

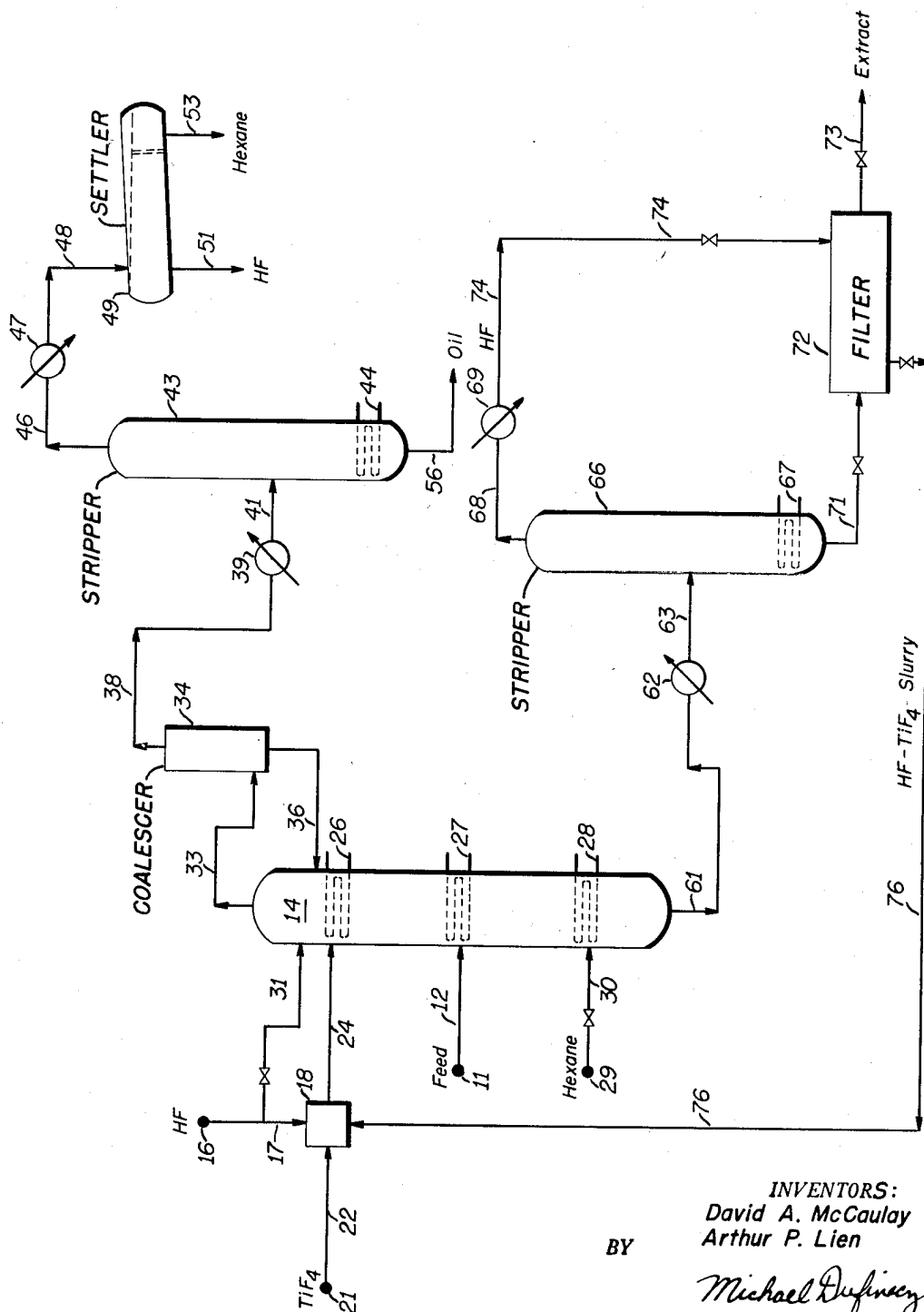
Nov. 8, 1955

D. A. McCAULAY ET AL

2,723,218

REFINING OF HYDROCARBON OILS WITH HF AND  $TiF_4$

Filed Nov. 29, 1951



INVENTORS:  
David A. McCaulay  
Arthur P. Lien  
BY  
*Michael Dufinney*  
ATTORNEY

1

2,723,218

REFINING OF HYDROCARBON OILS  
WITH HF AND  $TiF_4$ David A. McCaulay, Chicago, Ill., and Arthur P. Lien,  
Highland, Ind., assignors to Standard Oil Company,  
Chicago, Ill., a corporation of Indiana

Application November 29, 1951, Serial No. 258,918

8 Claims. (Cl. 196—13)

This invention relates to the refining of mixed hydrocarbon oils. More particularly, it relates to the refining of hydrocarbon oils containing aromatics, organic sulfur compounds, oxygenated compounds and nitrogen compounds. Still more particularly, it relates to the refining of petroleum distillates boiling in the heavier-than-gasoline range.

