March 25, 1952 B. C. BENEDICT 2,590,490

PROCESS FOR REFINING LUBRICATING OIL

Filed May 24, 1948 2 SHEETS—SHEET 1

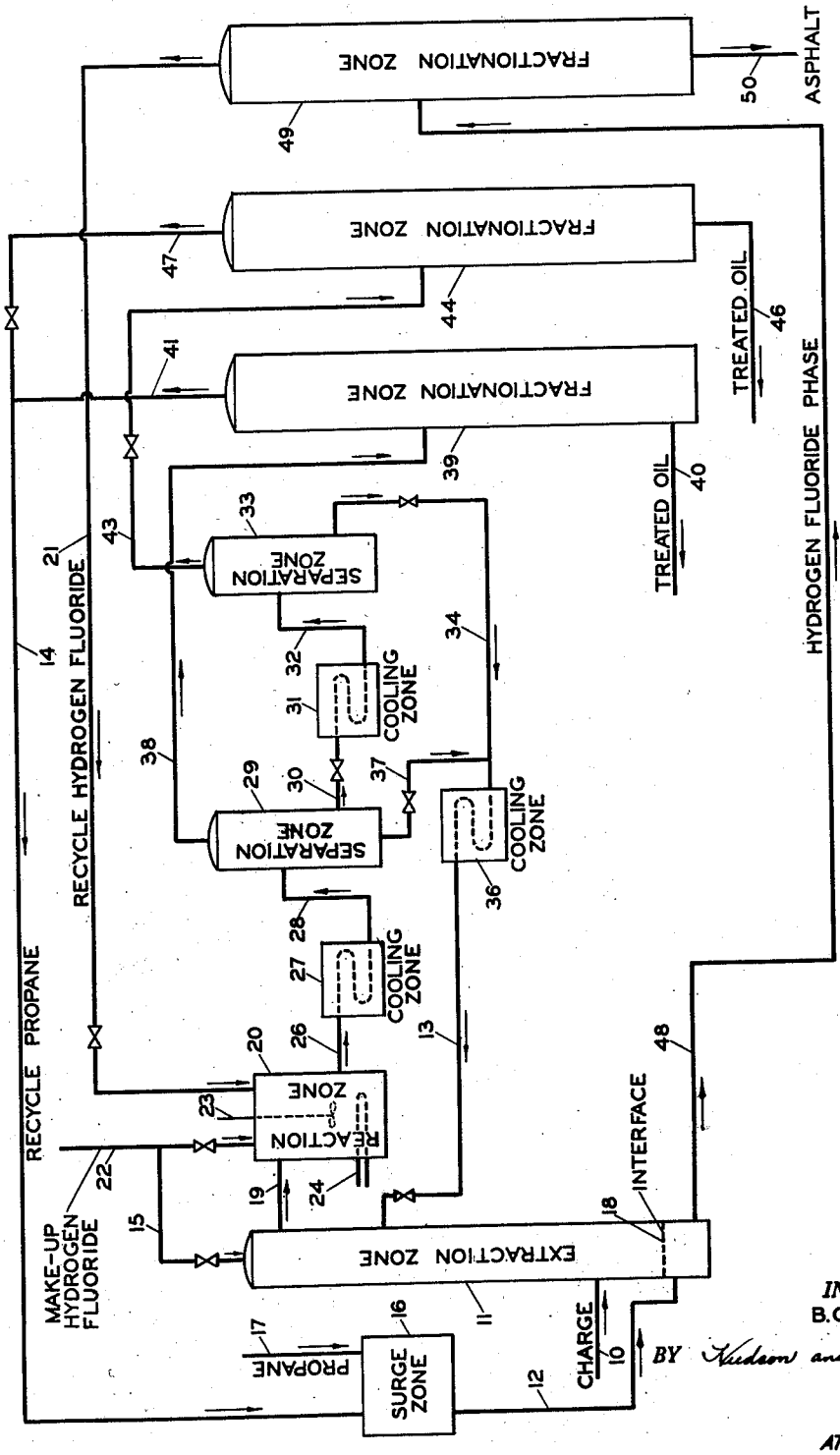


FIG. 1

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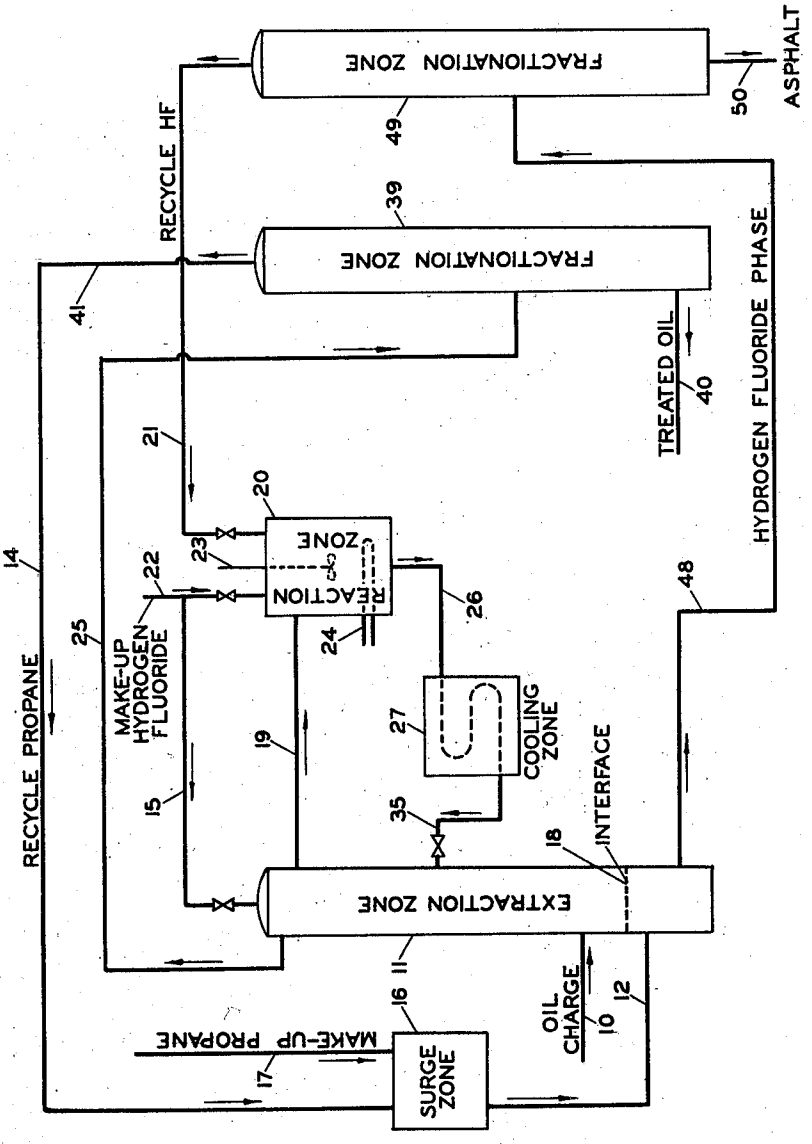


FIG. 2

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PROCESS FOR REFINING LUBRICATING OIL

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This invention relates to a process for refining lubricating oil. In one of its more specific aspects it relates to a process for producing an improved lubricating oil. In a preferred emobdiment of this invention lubricating oil of improved properties is produced by a two-step refining process utilizing hydrogen fluoride and a hydrocarbon solvent.

Lubricating oils of high quality have been manufactured from crude oil fractions having suitable boiling ranges by many processes, including sulfuric acid refining, aluminum chloride refining, and solvent extraction. In sulfuric acid or aluminum chloride processes, the treating reagents are consumed by reaction with the oil and are not economically recoverable from the resulting sludges. In solvent refining, the action is simply one of separating high quality lubricating ingredients from the crude oil, or removing the undersirable or low quality constituents; thus the yield of finished lubricating oil can be no greater than the proportion of lubricating oil-grade hydrocarbons in the raw material.

An object of this invention is to produce high quality lubricating oil in high yeld by a chemical process in which the refining agents are recoverable.

