

June 11, 1963

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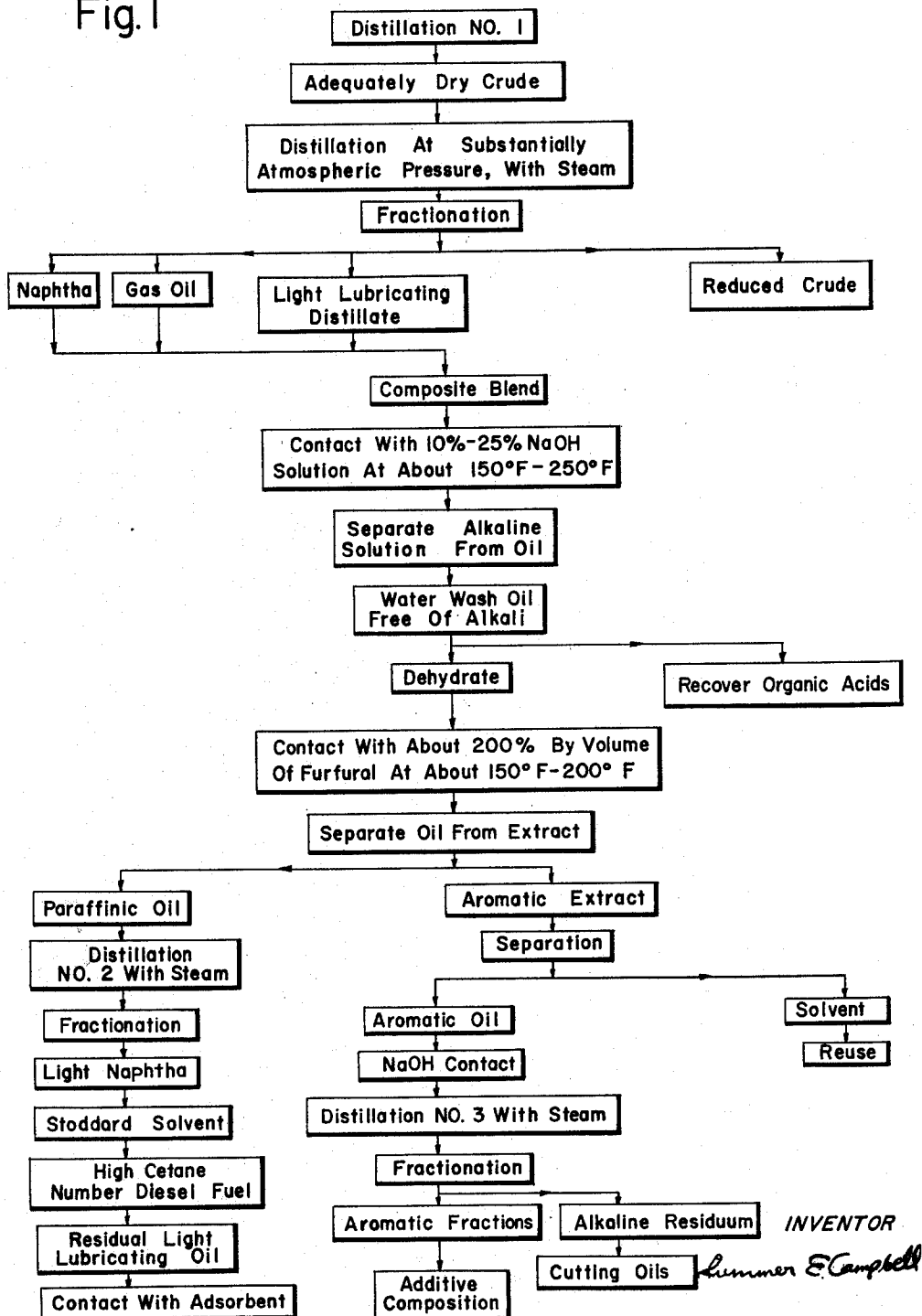
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REFINING OF CRUDE PETROLEUM