Naturally occurring hydrocarbon oils are mixtures of various classes of hydrocarbons and various organic compounds containing one or more of the elements sulfur, oxygen and nitrogen. For some uses many hydrocarbon oils contain an objectionable amount of aromatic hydrocarbons, for example, diesel oils, kerosenes, domestic fuel oils and lubricating oils. For some uses hydrocarbon oils should not only be low in aromatics, but also low in organic sulfur compounds. In some cases such as coal tar distillate, the oil contains substantially only aromatics and some organic sulfur compounds, and it is desired to remove the sulfur compounds only. In the case of shale oil, it is desirable to remove not only sulfur compounds, but also nitrogen compounds and oxygen compounds. One of the better methods for refining of a mixed hydrocarbon oil containing objectionable amounts of aromatic hydrocarbons and organic sulfur compounds is to treat with liquid hydrogen fluoride containing boron trifluoride. The HF- $BF_3$  treating agent acts very much like a selective solvent. However, this process has the serious disadvantage of having to operate at high pressures when temperatures above ambient are used because the  $BF_3$  is a very volatile gas.

It is an object of our invention to refine mixed hydrocarbon oils by an extraction method. Another object is to remove organic sulfur compounds and/or aromatic compounds from hydrocarbon oils containing objectionable amounts of these materials. Still another object is to develop a process for refining hydrocarbon oils, which process operates at about the vapor pressure of liquid HF. Still another object of this invention is to refine petroleum distillates which boil above about the gasoline range. Yet another object is to develop a process for removing organic sulfur compounds from hydrocarbon oil, which compounds are difficultly removable by other processes.

The above objects and other objects which will appear later in this specification are attained by treating hydrocarbon oils which contain objectionable amounts of aromatic hydrocarbons, other than benzene and toluene, and/or organic sulfur compounds, and/or phenolic compounds by treating said hydrocarbon oils with titanium fluoride in the presence of sufficient liquid HF to form a separate phase.

$TiF_4$  is a crystalline solid having a boiling point of  $543^\circ F$ . The solid is only slightly soluble in liquid HF. The solubility of  $TiF_4$  in liquid HF is enormously increased when a polyalkyl, polynuclear aromatic organic-sulfur compound, or phenolic compound is brought into contact with the  $TiF_4$ , in the presence of liquid HF. For example, a slurry of  $TiF_4$  and liquid HF is rapidly con-

2

verted to a clear reddish liquid when the slurry is contacted with a sufficient amount of xylene.

Liquid HF is a well known solvent for organic sulfur compounds and for polynuclear aromatics. However, the solvent power for organic sulfur compounds is somewhat limited. The inability to remove mononuclear aromatics seriously detracts from the usefulness of liquid HF as a selective solvent for oils containing these aromatics in addition to nonaromatics.

No improvement in quality is obtainable by the treatment of a mixed hydrocarbon oil with solid  $TiF_4$  in the absence of liquid HF.

We have discovered that organic sulfur compounds and some aromatic compounds not amenable to removal by liquid HF treatment are removable from the raw oil by treating said oil with  $TiF_4$  in the presence of sufficient liquid HF to form a separate HF-rich phase. The HF-rich phase, hereafter called the extract phase, contains liquid HF, aromatics, organic sulfur compounds, phenolic compounds, some non-aromatics and  $TiF_4$ , i. e., if all of these organic compounds are present in said oil. It is believed that the  $TiF_4$  in the extract phase exists in the form of a coordination compound or adduct with the aromatics and organic sulfur and phenolic compounds. Benzene and toluene can exist in the extract phase in about the amount soluble in liquid HF alone, which amount is about 2-3 volume percent based on HF. By using a sufficient amount of  $TiF_4$  and a sufficient amount of liquid HF, it is possible to produce a refined oil which contains substantially no compounds other than non-aromatics and benzene and/or toluene, if these aromatics are present in the raw oil.

Some improvement in quality of the oil can be obtained by using even a trace amount of  $TiF_4$  and further improvements can be obtained by increasing the amount of  $TiF_4$  until substantially all the materials removable by the liquid HF- $TiF_4$  treating agent have been removed. In general, the larger the amount of extractable materials present, the more  $TiF_4$  needed in the treatment. The upper limit on  $TiF_4$  usage is readily determined by the fact that when a solid  $TiF_4$  phase appears, no further improvement is obtainable. By the time that this third phase of solid  $TiF_4$  appears, a sufficiently refined oil has been attained. Thus we can use between a trace amount of  $TiF_4$  and an amount of  $TiF_4$  that will not dissolve completely into the extract phase. Expressing the  $TiF_4$  usage in another way, we can use from 0.1 weight percent to about 25 weight percent and, in some cases to about 100 weight percent, based on the raw oil. The amount of  $TiF_4$  needed to obtain a particular degree of refinement is readily determinable by small scale treatment of samples of the raw oil.