Another object is to provide a two step process for manufacturing an improved lubricating oil.

Another object is to combine advantageously into a process for manufacturing lubricating oil, the treatment of an oil with hydrogen fluoride and a hydrocarbon solvent.

Other objects and advantages of this invention will be apparent to one skilled in the art from the accompanying disclosure and discussion.

According to my invention, in a first step a lubricating oil stock is extracted with a hydrocarbon solvent and a hydrogen fluoride-rich phase from a second step; and in the second step a hydrocarbon solvent-oil mixture is treated with liquid hydrogen fluoride. The above lubricating oil stock may if desired contain both light and heavy materials outside the lubricating oil boiling range which may be easily removed by such means as fractionation subsequent to the refining treatment.

In a preferred embodiment of my invention a crude oil fraction having a suitable boiling range is extracted in step one with propane and a hydrogen fluoride-rich phase from a second step, the propane and oil passing countercurrently to the hydrogen fluoride phase. The propane used acts as a precipitating solvent for the asphalt, and the hydrogen fluoride-rich phase acts

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as a selective solvent for the asphalt and resins. Step two of the process is a reaction step wherein the propane-oil phase from the extraction step is treated with anhydrous liquid hydrogen fluoride, stirring vigorously. The effluent from step two is separated into an oil rich layer and a hydrogen fluoride-acid soluble oil layer, the latter mixture being injected back into the step one extratction process as one of the extractive media. The oil rich phase, that is, the phase containing both oil and propane, is separated in such a manner that the propane is recycled to the countercurrent extraction step, and the oil is recovered as the process product.

By this process the molecules of least stability are removed from the oil by solvent action and hydrogen fluoride extraction leaving only those of more stable structure to be acted upon in the reaction zone by the hydrogen fluoride. Thus, with the most unstable molecules such as asphalt, olefinic materials, and some armoatics removed, the control of the reaction is improved, and it is no longer necessary to produce excessive reaction with the most reactive constituents in order to produce sufficient reaction with the less reactive components. Since the most reactive portions of the oil have already been removed by extractive means, the activity of the hydrogen fluoride is maintained better and with less consumption of the reagent. Another advantage is that the hydrogen fluoride layer from the reaction step with its dissolved hydrocarbons is countercurrently extracted in the extraction step with the oil-solvent mixture to remove any desirable oil which may be occluded mechanically or be in solution with the hydrogen fluoride. At the same time the hydrogen fluoride extracts the asphaltic and resinous materials and especially the color bodies, giving an oil of improved appearance as well as improved viscosity index and stability.

Because the two treatments of the oil with hydrogen fluoride are in separate zones, each may be maintained at its optimum operating temperature and contact time. Thus, the chemical treatment in the reactor may take place under conditions of elevated temperature and very vigorous agitation, whereas the extraction step may be carried out at lower temperatures commensurate with the amount of materials which must necessarily be removed by extraction and with the desired contact time.

My process is not limited to treatment of one specific oil, but may be modified within the scope of the invention to adapt it to any type of lubri-

cating oil or lubricating oil stock to be treated and to the products which are desired. For example, an oil may be reacted at a high temperature so that a large portion of it is dissolved in the hydrogen fluoride phase. This dissolved material may include asphaltic or resinous substances not already removed by the extraction step, most of the naphthenes, and a portion of the paraffins. Separation of the oil-hydrocarbon solvent phase from this treatment gives an oil of the highest viscosity index obtainable from the particular charge stock. Cooling of the hydrogen fluoride phase will cause the less soluble of the extracted hydrocarbons to separate out, thus giving an additional oil product. If cooling is accomplished in steps and separation is made following each cooling step, several fractions of hydrogen fluoride-soluble oil may be obtained, ranging from oil of improved viscosity index to that with a viscosity index less than the treated oil.

The extractive hydrocarbon solvent may be any solvent which preferentially dissolves the desirable components of the oil, and produces an oil-solvent mixture at operating ratios the density of which is less than that of the hydrogen fluoride or the hydrogen fluoride with its dissolved components. This extractive solvent should also be non-reactive with the hydrogen fluoride at operating temperatures. In general, a paraffin hydrocarbon having from 2 to 6, but preferably 2 to 4, carbon atoms per molecule meets these requirements. One such solvent which has already been mentioned is propane; another is n-butane.

