amounts within the range of from about 0.10 to 10.0 pounds of H_3PO_4 per gallon of raffinate, with 0.25 pound being generally sufficient for most feeds. Further, I have found that by first treating the feed with alcohol and then with H_3PO_4 within the noted concentration range, the acid is regenerable, which is not true in many of the treating processes heretofore employed, including those wherein H_3PO_4 is employed alone, a result which is apparently attributable to the presence of the more basic nitrogen compounds present in the extract. Furthermore, since the H_3PO_4 extracts essentially only the less basic nitrogen and organo-metallic compounds, stock losses are low (in the order of 4 to 5 weight percent),

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whereas in HF and H₂SO₄ treating (which are not as selective to the nitrogen and metal compounds) stock losses run up to 15% and more due to the removal of additional hydrocarbons. Also, the quantity of H₃PO₄ required for the treating step in the present invention is lower than were H₃PO₄ to be employed alone because of the removal of a considerable amount of the nitrogen compounds by the less expensive alcohol.

To facilitate understanding of the invention, reference is made to the attached drawing, the single figure of which is a diagrammatic representation of the process of the present invention as applied to the treatment of charging stock to a catalytic cracking unit.

In the drawing, a hydrocarbon feed containing basic nitrogen and/or organo-metallic compounds is passed by line 11 into solvent contacting zone 12. The hydrocarbon feed is one suitable for catalytic cracking purposes such as straight-run distillate gas oils and the like. In zone 12 the hydrocarbon feed is contacted with a low molecular weight alcohol, preferably methanol, to remove the highly basic nitrogen compounds, said alcohol being passed into zone 12 by line 13. Zone 12 may be any conventional apparatus or equipment for intimately contacting the alcoholic solvent and the feed.

A first extract composed essentially of solvent along with highly basic nitrogen compounds is removed from zone 12 by line 14 and is passed into a primary distillation zone 15 wherein the solvent is separated from the nitrogen bases by conventional distillation methods, the overhead alcohol fraction being recycled by lines 16 and 13 to the solvent contacting zone for reuse. The basic nitrogen compounds are removed as a bottoms fraction by line 17.

A first raffinate from zone 12 is passed from solvent contacting zone 12 by line 18 into secondary distillation zone 19 wherein any solvent present in the first raffinate is distilled overhead by line 20. The solvent-free first raffinate is then passed from zone 19 through line 21 into a zone 22 where the raffinate is contacted with concentrated phosphoric acid (introduced into zone 22 by line 23) having a concentration of from about 90 to 116% H₃PO₄, said acid being employed in an amount of about 0.25 pound acid per gallon of solvent-free first raffinate. This acid contacting step may be practiced at ambient temperature since it has been found that temperature has little influence upon the effectiveness of the acid treatment.

The acid-hydrocarbon mixture is passed from acid contacting zone 22 by line 24 into a primary settling zone 25 wherein a second raffinate consisting essentially of hydrocarbons separates as an upper layer, while a second extract, consisting essentially of phosphoric acid along with less basic nitrogen compounds and any organo-metallic compounds present, separates as the lower layer. The second raffinate is removed from zone 25 by line 26 and is passed into acid removal zone 27 wherein the second raffinate is treated by water washing or the like to remove any acidic materials contained therein, the acid being removed through line 28. The acid-free second raffinate is then passed by line 29 into zone 30 where it is contacted with a catalytic cracking catalyst under cracking conditions by any of the conventional processes such as Houdrifiow, Thermoform, or fluid-bed type moving catalyst process. Gas and gasoline are removed from zone 30 by line 31, while light and heavy cycle oils are removed by lines 32 and 33 respectively.