Sufficient liquid HF must be present in the extraction zone to form a separate HF-rich phase, i. e., extract phase. The liquid HF should be substantially anhydrous, i. e., the HF should contain not more than about 1 or 2% of water. The minimum amount of liquid HF needed will vary somewhat with the type of oil being treated and the extractable materials content of the raw oil. The viscosity of the raw oil affects phase separation and, in general, the more viscous the raw oil, the more HF needed to obtain good phase separation. The presence of extractable materials in the liquid HF increases the viscosity of the extract phase so that good phase separation may be difficult when treating raw oils containing large amounts of extractable materials with small amounts of HF. When treating naphthas and light gas oils the minimum HF usage may be as low as 5 volume percent, based on the raw oil. When treating lube stocks such as distillate for the production of S. A. E. 20 oil, as much as 20 volume percent of liquid HF may be needed to obtain good phase separation. We prefer to use more than the bare minimum

amount of liquid HF. As much as 1500 volume percent liquid HF has been used without detrimental effect. However, little significant gain in refinement is obtained by using very large amounts of liquid HF. For most raw oils satisfactory phase separation and a satisfactory degree of refinement can be obtained by using from about 10 to about 500 volume percent of liquid HF. We prefer to use between about 30 and 300 volume percent.

Since viscosity does have an appreciable effect on the cleanness of the phase separation, the viscosity of the raw oil can be reduced by adding an inert diluent thereto. The diluent should be relatively inert to the solvent action of the treating agent and also to the catalytic action of the treating agent. Additionally, the diluent should be readily separable by distillation from the refined oil, although in some cases it may be desirable to leave the diluent in the refined oil. Suitable diluents are pentane, hexane, petroleum ether, cyclohexane, benzene, toluene, various naphtha fractions low in extractable materials, etc. Materials such as heptane or octane can be used when the treating is at about ambient temperatures. However, diluents containing about 6 or more carbon atoms are readily isomerized and even cracked by our treating agent at temperatures above about 250° F., so that their use at elevated temperatures is undesirable. In general, olefinic hydrocarbons are not suitable diluents. The amount of diluent used will be dependent upon the type of raw oil being charged, but in general, will be between about 10 and 200 volume percent based on raw oil. When using a diluent it may be possible to reduce the amount of liquid HF ordinarily used and still obtain a satisfactory phase separation.

The temperature of treating is of considerable importance in our process because the liquid HF-TiF<sub>4</sub> treating agent is a very powerful catalyst for isomerization, alkylation, cracking and other reactions. In order to avoid side reactions due to catalytic effects, the temperature of contacting should be below about 200° F. Temperatures below 30° F. may be used where the properties of the feed oil do not interfere with phase separation and/or where very large amounts of HF are being used. The treating temperature should always be above the pour point of the (diluted) raw oil in order to avoid difficulty in phase separation. We prefer to operate at from about 50° to about 100° F.

Contacting time will be dependent on the type of raw oil, the amount of liquid HF-TiF<sub>4</sub> treating agent and the temperature of operation. In general, times between about 5 minutes and 60 minutes in each extraction stage will be sufficient to obtain the desired degree of refining.

We have found that in some cases a better product can be obtained by taking advantage of the catalytic action of our treating agent at elevated temperatures. By contacting the oil at temperatures between about 200° and 500° F., and preferably between about 300° and 500° F. and then cooling to below about 100° F. before making the phase separation, it is possible to obtain a refined oil in greater yield and/or better quality. The higher the temperature in the contacting zone, the shorter should be the contacting time. At 500° F. the contacting time should be between 1 and 10 minutes. Prolonged contacting times may be harmful to product quality and/or yield.

We have also discovered that in many cases it is advantageous to operate in a two-step process. Liquid HF alone is used as the treating agent in the first step and in the second step our liquid HF-TiF<sub>4</sub> treating agent is used to treat the raffinate from the first step. In this method of operation we treat with from about 5 to 300 volume percent of liquid HF, based on raw oil, at temperatures below about 250° F. The extract phase from this HF treatment contains organic sulfur compounds and polynuclear aromatics. The raffinate phase from the HF treatment is treated with our liquid HF-TiF<sub>4</sub> treating agent, as though it were a raw oil, to obtain an extract

phase containing refractory organic sulfur compounds and polyalkyl aromatics. In some cases it is advantageous to carry out the liquid HF extraction at temperatures from about 250° to 500° F. and to treat the raffinate phase from this first step with our HF-TiF<sub>4</sub> treating agent at temperatures below about 200° F. It is to be understood that when operating above the boiling point of HF, super-atmospheric pressures must be used in order to keep the HF in the liquid state.