In the following descriptions two methods of operating my process are specifically disclosed. It is understood, however, that while they are representative in general of my process, various minor changes may be made in adapting the process to the various conditions within the scope of this invention. The drawings are schematic flow diagrams and are to be referred to in conjunction with the following discussion. Various additional valves, pumps, and other conventional equipment, necessary for the practice of this invention, will be familiar to one skilled in the art and have been omitted from these drawings for the sake of clarity.

In Figure 1, oil to be treated is introduced to extraction zone 11 through line 10, propane is introduced through line 12, and a hydrogen fluoride-rich phase is introduced through line 13. It is preferred that at least a portion of the propane be introduced below the interface formed by the propane-oil phase and the hydrogen fluoride-rich phase in sufficient quantity and sufficiently below the oil introduction point to give a withdrawn hydrogen fluoride-rich phase free from occluded unreacted (undissolved) oil. A suitable ratio of oil charge to propane is 1:3 to 1:12. The propane is either recycled propane from line 14 which is passed through surge zone 16, or makeup propane introduced through line 17 and also passed through surge zone 16 or a mixture of both. The recycle propane may contain minor portions of hydrogen fluoride from the reaction step hereinafter described; however, this is not detrimental. Any suitable extraction equipment may be used such as a vertical column packed with Raschig rings, helices, or other similar packing, or a column containing bubble plates, baffles, etc. However, my process is not to be limited by the specific type of extraction equipment and other apparatus used. The materials are charged to extraction zone 11 at a temperature in the range of 100 to 200° F., but preferably at about 180° F. The flow of materials to the extraction zone is so controlled that the interface between the propane-oil phase and the hydrogen fluoride-rich phase may be varied; however, the preferred level is slightly above the point where the propane is introduced through line 12, as indicated by reference numeral 18. Make-up hydrogen fluoride is introduced to extraction zone 11 through lines 22 and 15. A suitable extraction temperature is between 100 and 210° F. and preferably between 180 and 205° F.

The pressure within extraction zone 11 should be maintained slightly above the vapor pressure of the constituents to prevent vaporization and to maintain the constituents in substantially liquid phase. The solubility of the oil will vary with the pressure, thus control of the pressure is essential. The preferred pressure would be such that the constituents are maintained substantially in liquid phase, and not greater than about 1000 pounds per square inch gauge.

The oil rich phase from extraction zone 11 is withdrawn through line 19 and passed to reaction zone 20 where it is reacted with recycle hydrogen fluoride introduced through line 21 and/or make-up hydrogen fluoride introduced through line 22, at a temperature above that in the extraction zone and in the range of 100 to 500° F., but preferably at about 350° F. The recycle hydrogen fluoride may contain some propane which is not objectionable since the oil already contains propane. The amount of hydrogen fluoride used may vary within the range of 0.05 to 5 volumes per volume of the oil rich phase, but preferably 1 volume is used per volume of oil and propane. The contact time for the materials in reactor 11 is from 10 minutes to 5 hours, however, the preferred time is about 2 hours. Suitable means for mixing the constituents in reaction zone 20 is represented by stirrer 23, and a suitable means is used for maintaining the desired temperature, such as heater 24.

Effluent from reaction zone 20 is passed through line 26, cooling zone 27, and line 28 to separation zone 29. The hydrogen fluoride layer is withdrawn from separation zone 29 through line 30 and passed through cooling zone 31 and line 32 to separation zone 33. The hydrogen-fluoride layer from separation zone 33 is removed through line 34 and passed to cooling zone 36 where its temperature is adjusted to that of the extraction zone 11 into which it is to be introduced. From there it is passed through line 13 and introduced to extraction zone 11 as described heerinabove. If it is desirable not to use separation zone 33, the hydrogen fluoride layer in separation zone 29 is withdrawn through line 37 and passed through line 34, cooling zone 36, and line 13 to extraction zone 11. If desired, a portion of the HF phase from zone 29 may be withdrawn and passed along with the HF phase from zone 33 to the extraction zone 11.