The second extract, or acidic lower layer formed in settling zone 25 is passed through line 34 into a dilution zone 35 where the acid is diluted with water supplied through line 36 to a concentration of from about 40 to 50% H₃PO₄. The diluted acid is passed by line 37 into a secondary settling zone 38 where the liquid separates into an upper layer composed essentially of nitrogen and organo-metallic compounds, and a bottom layer composed essentially of dilute H₃PO₄. The upper layer is removed

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by line 39 while the bottom layer is passed by line 40 into an acid reconcentration zone 41 wherein the phosphoric acid is brought to a concentration of from about 90 to 116% H₃PO₄, the water removed from the acid being discharged through line 42, while the reconcentrated acid is recycled by line 43 to the acid contacting zone 22.

The process of the present invention is demonstrated in the following example:

EXAMPLE

A heavy gas oil containing 0.37 weight percent nitrogen (in the form of basic nitrogen compounds) and 6 parts per million (p. p. m.) of organo-metallic compounds was intimately mixed with 1.5 volumes of methanol per volume of gas oil. A first extract consisting essentially of methanol and nitrogen bases was recovered, and the first raffinate distilled to remove traces of methanol present therein. The raffinate was then treated with 0.28 lbs. of 99.9% H₃PO₄ per gallon of stock. The resulting mixture was allowed to settle, and an upper layer, second raffinate was recovered which was then water washed and subjected to a catalytic cracking operation. Conditions and results of the above operation, along with the results of operations wherein the identical heavy gas oil was catalytically cracked without pretreatment with the methanol and acid, are shown in Table I below.

Table I

	No Pretreatment	Example
Feed Stock.....	Heavy Gas Oil.	Heavy Gas Oil.
A. P. I. Gravity.....	22.9.....	22.9.....
Nitrogen (p. p. m.).....	0.37.....	0.37.....
Metals (p. p. m.).....	6.0.....	6.0.....
Methanol Treatment.....	none.....	1.5 Vol. of Methanol/Vol. feed.
First Raffinate:		
Nitrogen (Wt. Percent).....	do.....	0.26.....
Metals (p. p. m.).....	do.....	8.7.....
H ₃ PO ₄ Treatment:		
H ₃ PO ₄ Concentration, Percent.....	do.....	99.9.....
Temperature, ° F.....	do.....	125.....
Contact time (minutes).....	do.....	5.....
Acid Rate (Gallons/hr.).....	do.....	577.....
Lbs. Acid/Gallon of Feed.....	do.....	0.28.....
Second Raffinate:		
Nitrogen (Wt. Percent).....	do.....	0.11.....
Metals (p. p. m.).....	do.....	1.7.....
Total Stock Loss (Percent of total feed).....	do.....	10.1.....
Catalytic Cracking:		
Catalyst.....	Silica-Alumina.	Silica-Alumina.
Temperature, ° F.....	900.....	900.....
Space Rate, Vol. of feed/hour/Vol. of catalyst.....	1.5.....	1.5.....
Catalyst/Oil Ratio, Vol./Vol. Yields—	1.5.....	1.5.....
Gas, Wt. Percent.....	8.0.....	13.0.....
Carbon, Wt. Percent.....	3.8.....	3.9.....
Gasoline, 410° F. Cut Point, Vol. Percent.....	23.9.....	33.8.....
Ratio, Gasoline/Carbon, Vol. Percent/Wt. Percent.....	6.3.....	8.7.....
Ratio, Gasoline/Gas, Vol. Percent/Wt. Percent.....	3.0.....	2.36.....
Conversion, Percent.....	32.0.....	46.1.....

By comparing the results achieved in the present process with the catalytic cracking of raw feed, it can be seen from Table I that the gasoline motor fuel production from the heavy gas oil was increased from 23.9 volume percent to 33.8 volume percent, an increase of 42.4%. Also, it should be noted that the total stock loss of both treating steps was approximately 10%.

A modification of the present invention is in the disposition of the basic nitrogen compounds removed from the hydrocarbon feed as shown in the figure by lines 17 and 39. Various alternatives to their subsequent treatment, either separately or in admixture with each other, are available. For example, they be subjected to destructive distillation to form coke and valuable light-hydrocarbon products (coking), to thermal cracking or to catalytic hydrogenation under conditions of temperature, pressure,

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and space velocity so as to effect substantial hydro-cracking.