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2 Sheets-Sheet 1

Fig. 1



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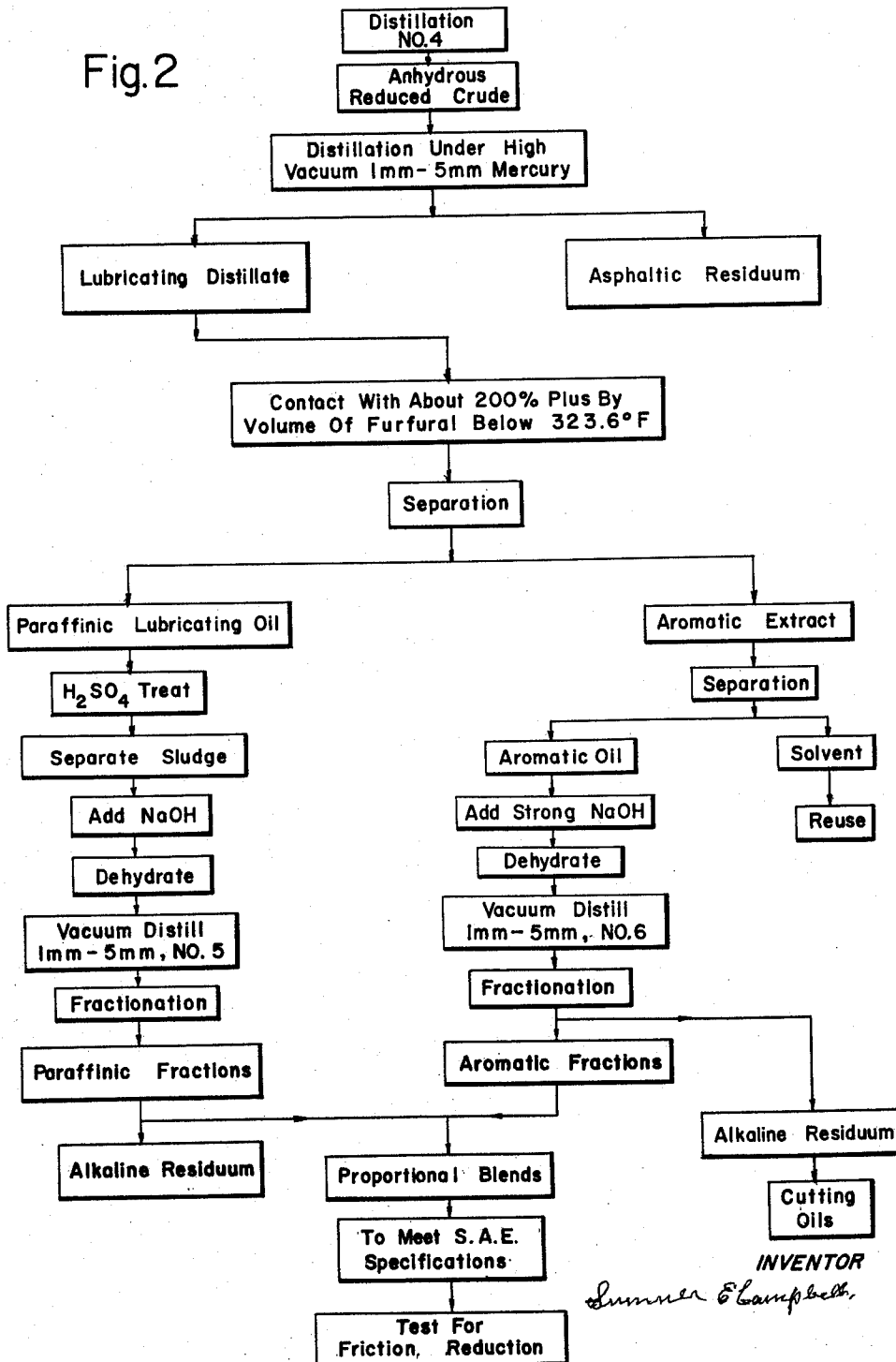
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Fig. 2



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REFINING OF CRUDE PETROLEUM

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2 Claims. (Cl. 208—221)

This invention relates to an improved processing procedure for refining crude petroleum containing 20% or more of an homologous series of aromatic hydrocarbons.