The oil layer from separation zone 29 is withdrawn through line 38 and pased to fractionation zone 39. Treated lubricating oil is recovered from zone 39 through line 40. Propane is recycled to surge zone 16 from fractionation zone 39 through lines 41 and 14. The oil layer from separation zone 33 is passed through line 43 to fractionation zone 44. Treated oil is recovered through line 46 and propane is recycled through lines 47 and 14 to surge zone 16. The product oils recovered through lines 40 and 46

may be freed from traces of propane in a steam stripping zone not shown and then alkali washed or clay treated to remove traces of hydrogen fluoride.

The hydrogen fluoride phase from extraction zone 11 is removed through line 48 and passed to fractionation zone 49. Here the hydrogen fluoride is separated from the asphaltic and resinous materials and passed through line 21 to reaction zone 20. The asphalt and similar materials are removed from fractionation zone 49 through line 50. Traces of hydrogen fluoride may be removed from the asphaltic materials by azeotropic distillation with propane or by steam stripping.

Referring now to Figure 2 which is a second embodiment of my invention the lines and zones serving the same purpose as those in Figure 1 are similarly numbered. Where it is necessary to minimize the equipment required for economic or other reasons, my process may be operated as shown by Figure 2 and as described hereinafter. For the sake of brevity, the reaction conditions will be omitted in this discussion since they are the same as those given for Figure 1.

The oil to be treated is introduced through line 10 to extraction zone 11. Propane is introduced through line 12, and a hydrogen fluoride rich phase, hereinafter described, is introduced through line 35. The propane is obtained from surge zone 16 which is fed by lines 14 and 17. When desirable, make-up hydrogen fluoride is introduced through lines 22 and 15. A portion of the oil rich phase which also contains most of the propane is removed from extraction zone 11 through line 19 and passed to reaction zone 20. This zone is equipped with a stirrer 23 and a heater 24. Recycle hydrogen fluoride and make-up hydrogen fluoride are introduced to the reaction zone through lines 21 and 22, respectively. Effluent from reaction zone 20 is passed through line 26, cooling zone 27, and line 35 to extraction zone 11. This effluent includes the hydrogen fluoride phase mentioned hereinabove. In Figure 1 the hydrogen fluoride phase and oil phase were passed to separation zones where the oil layers were removed and passed to fractionation zones, and only the acid phase was recycled to the extraction zone. In this embodiment the total effluent from reactor 20 is introduced to extraction zone 11, which thus serves the dual function of extraction column and phase separator. A highly simplified flow system is thus obtained.

The remaining portion of the oil rich phase in extraction zone 11 is removed through line 25 and passed to fractionation zone 39. Here the propane is removed through line 41 and recycled through line 14 to surge zone 16. The treated oil is removed from fractionation zone 39 through line 40. The hydrogen fluoride phase from extraction zone 11 is removed through line 48 and passed to fractionation zone 49. The hydrogen fluoride is separated and removed through line 21 to reaction zone 20. The asphaltic materials are removed through line 50.

Advantages of this invention are illustrated by the following example. The reactants and their proportions, and other specific ingredients are presented as being typical and should not be construed to limit the invention unduly.

Example

In a system similar to that shown in Figure 2, one volume per hour of a 14.3 volume per cent residue fraction from West Edmund crude oil and 8 volumes per hour of propane are charged to an extraction column at a temperature of 180° F. A hydrogen fluoride-oil-propane stream is also injected as described hereinafter. The oil is extracted by the propane and hydrogen fluoride, the propane and oil passing countercurrently to the hydrogen fluoride, at a top column temperature of 202° F. Five volumes per hour of oil-propane mixture are removed from the column as a side stream and reacted with one volume per hour of hydrogen fluoride in a reaction chamber so designed that the average contact time is 2 hours, at a temperature of 350° F. The effluent from the reactor is cooled to 190° F. and then injected back into the extraction column as mentioned hereinabove. A treated oil-propane mixture is removed from the top of the extraction column. After removal of the propane and traces of hydrogen fluoride from the oil, it has the following properties as compared with the oil charge and with a portion of the same oil treated only with propane.