The figure and much of the description of the present invention has been directed to the removal of nitrogen bases and organo-metallic compounds from hydrocarbons employed as charging stock to a catalytic cracking unit. However, it must be borne in mind that the subject process is applicable for the removal of nitrogen bases from other petroleum fractions commonly found in the petroleum refining art. Furthermore, the treatment of oils derived from "kerogen" in shale is within the scope of this invention.

I claim:

1. In a process for removing basic nitrogen and organo-metallic compounds from a hydrocarbon feed, the steps comprising extracting said feed with a low molecular weight alcohol, recovering a first extract and a substantially alcohol-free first raffinate, extracting said first raffinate with concentrated phosphoric acid (H_3PO_4), and recovering a second extract and a substantially acid-free second raffinate product, said extracting steps being practiced under essentially ambient temperature conditions.

2. The process of claim 1 wherein the concentration of the phosphoric acid lies in the range of from about 90 to 116% H_3PO_4 .

3. The process of claim 1 wherein the alcohol is methanol.

4. In a process for removing basic nitrogen and organo-metallic compounds from a hydrocarbon feed, the steps comprising contacting said hydrocarbon feed at essentially ambient temperatures with a low molecular weight alcohol solvent; recovering a solvent-free first raffinate and a first extract composed essentially of solvent and containing the more highly basic nitrogen compounds contained in the feed; contacting said first raffinate, under essentially ambient temperatures, with phosphoric acid of concentration in the range of from about 90 to 116% H_3PO_4 in an amount in excess of 0.10 pound of acid per gallon of first raffinate; recovering a second raffinate and a second extract composed essentially of phosphoric acid and containing organo-metallic compounds and the relatively less basic nitrogen compounds contained in said first extract; removing essentially all of the acidic materials from said second raffinate; and recovering relatively pure solvent from said first extract and relatively pure H_3PO_4 from said second extract.

5. The process of claim 4 wherein the solvent is methanol.

6. In a process for the conversion of hydrocarbon oils which contain basic nitrogen compounds and organo-metallic compounds, the steps comprising contacting said

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hydrocarbon oils with methanol in a solvent contacting zone; recovering a first raffinate and a first extract composed essentially of methanol and highly basic nitrogen compounds; passing said first extract into a primary distillation zone wherein said first extract is separated into an overhead fraction composed essentially of methanol and a bottoms fraction composed essentially of highly basic nitrogen compounds; passing said first raffinate into a secondary distillation zone wherein any methanol in said first raffinate is removed overhead; passing said methanol-free first raffinate into an acid contacting zone and there contacting the raffinate with 90 to 116% phosphoric acid in an amount in excess of 0.10 pound of acid per gallon of raffinate; passing the resulting acid-raffinate mixture into a primary settling zone; recovering from said settling zone as the bottom layer a second extract composed essentially of phosphoric acid and containing organo-metallic compounds and nitrogen compounds less basic than the basic nitrogen compounds contained in said first extract, and as the top layer a second raffinate; passing said second extract into an acid dilution zone and there adding water to dilute the acid to a concentration of from about 40 to 50% H_3PO_4 ; passing said diluted acid into a secondary settling zone and recovering an upper layer composed essentially of nitrogenous compounds and organo-metallic compounds and a bottoms layer composed essentially of dilute H_3PO_4 ; passing said dilute acid bottoms layer into an acid concentration zone wherein water is removed and the H_3PO_4 is concentrated to the range of from about 90 to 116%; treating said second raffinate so as to remove substantially all of the acid therefrom; and contacting the acid-free second raffinate with a catalytic cracking catalyst under cracking conditions to form substantial amounts of low boiling hydrocarbons.

7. The process of claim 6 wherein the overhead fraction from the primary distillation zone is recycled to the solvent contacting zone.

8. The process of claim 6 wherein the acid from the concentration zone is recycled to the acid contacting zone.

9. The process of claim 7 wherein acid from the concentration zone is recycled to the acid contacting zone.

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