

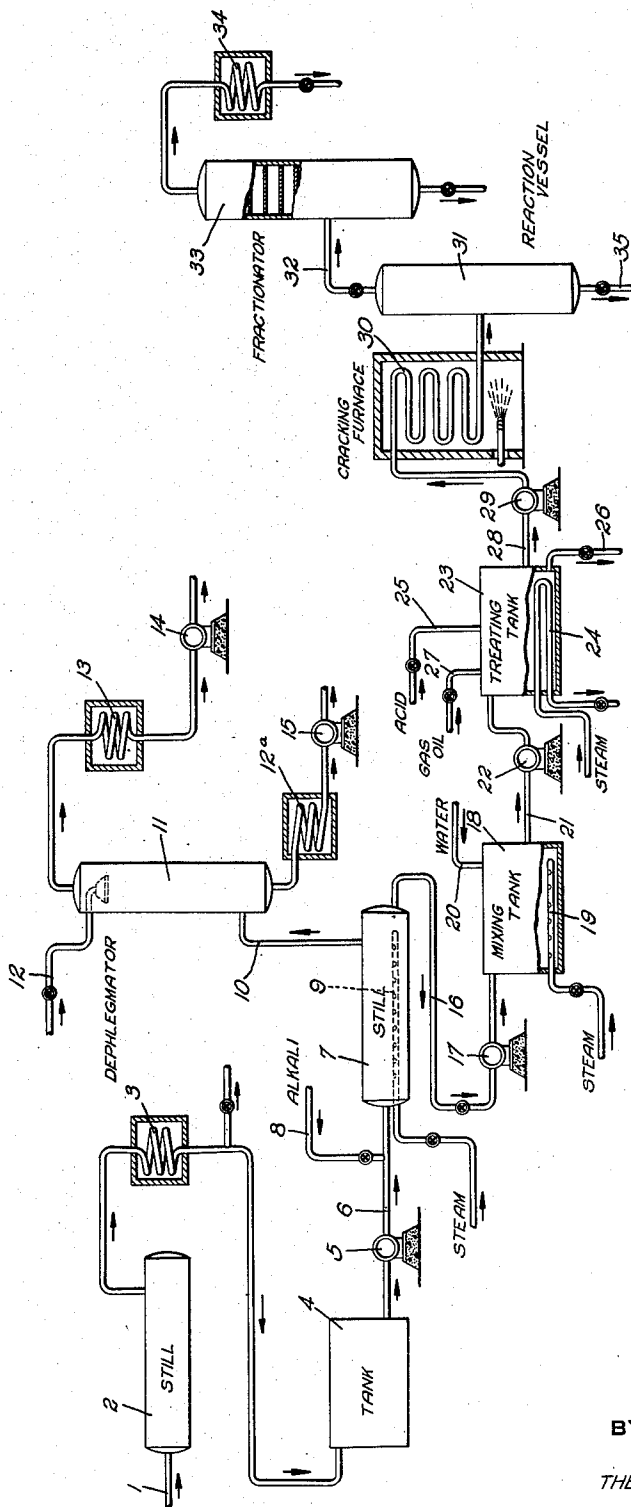
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PROCESS OF TREATING HYDROCARBON OIL CONTAINING NAPHTHENIC ACIDS

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PROCESS OF TREATING HYDROCARBON OIL
CONTAINING NAPHTHENIC ACIDSGus Kaufman and Carl E. Lauer, Port Arthur,
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This invention relates to the treatment of hydrocarbon oils and more particularly to a process for the treatment of petroleum hydrocarbons containing organic acids, such as naphthenic acids and the like, for the production of valuable products therefrom.

The invention contemplates broadly a process for treating petroleum oil, particularly of the naphthene base type, containing naphthenic and other organic acids, for the preparation of distillate fractions of desired characteristics and the formation of a residual fraction composed largely of naphthenic acids, which is subjected to thermal conversion for the production of low boiling hydrocarbons adapted for use as motor fuel.

Certain crude or distillate oils of the so-called naphthene base type comprise fractions which are particularly suitable for use in the manufacture of lubricating oils. These crude or distillate oils contain substantial amounts of naphthenic acid, or other organic acids of somewhat similar nature, and it is, therefore, advantageous to add an alkali, such as caustic soda, to the still during distillation of these oils for the production of desired lubricating oil fractions free from acidic constituents.