Crude petroleum consists of a complex mixture of hydrocarbons of different boiling points, with which may be associated certain compounds considered impurities, such as sulphur compounds, organic acids and nitrogenous bases. Crude petroleum varies widely in its chemical constitution. For example, that produced in the State of Pennsylvania is relatively rich in the paraffin series of hydrocarbons. Crude petroleum, however, produced in the Smackover Field of southern Arkansas, is asphaltic, and comparatively rich in aromatic hydrocarbons which occur in this crude in an homologous series, boiling over a range of temperature. Crude petroleum produced in California usually is also relatively rich in hydrocarbons of the aromatic series. Pennsylvania crude is low in sulphur, and contains substantially no nitrogen compounds or organic acids. This highly paraffinic oil usually has a high content of paraffin wax, which must be removed to obtain sufficiently low pour points for lubricating oils. Smackover crude is generally of two types in one of which there is sufficient paraffin wax to make it necessary to separate this element, if the crude is to be used in the production of lubricating oils. There is also produced in this field, crude that is relatively free of paraffin wax, so that no special processing is necessary for the production of very low pour point lubricating oils. While Pennsylvania crude is substantially free of such compounds as naphthenic acids, Smackover crude is comparatively rich in these acidic compounds, which must be removed, both for the production of high quality lubricating oil, as well as to recover them as valuable by-products. Crude petroleum, as produced in California, is richer in nitrogen compounds than that usually produced anywhere else in the United States. In this last mentioned crude, these nitrogen compounds are present in two forms, about 50% being basic in nature and these are termed, "nitrogenous bases." If California crude is being refined, it is highly desirable to remove nitrogenous basic compounds from the distillates being refined, such as naphtha distillate. This, briefly, describes three classes of crude generally produced.

The type of crude petroleum to be used in reducing this invention to practice should be substantially wax-free, and have an A.P.I. gravity ranging from about 15.0 to 25.0. Smackover crude is cited to illustrate the type of oil used in the refining steps employed, as described below, which will be clearly understood by referring to the accompanying diagrams.

The adequately dry crude is first passed through a heating system, such as a tubular heater, in which the temperature is raised sufficiently to vaporize that portion of the oil it is desired to distill. Such a distillation system is provided with suitably designed towers in order to obtain the necessary fractionation. In this operation steam is introduced for two purposes: one, to facilitate distillation and, two, to avoid any tendency toward decomposition, or "cracking," of the hydrocarbons composing the oil. It

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is usual practice to introduce anhydrous ammonia at the proper point in the system to prevent any corrosion of the equipment, which may occur, particularly at distillation temperatures, when the crude being refined contains corrosive elements, such as sulphur compounds and organic acids.

In the first refining step of the subject process, distillation (No. 1) is conducted at substantially atmospheric pressure; the heated vapors and steam pass upwardly through the fractionating tower, the most volatile constituents pass out of the top of the tower to a condenser, where they are converted to liquids, and the first fraction, naphtha, is recovered, the condensed steam being discarded as water. The next and less volatile constituents, pass out of the tower lower down, into another condenser, are liquefied, and the second fraction, gas oil, is recovered. The next, and still less volatile constituents, pass out of the tower at a still lower level, into another condenser, are liquefied, and the third fraction, light lubricating distillate, is recovered.

In this new processing procedure, the three normally obtained distillates, having the approximate yields as indicated, naphtha 10%, gas oil 20%, and light lubricating distillate 10%, are incorporated as a single oil.

The remaining portion of the oil, reduced crude, is not vaporized, and is used as the charging stock for distillation (No. 4) under high vacuum of 1 mm.—5 mm. mercury absolute pressure.

Since the type of oil being described contains an appreciable proportion of organic acids, such as naphthenic acids and phenolic compounds, and usually has a relatively high sulphur content, it is necessary to remove these acidic compounds by contacting the oil to render it alkaline with a solution of caustic soda, or its equivalent, of about 10–25% concentration, at about 150° F.—200° F. The alkaline solution containing these acidic impurities, as well as certain sulphur compounds which it removes, is separated and the alkaline oil is next thoroughly washed with water to remove any traces of entrained alkali. From the separated alkaline solution organic acids are recovered as by-products of value, and the sulphur content of the oil is reduced.