The feed to our process can be: various fractions obtained from the distillation of crude oil, for example, naphthas, kerosenes, heater oil, lube oils, etc., or the crude oil itself, or reduced crudes. Another class of materials suitable as a feed may be oils derived from the treatment of the above materials, for example, raffinates and extracts from the solvent treatment of kerosenes or lube oils. Shale oil, and its various fractions, is a suitable feed to our process. The so-called light oil from the coking of coal is an exceptional feed to our process since the sulfur compounds in the benzene and toluene fractions are extremely refractory to conventional desulfurization methods. The liquid products from the hydrogenation of coal or the Fischer-Tropsch process are suitable feeds to our process. Liquid HF-TiF<sub>4</sub> is a powerful catalyst for alkylation purposes. Appreciable amounts of olefins can be eliminated from olefin-containing feeds by treatment with liquid HF-TiF<sub>4</sub>; the alkylate may or may not be extracted into the extract phase. In general, oils containing large amounts of olefins are not a desirable feed to our process. In general, the most suitable feed stocks are petroleum distillates boiling in the heavier-than-gasoline range, that is, above about 350° F. and below about 750° F., and particularly those distillates derived from high sulfur and high aromatic content crudes, such as, West Texas crude, Winkler crude, etc.

The raffinate phase will usually contain some dissolved liquid HF and also some entrained HF; small amounts of solid TiF<sub>4</sub> may also be entrained. The TiF<sub>4</sub> can be recovered by filtration, by a coalescing operation or in some cases by distilling the raffinate oil. The liquid HF is readily removed from the raffinate phase by distillation at temperatures of about 100° F., at atmospheric pressure. In some cases the raffinate may contain minor amounts of alkyl fluorides; these can be readily removed by percolation through bauxite.

The extract phase is readily decomposed by treatment with water, preferably cold water or ice; the upper layer of extract oil can be decanted from the lower aqueous layer. The extract oil contains the extracted materials, i. e., hydrocarbons and/or organic sulfur compounds. The lower aqueous layer consists of a mixture of hydrofluoric acid and TiF<sub>4</sub>. The extract oil can be freed of traces of HF by treatment with dilute caustic. This method is particularly suitable for laboratory operations.

We prefer to decompose the extract phase as follows: The extract phase is placed in a vessel, usually provided with a few fractionation trays, wherein the temperature of the extract phase is raised until the HF vaporizes and passes out of the vessel. The top temperature in the decomposing vessel is held at about the boiling point of HF in order to prevent the removal of extract materials along with the HF. In the bottom of the decomposer after the removal of HF, there exists a slurry of extract materials and solid finely divided TiF<sub>4</sub>. This slurry is passed to a filter which retains the solid TiF<sub>4</sub>. The TiF<sub>4</sub> can be reused in the process. In the case of lower boiling extract materials, the extract materials may be distilled leaving behind the solid TiF<sub>4</sub>. By operating under vacuum, the HF may be removed at low temperatures. We operate at from about 200° to 500° F.; the lowest possible temperature is preferred because of the side-reactions resulting from the catalytic action of the treating agent. Where it is desired to avoid as much as possible side-reactions in the extract phase, the decomposer may be operated under vacuum in order to remove a

major part of the liquid HF at temperatures below about 100° F.; and then the partially dennuded extract phase is heated to from about 200° to 500° F. to remove the remainder of the HF.

Normally the raffinate from our process will be the desired product. However, the low sulfur, low aromatic content thereof makes the refined oil a very suitable feed to a catalytic cracking operation; thus our process may be used to treat cycle gas oils which are low quality catalytic cracking feeds in order to improve their suitability for catalytic cracking. These cycle oils may be derived from thermal cracking, coking, or catalytic cracking.

We have found that the organic sulfur compounds present in the extract from the treatment of heavy naphtha and gas oils boiling between about 350° and 600° F. are very readily catalytically cracked to produce a high octane, low sulfur product. Particularly good results are obtained when the extract is fractionated and that portion boiling below about 450° F. is charged to the catalytic cracking operation.

We have discovered that  $TiF_4$  in the presence of liquid HF forms a coordination compound or adduct, hereafter called a complex, with polyalkylbenzenes, such as, xylene, mesitylene, diethylbenzene, hexamethylbenzene, etc. The polyalkylbenzene- $TiF_4$  complex contains for each mol of complex 2 mols of  $TiF_4$ , 1 mol of polyalkylbenzene and (we believe) at least 1 mol of HF. We have found that substantially all the xylenes can be extracted from a mixture of benzene, toluene and xylene by treating said mixture with  $TiF_4$  in an amount greater than the theoretical 2 mols of  $TiF_4$  per mol of xylene present and with sufficient liquid HF to form an extract phase.