Heretofore the residuum resulting from the distillation, and which consists largely of naphthenic acids, has been disposed of as fuel oil, or by laborious procedure has been refined into more or less pure naphthenic acids. However, this residual material, after suitable treatment, may be subjected to cracking for the production of hydrocarbons of the gasoline class suitable for use as high grade motor fuel, possessing high anti-knock qualities and substantially free from acidic constituents.

Our process, therefore, comprises distilling crudes of the class described to produce a lubricating oil fraction containing substantial amounts of naphthenic acids and then distilling this fraction in the presence of alkali, preferably under vacuum, to produce lubricating oils substantially free from naphthenic or other organic acids and a residual fraction containing these organic acids in the form of non-volatile salts. This residual fraction may then be commingled with water to form an emulsion or a mixture to which a mineral acid is added, preferably in just sufficient quantity to liberate or displace the organic acids and leave the mixture just slightly on the acid side. It is of advantage, in many instances, to mix the residual matter directly with a dilute acid instead of first mixing with water, thereby simplifying the neutralizing operation. The substantially neutralized mixture is then subjected to stirring by the introduction of exhaust steam thereto which also serves to

heat the mixture and facilitate the separation of water and inorganic salts dissolved or suspended therein. The mixture is then permitted to settle into an aqueous layer and an oily layer, the latter containing the hydrocarbon oil and the organic acids, the organic acids comprising at least 25% of the oily layer, and usually from 50% to 80%. After removing the separated water and dissolved or suspended salts, the remaining oily mixture may be diluted with a relatively low boiling hydrocarbon oil, such as gas oil, and the diluted mixture subjected to further settling while maintained in a heated condition to bring about still more complete separation of water.

The oil mixture, either alone or diluted as above indicated with a cracking stock such as gas oil, is then subjected to cracking, preferably under superatmospheric pressure, at temperatures ranging from about 750° F. to 950° F. or higher, preferably 775° F. to 825° F. In this operation, the naphthenic or organic acids are decomposed practically quantitatively into carbon dioxide and hydrocarbons, a large proportion of which is of the boiling range of gasoline. The vapors from this cracking step are subjected to fractionation to separate the motor fuel or gasoline fraction from the heavier oils.

In the case where the naphthenic acid oil residue is diluted with a gas oil prior to the cracking step, the mixture is rendered more fluid and it is believed that the cracking operation may then be carried out with the maximum production of motor fuel and minimum production of coke and fixed gases.

The accompanying drawing to which reference will now be made diagrammatically illustrates a method of carrying out our invention.

Crude oil containing naturally occurring naphthenic acids is conducted through a pipe 1 to a still 2 wherein it is subjected to distillation for the production of a distillate lubricating oil fraction which is withdrawn through a condenser 3 to a tank 4. This oil, containing naphthenic acids, is drawn from the tank 4 by a pump 5 and charged through a pipe 6 to a vacuum still 7. Caustic soda or other suitable alkaline material, from a source not shown, is introduced through a connection 8 to the stream of oil entering the still through the pipe 6, and wherein it is brought into intimate mixture with the oil to react under the influence of heat with the organic acids contained therein and form non-volatile salts. Steam may be introduced to the still through a spray 9. Where the distillate comprises lubricating fractions, the still temperature will ordinarily not exceed about 650° F. while maintaining a vacuum within the still of from 25 to 30 inches of mercury.

The evolved vapors comprising lubricating oil fractions and steam are removed from the still

through a vapor line 10 and conducted to a dephlegmator 11 into the top of which a cooling medium, such as water or hydrocarbon liquid, may be sprayed as a reflux liquid through a spray 12. The lubricating oil vapor is condensed therein and withdrawn through a cooling coil 12a. Uncondensed vapors consisting largely of steam are removed from the top of the dephlegmator through a condenser 13. A vacuum pump 14 and a condensate pump 15 are provided to remove these products and thus maintain a vacuum within the still and dephlegmator. The residual oil fraction formed in the still 7, and containing the non-volatile salts of the organic acids, is withdrawn through a pipe 16 by means of a pump 17 and introduced to a mixing tank 18 provided with a steam spray 19 as well as a pipe 20 through which water may be introduced to the tank.