In conducting tests on the three distillates mentioned above, obtained from the cited crude, it has been found that from each of them there is extractable 20% or more of hydrocarbons of the aromatic series, which are soluble in furfural.

The water washed oil is next dehydrated, and then contacted with about 200% by volume of furfural at about 150° F. The oil being processed is separated into two parts; an extract consisting of the selective solvent and the aromatic hydrocarbons it extracts, and a portion which is composed of paraffinic and naphthenic hydrocarbons. This processing operation is conducted by well known procedures, the furfural separated and recovered for reuse as the selective solvent.

Having separated the oil from the extract and entirely freed it of the solvent, there is obtained a highly paraffinic oil which is next distilled (No. 2) at substantially atmospheric pressure, introducing steam as already mentioned. The oil is then separated into the following fractions; light naphtha, Stoddard solvent, high cetane number diesel fuel, and residual light lubricating oil. These highly paraffinic fractions are of increased utility because of their chemical constitution. For example, the light

naphtha is usable as lighter fluid since this product must not contain aromatic hydrocarbons or other impurities which affect its quality and efficiency in operation. There are other uses for such a light paraffinic naphtha which will be readily apparent to one skilled in the art. The next fraction listed on the accompanying diagram, Stoddard solvent, when produced by this process, will be found to meet A.S.T.M. Designation: D484-52. The next fraction, of lower volatility, to be used as fuel for the operation of diesel engines, will be found to have a cetane number of 50 or higher, as required in U.S. Navy specifications, and is also in accordance with A.S.T.M. Designation: D975-53T. This diesel engine fuel, which is substantially devoid of aromatic hydrocarbons, appreciably decreases contribution to smog formation, and is therefore highly important in combating this difficult problem. The residual light lubricating oil, having a viscosity of about 100-110 S.U.S. at 100° F., obtained in this distillation, is contacted with a suitable adsorbent, such as silica gel, for lightening its color to the desired degree, which may be water white if the oil is to be used, for example, in the production of cosmetic compositions, or for other purposes.

Referring to the extract, the separated aromatic hydrocarbons composing this fraction are entirely freed of furfural and next thoroughly contacted with a solution of caustic soda, or its equivalent, of about 10-25% concentration, to render the oil alkaline, the mixture sufficiently dehydrated to permit distillation (No. 3) and fractionation, introducing steam, only if required, to separate the aromatic hydrocarbon composition into desired fractions, such as benzene, toluene, the xylenes and higher homologues of aromatic hydrocarbons. This treatment accomplishes further reduction of the sulphur content of this aromatic oil, which greatly improves its quality and utility. This separated anhydrous aromatic oil is utilized for two purposes: one, to obtain the desired fractions as mentioned above, and, two, because of the chemical constitution of this aromatic hydrocarbon mixture, to provide high solvency for asphaltic binders which hold carbon particles together to form carbon deposits in internal combustion engines; as well as to provide essential friction reducing characteristics, which are furnished by that portion of the aromatic hydrocarbon mixture that is of higher viscosity and molecular weight. This entire aromatic composition is added, in necessary and regulated amount, to the lubricating oil used in internal combustion engines, to provide the lubricity, especially where clearances are very close, as is the case with hydraulic valve lifters, in which the highly paraffinic oils are deficient, as well as to furnish solvency that continues its beneficial effect, without being lost by volatilization, even at high operating temperatures in an internal combustion engine. The alkaline residuum obtained from this distillation (No. 3) in which sulphur compounds have been highly concentrated, is used as the source material for the production of cutting oil compositions.

In the next step of the process, the anhydrous reduced crude is sufficiently heated, and distilled (No. 4) under high vacuum of 1 mm.-5 mm. of mercury absolute pressure. In this operation the oil is separated into two parts: lubricating distillate, which must be further refined for the production of high quality lubricating oils, and asphaltic residuum, which is further distilled for the production of road oil compositions, roofing material, and various grades of asphalt.