We have also discovered that the complex formed by the three isomers of xylene—ortho, meta and para—have different dissociation constants; the meta isomer forms the most stable complex. By treating a mixture of meta-xylene and para-xylene (or ortho-xylene or both) with  $TiF_4$  in the presence of liquid HF, it is possible to produce an extract containing a higher meta/para ratio than the feed and a raffinate containing a lower meta/para ratio than the feed. By using a sufficient number of extraction stages and a liquid HF- $TiF_4$  treating agent containing about 2 mols of  $TiF_4$  per mol of meta-xylene present in the feed, it is possible to obtain a substantially pure meta-xylene product.

We have also discovered that the monoalkylbenzenes, other than toluene, are rapidly disproportionated when treated with liquid HF- $TiF_4$  at about ambient temperatures; for example, ethylbenzene is rapidly converted to benzene and meta-diethylbenzene when contacted with our treating agent at about 70° F. In the case of the monoalkylbenzenes having three or more carbon atoms in the side chain not only does disproportionation occur, but also isomerization of the side chain and even cracking of the side chain. These effects can be avoided by reducing the temperature at which the disproportionation reaction takes place. In general, when treating propyl and butylbenzene, the temperature of contacting should be below about 50° F. By the use of this discovery we are able to treat a mixture of benzene, toluene and  $C_8$  aromatics to produce a raffinate of benzene and toluene and an extract containing xylenes, ethylxylene and meta-diethylbenzene. The diethylbenzene and ethylxylene are readily separable by distillation from the xylenes. A further treatment of the xylene fraction will produce substantially pure meta-xylene and an ortho-para-xylene fraction which is separable by superfractionation into substantially pure ortho and para-xylenes.

We have also discovered that the polyalkylbenzenes are readily isomerized by our liquid HF- $TiF_4$  treating agent. When operating at temperatures below about 90° F., it is possible to convert a mixture of xylene isomers into a substantially pure meta-xylene product. In order to achieve this result it is necessary to operate with a

homogeneous phase system wherein no raffinate phase of either aromatic or non-aromatic hydrocarbons is present; this homogeneous phase is achieved by using at least 2 mols of  $TiF_4$  per mol of polyalkylbenzene in the feed. The more carbon atoms in the alkyl group, the lower the temperature of operation needed in order to prevent side-reactions.

We have also discovered that a mixture of xylenes can be disproportionated to a mixture of toluene and 1,3,5-trimethylbenzene by treatment with liquid HF- $TiF_4$  treating agent at temperatures above about 100° F. and long contact times. Homogeneous phase treatment decreases the contact time needed when operating at temperatures of about 100° F. It is possible to obtain a mixture of tetramethylbenzene and hexamethylbenzene by treating pentamethylbenzene with liquid HF- $TiF_4$  at temperatures of above about 100° F., preferably in a homogeneous phase operation. It is possible to obtain substantially pure 1,3,5-triethylbenzene by treating in the homogeneous phase with liquid HF- $TiF_4$  at temperatures below about 125° F. a substantially pure diethylbenzene.

Several examples of the results obtainable with our process are set out below. In all cases the contacting was carried out in a carbon steel reactor equipped with a 1725 R. P. M. stirrer. The experimental procedure was to add a quantity of  $TiF_4$  to the reactor, followed by liquid HF and then by the feed oil. The contents of the reactor were stirred for a selected time at the selected temperature; at the end of the contacting time the contents of the reactor were settled for a selected time. The lower extract phase was withdrawn into a vessel containing cracked ice; the extract oil was decanted from the lower aqueous layer. The extract oil and the raffinate phase were washed with dilute aqueous caustic to eliminate traces of HF. The refined oil and extract oil were analyzed by the usual methods and also where possible by ultraviolet and infrared absorption methods.

#### Run 1

In this run 379 g. of feed were prepared by blending 300 ml. of heptane with 100 ml. each of m-xylene and p-xylene—a total of 1.6 mol of xylenes. Solid  $TiF_4$  was added to the reactor—1.38 mols (177 g.); this corresponds to 47 wt. percent on the feed. Liquid HF—390 ml.—78 volume percent based on feed was added and then the feed was added. The reactor was agitated for 30 minutes at 38° F.; the contents were allowed to settle for 15 minutes. The raffinate and extract were analyzed and found to consist of:

	Raffinate	Extract
Yield, Vol. Percent.....	83.2	16.8
Composition, Vol. Percent:		
Heptane.....	70.0	11.6
m-Xylene.....	7.8	74.3
p-Xylene.....	22.2	14.1
Ratio m/p.....	0.28	5.25

The extract phase contained no solid  $TiF_4$ ; all had been dissolved into the extract phase. Based on the mols of xylene in the extract, each 2 mols of  $TiF_4$  had complexed with 0.9 mol of xylene.