This residual oil containing the non-volatile organic acid salts of the alkali may be mixed in the tank 18 with water in approximately the ratio of 3 parts of water to 1 part of residual matter and the resulting mixture subjected to agitation and heating by means of exhaust steam which is introduced through the spray 19.

The resulting emulsified mixture is then withdrawn from the mixing tank 18 through a pipe 21 by a pump 22 and introduced to a treating tank 23 provided with a closed steam-heating coil 24. A dilute acid solution, containing from about 3% to 5% sulphuric acid, is introduced to the tank 23 in sufficient quantity, through a pipe 25 leading from a source not shown, to displace the organic acids contained in the residual oil and leave the mixture slightly on the acid side. During the acid addition, and for about a half-hour thereafter, the mass is kept constantly stirred as, for example, by introducing air thereto, and while maintaining the contents of the tank in a heated condition by the introduction of steam to the heating coil 24, the temperature being preferably maintained at around the boiling temperature of water. The mixture may then be allowed to stand in an undisturbed condition to permit drawing off, through a pipe 26, separated water and suspended or dissolved inorganic matter such as sodium sulphate and other salts.

Following this, a relatively low boiling hydrocarbon oil, such as gas oil, may if desired be introduced to the tank 23 through a pipe 27 to form a diluted mixture in the proportion of about 1 part of diluent to 3 parts of treated residual matter. This diluent may advantageously consist of a refractory recycle gas oil accumulating in the subsequent cracking operation. The dilute mixture is subjected to continued settling while maintained in a heated or warmed condition to thereby effect the settling out of the final traces of water and inorganic matter, leaving behind a mixture consisting chiefly of naphthenic acids and asphaltic tarry matter in admixture with the diluent hydrocarbon oil.

The water-free mixture is then withdrawn from the tank 23 through a pipe 28 by a pump 29 and conducted through a heating coil 30 located in a furnace wherein it is heated to a conversion temperature of about 775° F. following which the heated oil is introduced to a reaction vessel 31 wherein the cracking reaction is continued to the desired extent under a pressure of approximately 250 pounds per square inch gauge producing a cracked vaporous frac-

tion which is removed through a vapor line 32 to fractionating means 33 for the production of a fractionated gasoline vapor which is withdrawn through a condenser 34. The resulting gasoline condensate, after suitable chemical treatment, is particularly valuable for use as a motor fuel.

The heavy tar formed during conversion within the reaction vessel 31 is withdrawn through a pipe 35 to suitable stripping means not shown to strip out the retained cracked gasoline constituents as well as its relatively higher boiling gas oil constituents, which latter may subsequently be used as the diluent recycle gas oil for mixing with fresh residual oil in the tank 23.

While dilution of the chemically treated residual oils with gas oil has been described, it may be of advantage, in many instances, to omit this particular step, depending on the nature and viscosity of the residual material undergoing treatment, and in which case such dilution may be unnecessary since the complete separation of water and inorganic matter may be effected merely by settling in a heated condition for a sufficient length of time.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for treating hydrocarbon oil containing naphthenic acids for the production of substantially acid-free distillate stock and a motor fuel distillate stock having a substantial anti-knock value comprising distilling the oil in the presence of alkali to remove distillate fractions thereof substantially acid free and form a residual oil fraction containing the neutralized naphthenic acids, emulsifying the residual fraction with water, mixing mineral acid therewith to liberate the naphthenic acids therein, subjecting the acidified residual oil fraction to settling while in a heated condition, removing from the said residual oil fraction the separated water and inorganic salts, and subjecting the said residual oil fraction comprising liberated naphthenic acids and associated residual hydrocarbons to thermal conversion for the production of low boiling hydrocarbons suitable as motor fuel and having a substantial anti-knock value.