The lubricating distillate, having a Saybolt Universal viscosity of about 65 seconds at 210° F., is contacted with a selective solvent such as, preferably, furfural, for the purpose of separating hydrocarbons of the aromatic series from paraffins and naphthenes. The volume of furfural to be used, which may range between about 200% to 300% by volume, will depend on the character of the oil being refined. If it has a high viscosity, a

greater volume of furfural may be required to obtain efficient separation of the extract from the oil. As already mentioned, usual and well-known processing procedures are employed in the use of furfural as the selective solvent. In the process step being described, the treatment with furfural is conducted at adequately elevated temperature, but sufficiently below the boiling point of the solvent. By this treatment there are obtained two portions; a paraffinic lubricating oil, and an aromatic extract. The anhydrous paraffinic lubricating oil, when entirely freed of furfural, is efficiently contacted with only the necessary and minimized amount of 98% sulphuric acid to accomplish the required purification and decolorization. The acid sludge produced in this treatment is separated, preferably, by centrifuging, and the acid oil contacted with a solution of caustic soda of about 10% concentration, for neutralization of any acidic compounds present. The alkaline oil is next dehydrated, distilled and fractionated under high vacuum of 1 mm.-5 mm. of mercury absolute pressure, securing desired fractions of highly paraffinic oils from which blends are produced to meet the specifications for the various S.A.E. grades of lubricating oil. The residual oil containing the caustic soda used consists of an alkaline residuum of about 5% or less in volume. Water is added to this residual oil to separate the alkali and recover the highly viscous paraffinic oil, which then must be preferably hot water washed free of alkali, and dehydrated, to be available for various uses.

Referring now to the aromatic extract, which consists of the furfural used and the aromatic hydrocarbons which it separates: when this aromatic oil has been entirely freed of furfural, and the solvent recovered for reuse, the highly aromatic oil is next efficiently contacted with a solution of caustic soda of about 25% concentration to render the oil alkaline, the mixture dehydrated, distilled under high vacuum of 1 mm.-5 mm. of mercury absolute pressure, and fractionated to separate this aromatic oil into desired fractions, having viscosities falling within the limits specified by the S.A.E. for each particular grade of lubricating oil. A necessary and regulated amount of the particular aromatic fraction which has the viscosity limits specified by the S.A.E. for a designated grade of lubricating oil, is added to that fraction of paraffinic lubricating oil obtained by the described treatment, which meets the same S.A.E. viscosity specification; the purpose being to provide these highly paraffinic oils with the friction reducing characteristics in which they are deficient, so that the blended lubricating oil produced will take just 20 one-pound weights, when tested on a friction machine, to produce a score of about $\frac{1}{16}$ of an inch on a test bearing. For the purpose of obtaining this information an instrument has been developed which very efficiently determines the ability of an oil to reduce friction (see Patent No. 2,097,716). Other means of securing this information can be used, but an accurate measurement of the percentage of the aromatic fraction to be added to a given paraffinic fraction is highly important, in order to add only that quantity of aromatic oil necessary to obtain the required friction reducing characteristics, but not an excessive amount which degrades the quality of the oil. The remaining aromatic fractions, of higher viscosity and of reduced sulphur content, are added to the asphaltic residuum to provide and increase the ductility of various grades of asphalt, including roofing materials, produced from this type of crude.

I. In the refining procedure above described (distillations No. 1 and No. 2) there are obtained products composed substantially of hydrocarbons of the

A. Paraffin series:

- (1) Light naphtha
- (2) Stoddard solvent
- (3) High cetane number diesel fuel
- (4) Light lubricating oil

(5) The reduction of sulphur content of these refined products increases their value and utility

B. Aromatic series:

(1) The extracted aromatic hydrocarbons obtained in this distillation (No. 3), efficiently fractionated, increases the value of these separated, fractions of lowered sulphur content

(2) This entire aromatic hydrocarbon mixture is utilized, when added to lubricating oil, in necessary amount, to improve the functioning of internal combustion engines and to maintain them in highly efficient operation

(3) The reduction of sulphur content of these products increases their value and utility

(4) The alkaline residuum in which sulphur compounds are concentrated provides source material for cutting oil compositions

II. Referring to the refining procedure described under distillations No. 4 and No. 5, there are obtained

A. Highly paraffinic purified, lubricating oil fractions of reduced sulphur content

B. Highly aromatic fractions of reduced sulphur content

C. Highly viscous aromatic fractions of reduced sulphur content added to the asphaltic residuum, imparting increased ductility