#### Run 2

In this run a comparison was made between HF extraction alone and HF- $TiF_4$  treatment of an oil which had been previously extracted with liquid HF alone. A gas oil having a sulfur content of 1.46 wt. percent and a boiling range of 425° to 675° F. was treated with 23 volume percent of liquid HF at about 105° F. The raffinate from this treat had inspections as given below.

Parallel treats were made on this feed using in one

7

treat liquid HF alone and in the other liquid HF-TiF<sub>4</sub>. In each treat 500 ml.—427 g.—of feed and 30 volume percent, based on feed, of liquid HF was used. In the one treat, 26 g. 6.1 wt. percent based on feed, of solid TiF<sub>4</sub> was added to the reactor. In each treat the contents of the reactor were agitated for 60 minutes and settled for 60 minutes. The phases were separated and the raffinates and extracts were analyzed.

	Feed	HF only Raffinate	HF-TiF <sub>4</sub> Raffinate
Yield, Vol. Percent.....		98.4	91.5
Sulfur, Wt. Percent.....	0.51	0.44	0.20
Percent Desulfurization.....		14	61
Aniline Point, °C.....	75	76	80
n <sub>D</sub> <sup>20</sup> .....	1.4743	1.4732	1.4674
		Extract	Extract
Sulfur, Wt. Percent.....		7.3	3.8
n <sub>D</sub> <sup>20</sup> .....		1.5430	1.5568

This run shows very clearly the superiority of our treating agent for removing aromatics and refractory organic sulfur compounds from an HF treated gas oil.

## Run 3

The feed to this run was a distillate from a Winkler crude which is used for the manufacture of S. A. E. 20 motor oil. This distillate had the following inspections:

ASTM Distillation:		
Initial.....°F	631	
50%.....°F	733	
79% off.....°F	760	
°API.....	22.4	
NPA, color.....	1.5-2	
SSU (100° F.).....	308.0	
SSU (210° F.).....	48.4	
Viscosity index (Dean and Davis).....	41	
n <sub>D</sub> <sup>20</sup> .....	1.5125	
Sulfur, wt. percent.....	1.68	

For purposes of comparison two treats were made, one with liquid HF alone and one with liquid HF-TiF<sub>4</sub>. In one treat, the feed was contacted with 20 volume percent of liquid HF at 70° F. for one hour; the contents of the reactor were settled for one hour.

In the other treat, 49 g. of TiF<sub>4</sub> were added to the reactor; 100 ml. of liquid HF was added, and then 500 ml.—456 g.—of the feed was added. This represents a TiF<sub>4</sub> usage of 10.7 wt. percent based on feed. The contents were agitated at 70° F. for one hour and settled for 2 hours. Phase separation was quite poor because the two phases were about the same color and viscosity—the yields were unreliable and are not reported. A sample of the raffinate phase was obtained, which was substantially free of extract phase and analyzed. The results of these treats are,

	HF alone Raffinate	HF-TiF <sub>4</sub> Raffinate
SSU (100° F.).....	280.1	252.0
SSU (210° F.).....	48.2	47.2
Viscosity Index.....	52.3	63.5
n <sub>D</sub> <sup>20</sup> .....	1.5060	1.4988

## Run 4

This run differs from Run 3 essentially only in the amount of liquid HF used. In one run 700 ml. of the Winkler 20 oil was treated with 350 ml. of liquid HF at 70° F. for one hour, and then settled for two hours. In the other run 500 ml.—451 g.—of the Winkler 20 oil, 250 ml. of liquid HF and 50.2 g. of TiF<sub>4</sub> were used at a temperature of 70° F. at a one-hour contact time and

8

a two-hour settle. This represents a TiF<sub>4</sub> usage of 11.1 wt. percent on feed. In order to facilitate handling, the extract oil was diluted with benzene before the aqueous caustic washing step; the benzene was removed by distillation before analyzing the extract oil. The results of these two treats were,

	HF alone Raffinate	HF-TiF <sub>4</sub> Raffinate
Yield, Vol. Percent.....	86.7	81.0
SSU (100° F.).....	272	240.0
SSU (210° F.).....	47.6	46.7
Viscosity Index.....	55.5	65.0
n <sub>D</sub> <sup>20</sup> .....	1.5083	1.4982
Sulfur, Wt. Percent.....	0.91	0.87
Percent Desulfurization.....	46	66
ASTM Distillation:		
Initial, °F.....	630	624
50% off.....	723	729
80% off.....	760	
83% off.....		760
	Extract	Extract
Viscosity Index.....	-175	-156

Runs 3 and 4 show the superiority of our treating agent over HF alone in the refining of this very poor quality lube oil distillate from a high sulfur, high aromatic Winkler crude. Also the runs show that at about a constant TiF<sub>4</sub> usage, the effect of HF increase is noticed primarily in the improvement of phase separation.