	Oil Charge	Propane Treated Oil	Propane-Hydrogen Fluoride Treated Oil
Viscosity @ 210 SUS	241	77	72
Viscosity Gravity Constant	0.892	0.809	0.796
Viscosity Index	72		105
Gravity, API	15.1	28.2	30.2
Carbon Residue, Weight Per Cent	4.1	0.17	0.04
Yield	100	33.2	29.4

As may be seen by the above data, an oil of improved viscosity index is obtained. In addition the stability is improved as shown by the reduction in the carbon residue.

Although this process has been described and exemplified in terms of its preferred modifications, it is understood that various changes may be made without departing from the spirit and scope of the disclosure and of the claims.

I claim:

1. A process for refining lubricating oil which comprises introducing a lubricating oil stock, a normal paraffin hydrocarbon solvent containing not more than 4 carbon atoms per molecule, and a hydrogen fluoride-rich phase from a reaction zone to an extraction zone wherein said oil is extracted at a temperature in the range of 100 to 210° F. and a pressure above the vapor pressure of the constituents with said solvent and said hydrogen fluoride-rich phase, removing said hydrogen fluoride-rich phase from said extraction zone, removing a solvent-oil phase from said extraction zone to a reaction zone wherein it is reacted with hydrogen fluoride at a temperature in the range of 300 to 400° F. and for a reaction time in the range of 10 minutes to 5 hours, separating effluent from said reaction zone into a solvent-oil phase and a hydrogen fluoride-rich phase which latter is recycled to said extraction zone as aforesaid, and separating said solvent-oil phase from said extraction zone into solvent which is recycled to said extraction zone and treated oil which is recovered as a product of the process.

2. A process for refining lubricating oil which comprises introducing a lubricating oil stock and propane at a temperature in the range of 100 to 200° F., and a hydrogen fluoride-rich phase to an extraction zone wherein said propane is in-

troduced below the interface formed by the propane-and-oil phase and said hydrogen fluoride-rich phase, extracting said oil with said propane and said hydrogen fluoride-rich phase at a temperature in the range of 100 to 210° F. and a pressure above the vapor pressure of the constituents, said oil and said propane passing countercurrently to said hydrogen fluoride-rich phase, removing said hydrogen fluoride-rich phase from said extraction zone and separating hydrogen fluoride therefrom for recycle to a reaction zone, removing said propane-oil phase from said extraction zone to said reaction zone wherein it is reacted with hydrogen fluoride in a proportion of 0.05 to 5 volumes of hydrogen fluoride to one volume of propane and oil at a temperature in the range of 300 to 400° F. and a reaction time in the range of 10 minutes to 5 hours, separating effluent from said reaction zone into a propane-oil phase and a hydrogen fluoride-rich phase, said hydrogen fluoride-rich phase being recycled to said extraction zone as aforesaid, separating said propane-oil phase from said reaction zone into propane and treated oil, recycling said propane to said extraction zone and recovering said treated oil as a product of the process.

3. A process for refining lubricating oil which comprises introducing to a vertical extraction zone a lubricating oil stock and propane at a temperature of about 180° F., and a hydrogen fluoride-rich phase at the temperature of said extraction zone at the point of introduction, at least a portion of said propane being introduced below the point of introduction of said oil and below the interface formed by the propane-and-oil phase and said hydrogen fluoride-rich phase, extracting said oil with said propane and said hydrogen fluoride-rich phase at a temperature in the range of 180 to 205° F. and a pressure above the vapor pressure of the constituents and not above about 1000 pounds per square inch gauge, said oil and said propane passing countercurrently to said hydrogen fluoride-rich phase, removing said hydrogen fluoride-rich phase from a low point of said extraction zone, separating same into a hydrogen fluoride fraction and an acid-soluble material fraction including asphalt, recycling thus separated hydrogen fluoride to a reaction zone, removing said propane-oil phase overhead from said extraction zone to said reaction zone wherein it is reacted in liquid phase with hydrogen fluoride in a proportion of propane and oil to hydrogen fluoride of about 1:1, at a temperature of about 350° F., and for about 2 hours, separating effluent from said reaction zone into a propane-oil phase and a hydrogen fluoride rich phase and passing said hydrogen fluoride-rich phase to said extraction zone as above described, separating said propane-oil phase removed from said reaction zone into propane and treated oil, recycling said propane to said vertical extraction zone, and recovering said treated oil as a product of the process.