D. Alkaline residuum in which sulphur compounds are highly concentrated provides source material for cutting oil compositions

III. The purified highly paraffinic lubricating oils are deficient in their ability to reduce friction. Therefore, a necessary and minimized amount of that particular fraction of aromatic hydrocarbons, of reduced sulphur content, which has a viscosity within the viscosity range specified by the S.A.E. for a designated grade of lubricating oil (i.e. 5W-10W-20W-30-40-50) is added to a paraffinic fraction that has a viscosity also falling within that same range of viscosity required by the S.A.E. specification for the grade of lubricating oil that has designated. It is essential that the amount of aromatic fraction added to a paraffinic fraction of the same viscosity range specified by the S.A.E. for the particular grade of lubricating oil desired, be adequate, but not excessive, and regulated to meet the required friction reducing tests, in order to produce this higher quality oil. Distillations No. 1, No. 2 and No. 3 are shown on FIG. 1. Distillations No. 4, No. 5 and No. 6 are shown in FIG. 2.

I claim:

1. The process of refining crude petroleum containing 20% or more of an homologous series of aromatic hydrocarbons, which comprises: (A) distilling the adequately dry crude at substantially atmospheric pressure, introducing steam, producing a distillate fraction composed of naphtha, gas oil and light lubricating oil—and residual reduced crude; treating the composite distillate with caustic soda (NaOH) solution—forming sodium salts of naphthenic acids and phenolic compounds which are contained in the alkaline solution, reducing the sulphur content of the oil—and recovering the organic acids from the separated alkaline solution; dehydrating, and treating the oil with furfural, separating the mixture into a part composed predominantly of hydrocarbons of the paraffin series—and an extract composed of the furfural used and

hydrocarbons of the aromatic series which it separates; distilling, introducing steam, and fractionating the oil composed predominantly of hydrocarbons of the paraffin series, obtaining light naphtha, Stoddard solvent, high cetane number diesel fuel—and residual light lubricating oil, and treating the light lubricating oil with adsorbent; separating the furfural from the aromatic oil and recovering it for reuse as the selective solvent; treating the aromatic oil which has been freed of furfural, with sodium hydroxide (NaOH) solution, reducing the sulphur content, dehydrating, and distilling the alkaline oil, introducing steam, producing aromatic fractions, aromatic additive compositions—and an alkaline residuum; (B) distilling under high vacuum of 1 mm.—5 mm. of mercury absolute pressure, of the anhydrous reduced crude, producing lubricating distillate—and asphaltic residuum; contacting the anhydrous lubricating distillate with furfural at substantially atmospheric pressure and at elevated temperature, separating the mixture into a portion composed predominantly of hydrocarbons of the paraffin series, and an extract composed of the furfural and the aromatic hydrocarbons which it separates; treating the portion composed substantially of hydrocarbons of the paraffin series with concentrated sulphuric acid, and removing the formed acid sludge—neutralizing the acid oil with caustic soda (NaOH) solution, thereby further reducing the sulphur content—dehydrating, distilling and fractionating under high vacuum of 1 mm.—5 mm. of mercury absolute pressure, and recovering fractions composed predominantly of hydrocarbons of the paraffin series—and an alkaline residuum; mixing the alkaline residuum with sufficient water, heating the mixture to a temperature below 212° F., settling, and separating the alkaline solution from the oil, washing the alkaline oil with water for the complete removal of all traces of alkali, dehydrating, and producing an anhydrous, highly viscous, paraffinic lubricating oil; separating the furfural from the extract and recovering it for reuse as the selective solvent, obtaining an oil composed predominantly of hydrocarbons of the aromatic series; contacting this oil with sodium hydroxide (NaOH) solution, further reducing the sulphur content—dehydrating, and fractionating by distillation under high vacuum of 1 mm.—5 mm. of mercury absolute pressure, producing fractions composed predominantly of hydrocarbons of the aromatic series—and an alkali residuum.

2. The process as claimed in claim 1 wherein a portion of said aromatic fractions are blended with a portion of said paraffinic fractions of equivalent viscosity to produce a lubricating oil.

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