The figure illustrates a commercial size embodiment of our invention wherein the feed is a virgin distillate from a West Texas crude; this distillate has a boiling range between about 375° and 540° F., has a sulfur content of about 1.7 wt. percent and has a total aromatic content of about 20 volume percent.

In this embodiment we show a tower type of continuous countercurrent operation in the extraction step. This tower can be packed with HF-resistant materials, such as Raschig rings, Berl saddles, alumina balls, etc.; or, preferably, it is equipped with modified bubble trays. However, we are not limited to a tower operation and we can use a series of batch countercurrent extraction zones instead of a tower. Furthermore, in some cases, a satisfactory product oil can be obtained by a single-stage extraction, i. e., only a contactor and a single settler are needed in the extraction zone.

The feed distillate from source 11 is passed by way of line 12 into about the vertical midpoint of extraction tower 14. The exact point of feed entry will vary somewhat with the feed and the conditions of operation; in some cases, the point of feed entry can be near the bottom of the tower.

Liquid HF from source 16 is passed through line 17 into vessel 18, which vessel 18 is provided with agitating means not shown. Finely divided TiF<sub>4</sub> from storage 21 is passed by way of line 22 into vessel 18. Many methods are known in the art for introducing a finely divided solid into a line and conveying the material into a closed vessel; for example, storage 21 may be equipped with a star valve at the exit thereof and line 22 may be equipped with conveying flights for propelling the solid. In vessel 18, the liquid HF and the TiF<sub>4</sub> form a slurry—when, as is usually the case, more TiF<sub>4</sub> is used than is soluble in the liquid HF—which slurry is passed through line 24 into an upper part of tower 14. In this illustration the TiF<sub>4</sub> is added to the tower along with the liquid HF. However, the TiF<sub>4</sub> could be added along with the feed or could be injected into the tower directly—near the top, for example. In this case, we use 50 volume percent of liquid HF and 15 wt. percent of TiF<sub>4</sub>, both based on the feed. Another method of introducing the TiF<sub>4</sub> into the system, is to add TiCl<sub>4</sub>—a liquid—into vessel 18 where the chloride reacts with HF to produce TiF<sub>4</sub>; extra HF must be added to vessel 18 to participate in the reaction. Means for venting HCl should be provided on vessel 18.

Tower 14 is provided with heat exchangers 26, 27 and 28 which enable the tower to be operated at substantially constant temperature or with a temperature gradient throughout the length of the tower. In this embodiment of our process, we operate at a uniform temperature of 70° F. and at a pressure of about 10 p. s. i. g. The contact time per extraction stage in tower 14 is about 10 minutes.

In order to improve phase separation, and selectivity of the extraction, a hexane diluent from source 29, may be added to the tower at a point near the bottom thereof by way of valve line 30. The diluent can be added to the feed directly, if desired. The amount of diluent used will be dependent on the feed, the temperature of extraction and the amount of liquid HF and TiF<sub>4</sub> used. In this illustration, we use about 10 volume percent of hexane, based on the feed.

When operating with viscous feeds and low temperature, some TiF<sub>4</sub> and liquid HF may be entrained in the raffinate phase and pass out of the tower. In order to retain most of this entrained material, a stream of liquid HF can be introduced into the tower below the exit point of the raffinate phase. The wash liquid HF is introduced into tower 14 by way of valved line 31. The amount of liquid HF from lines 24 and 31 should be so adjusted that the total liquid HF in the tower does not exceed the desired amount. In this case, we prefer to operate without the addition of a liquid HF wash.

The raffinate phase, which contains some HF and TiF<sub>4</sub> occluded therein, is passed out of tower 14 by way of line 33 into coalescer 34. Coalescer 34 may be a baffled vessel or may be packed with steel wool. The occluded HF and TiF<sub>4</sub> coalesce and drain to the bottom of coalescer 34; the recovered material is returned to tower 14 by way of line 36.

The raffinate phase is passed out of coalescer 34 through line 38, heater 39 and line 41 into stripper 43, which is provided with internal heater 44. The temperature in stripper 43 is maintained high enough to remove dissolved HF and hexane—a vapor outlet temperature of about 160° F. at atmospheric pressure is suitable.

The vapors of HF and hexane are passed through line 46, condenser 47 and line 48 into settler 49. The liquid HF and hexane form two layers in settler 49. The lower HF layer is withdrawn by way of line 51 and is recycled to line 17 for reuse in the process, by lines not shown. The hexane is withdrawn by way of line 53 and is recycled to line 30 for reuse in the process, by lines not shown.

The product oil, which is now low in both aromatics and organic sulfur compounds and is suitable for use as domestic heating oil, is withdrawn from stripper 43 by way of line 56 to storage, not shown.

The extract phase consisting of liquid HF, TiF<sub>4</sub>, aromatics, organic sulfur compounds and some non-aromatics is withdrawn from tower 14 through line 61. The extract phase is passed through heater 62 and through line 63 into stripper 66, which is provided with an internal heater 67.