4. A process for refining lubricating oil which comprises introducing a lubricating oil stock, a normal paraffin hydrocarbon solvent containing not more than 4 carbon atoms per molecule, and a hydrogen fluoride-rich phase from a reaction zone to an extraction zone wherein said oil is extracted at a temperature in the range of 100 to 210° F. and a pressure above the vapor pressure of the constituents with said solvent and said hydrogen fluoride-rich phase, removing said hydrogen fluoride-rich phase from said extraction zone, removing a solvent-oil phase from said extraction zone to a reaction zone wherein it is reacted with hydrogen fluoride at a temperature in the range of 300 to 400° F. and a reaction time in the range of 10 minutes to 5 hours, passing effluent from said reaction zone back to said extraction zone wherein it is separated into a solvent treated oil phase and a hydrogen fluoride-rich phase, recovering from said extraction said solvent-treated oil phase and separating same into solvent which is recycled to said extraction zone and treated oil which is recovered as a product of the process.

5. A process for refining lubricating oil which comprises introducing a lubricating oil stock and propane in a ratio of 1:3 to 1:12 and a temperature in the range of 100 to 200° F., and a hydrogen fluoride-rich phase to an extraction zone wherein said propane is introduced below the interface formed by the propane and oil phase and said hydrogen fluoride-rich phase, extracting said oil with said propane and said hydrogen fluoride-rich phase at a temperature in the range of 100 to 210° F. and a pressure above the vapor pressure of the constituents, said oil and said propane passing countercurrently to said hydrogen fluoride-rich phase, removing said hydrogen fluoride-rich phase from said extraction zone and separating hydrogen fluoride therefrom for recycle to a reaction zone, removing said propane-oil phase from said extraction zone to said reaction zone wherein it is reacted with hydrogen fluoride in a proportion of 0.05 to 5 volumes of hydrogen fluoride to one volume of propane and oil at a temperature in the range of 300 to 400° F. and a reaction time in the range of 10 minutes to 5 hours, passing effluent from said reaction zone back to said extraction zone wherein it is separated into a solvent treated oil phase and a hydrogen fluoride-rich phase, recovering from said extraction said solvent-treated oil phase and separating same into solvent which is recycled to said extraction zone and treated oil which is recovered as a product of the process.

6. A process for refining lubricating oil which comprises introducing to a vertical extraction zone a lubricating oil stock and propane in a ratio of 1:3 to 1:12 and at a temperature of about 180° F., and a hydrogen fluoride-rich phase at the temperature of said extraction zone at the point of introduction, at least a portion of said propane being introduced below the point of introduction of said oil and below the interface formed by the propane-and-oil phase and said hydrogen fluoride-rich phase, extracting said oil with said propane and said hydrogen fluoride-rich phase at a temperature in the range of 180 to 205° F. and a pressure above the vapor pressure of the constituents and not above about 1000 pounds per square inch gauge, said oil and said propane passing countercurrently to said hydrogen fluoride-rich phase, removing said hydrogen fluoride-rich phase from a low point of said extraction zone, separating same into a hydrogen fluoride fraction and an acid-soluble material fraction including asphalt, recycling thus separated hydrogen fluoride to a reaction zone, removing said propane-oil phase overhead from said extraction zone to said reaction zone wherein it is reacted in liquid phase with hydrogen fluoride in a proportion of propane and oil to hydrogen fluoride of about 1:1, at a temperature of about 350° F., and for about 2 hours, passing effluent from said reaction zone back to said extraction zone wherein it is separated into a solvent treated oil phase and a hydrogen fluoride-

rich phase, recovering from said extraction said solvent-treated oil phase and separating same into solvent which is recycled to said extraction zone and treated oil which is recovered as a product of the process.

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