Stripper 66 is operated at a bottoms temperature great enough to distill the liquid HF from the extract phase. The top temperature in the stripper should be low so that substantially pure HF is taken overhead through line 68, which HF is condensed by cooler 69. The bottom temperature in stripper 66 may be from about 200 to 500° F. We prefer to operate at a low temperature of about 200° F. in order to minimize cracking and isomerization reactions in the extract phase.

After the removal of the HF, the bottom of the stripper contains the extract and solid, finely divided TiF<sub>4</sub>. These materials are withdrawn through valved line 71 and are passed into filter 72. Filter 72 may be any type of HF-resistant and HF-vapor tight filter, such as a plate and frame filter, or a rotary filter, or a centrifuge. We prefer to use a Sweetland-type filter. The TiF<sub>4</sub> is retained in the filter and the extract is passed to storage, not

shown, by way of valved line 73. It is to be understood that, even though we show only one filter, for continuous operation two or more filters would be used.

The TiF<sub>4</sub> is removed from filter 72 by means of a backwashing operation with liquid HF from condenser 69 and line 74. The slurry of liquid HF and TiF<sub>4</sub> is passed from filter 72 through line 76 to vessel 18 for reuse in the process.

We do not wish to be bound by the above embodiment as the only way of carrying out our process. Many other variations are possible and we include these within the scope of the invention. For example, when operating on low boiling distillates, stripper 66 could be operated as a flash drum by preheating the extract phase to a temperature so that all the extract liquids and HF would be vaporized and pass out through line 68. The extract and HF could be condensed and separated by decantation. The solid TiF<sub>4</sub> could be readily removed from the bottom of the stripper 66. Or instead of a flash distillation, all the extract liquids could be taken over by simple distillation in stripper 66.

Instead of using a filter, the slurry from stripper 66 can be sent into a separator and the TiF<sub>4</sub>-free extract decanted. A very thick slurry of TiF<sub>4</sub> and some extract can be recycled to the extraction step. Of course, additional TiF<sub>4</sub> is needed, in this method of operation, in order to recover the recycled extract materials.

We claim:

1. A refining process which comprises contacting, at a temperature between about 50 and about 100° F. for a time between about 5 and 60 minutes, a hydrocarbon oil containing materials selected from the class consisting of polyalkylbenzene, poly nuclear aromatics, organic sulfur compounds and phenolic compounds, with liquid HF in an amount between about 10 and about 500 volume percent and TiF<sub>4</sub> in an amount between about 0.1 and 100 weight percent, respectively, based on said oil, and separating an extract phase from a raffinate phase, which raffinate phase contains less of said materials than said oil.

2. The process of claim 1 wherein the amount of TiF<sub>4</sub> is between about 0.1 and 25 weight percent.

3. The process of claim 1 wherein said HF is present in an amount between about 30 and 300 volume percent.

4. The process of claim 1 wherein said oil is a petroleum distillate boiling within the range of about 375° to 750° F.

5. A process for refining a hydrocarbon oil containing polyalkylbenzenes, which process comprises contacting said oil at a temperature between about 50° and 100° F. for a time between about 5 and 60 minutes with from about 0.1 and 100 weight percent of TiF<sub>4</sub> in the presence of from about 10 to 500 volume percent of liquid HF, both based on said oil, and separating a raffinate phase from an extract phase.

6. The process of claim 5 wherein said extract phase is decomposed by heating, and liquid HF and TiF<sub>4</sub> are recovered therefrom, and wherein said recovered liquid HF and TiF<sub>4</sub> are reused in said contacting step.

7. A process for refining a lubricating oil stock, which process comprises the steps of (1) contacting said stock at a temperature below about 250° F. with 5 to 300 volume percent of liquid HF, based on said stock, (2) separating a first raffinate phase from a first extract phase, (3) contacting said first raffinate phase with from about 0.1 to 100 weight percent of TiF<sub>4</sub> in the presence of from about 10 to 500 volume percent of liquid HF, both based on said first raffinate phase, at a temperature below about 200° F., and (4) separating a second raffinate phase from a second extract phase.

8. A process for removing polyalkylbenzenes from a naphtha which contains substantially no other extractable materials, which process comprises contacting said naphtha with about 2 mols of TiF<sub>4</sub> per mol of polyalkyl-

11

benzene to be removed in the presence of about 5 to 500 volume percent, based on said naphtha, of liquid HF at a temperature between about 50° and about 100° F. for a time between about 5 and 60 minutes, and separating a raffinate phase from an extract phase, which extract phase contains extracted polyalkylbenzenes. 5

12

## References Cited in the file of this patent

## UNITED STATES PATENTS

2,378,762	Frey	June 19, 1945
2,428,455	Friedman	Oct. 7, 1947
2,514,866	Hovey	July 11, 1950