2. A process for treating hydrocarbon oil containing naphthenic acids for the production of substantially acid-free distillate stock and a motor fuel distillate stock having a substantial anti-knock value comprising distilling the oil in the presence of alkali to remove distillate fractions thereof substantially acid free and form a residual oil fraction containing the neutralized naphthenic acids, emulsifying the residual oil fraction with water, mixing mineral acid therewith to liberate the naphthenic acids therein, subjecting the resulting acidified residual oil fraction to settling while in a heated condition, removing from the said residual oil fraction the separated water and inorganic salts, and subjecting the said residual oil fraction comprising liberated naphthenic acids and associated residual hydrocarbons to cracking under a pressure of the order of 250 pounds per square inch or higher and a temperature of over 750° F. to convert said naphthenic acids and asso-

ciated hydrocarbons into a motor fuel having a substantial anti-knock value, and then fractionating the cracked products to separate the said motor fuel.

3. A process for treating hydrocarbon oil containing naphthenic acids for the production of substantially acid-free distillate stock and a motor fuel distillate stock having a substantial anti-knock value comprising distilling the oil in the presence of alkali to remove distillate fractions thereof substantially acid free and form a residual oil fraction containing the naphthenic acids in the form of salts of the alkali, mixing a dilute mineral acid therewith to liberate the said naphthenic acids in said residual oil fraction, subjecting the resulting acidified residual oil fraction to settling while maintained in a heated condition, removing water and separated inorganic salts therefrom, diluting the remaining portion of the residual oil fraction with recycle gas oil, formed during subsequent cracking, to increase the fluidity of the said residual fraction and facilitate settling out of remaining water and inorganic salts, subjecting the dilute residual oil fraction to settling while maintained in a heated condition to separate out said remaining water and suspended salts, subjecting the water-free residual oil fraction comprising oil residues of said original distilling operation, free naphthenic acids and diluent oil to thermal conversion to convert said naphthenic acids and oil into a motor fuel having a substantial anti-knock value, fractionating the cracked products to separate the said motor fuel, and returning a portion of the relatively higher boiling cracked products as a recycle gas oil for dilution of the acid-treated residual fraction.

4. The method of producing cracked motor fuel of high anti-knock properties for the production of substantially acid-free lubricating oil stock and a motor fuel distillate stock having a substantial anti-knock value which comprises distilling a naphthene base crude oil and separating therefrom a lubricating oil fraction containing a substantial amount of high boiling organic acids, subjecting the fraction to vacuum distillation in the presence of caustic soda to distill off the lubricating oil constituents substantially free of organic acids, thereby producing a heavy oil residue composed of heavy hydrocarbons admixed with the sodium salts of the said high boiling organic acids, treating this heavy oil residue with mineral acid in aqueous solution in sufficient quantity to liberate the organic acids, permitting the resulting mixture to settle to form an aqueous layer and an oily layer comprising a mixture of the heavy residual hydrocarbon oil and the said liberated organic acids, drawing off the layer of mixed oil and organic acids thus obtained, and subjecting it to cracking under a pressure of the order of 250 pounds per square inch or higher and a temperature of over 750° F. to convert the organic acids and the residual hydrocarbons into anti-knock motor fuel, and then fractionating the cracked products to separate the said motor fuel.

5. The method of producing cracked motor fuel of high anti-knock properties for the production of substantially acid-free lubricating oil stock and a motor fuel distillate stock having a substantial anti-knock value which comprises distilling a naphthene base crude oil and separating therefrom a lubricating oil fraction con-

taining a substantial amount of high boiling organic acids, subjecting the said lubricating oil fraction to vacuum distillation in the presence of caustic soda to distill off the lubricating oil constituents substantially free of organic acids, thereby producing a heavy oil residue composed of heavy hydrocarbons admixed with the sodium salts of the said high boiling organic acids, treating this heavy oil residue and organic acid salt mixture with mineral acid in aqueous solution in sufficient quantity to liberate the organic acids in said mixture, permitting the mixture to settle to form an aqueous layer and an oily layer comprising a mixture of the said heavy residual hydrocarbons and the liberated organic acids in which mixture the acids are present to the extent of at least 25%, drawing off the layer of mixed oil and liberated organic acids thus obtained, and subjecting it to cracking under a pressure of the order of 250 pounds per square inch or higher and a temperature of over 750° F. to convert the heavy hydrocarbon and acid mixture into a motor fuel having a substantial anti-knock value, and then fractionating the cracked products to separate the said motor fuel.

6. The method of producing cracked motor fuel of high anti-knock properties for the production of substantially acid-free lubricating oil stock and a motor fuel distillate stock having a substantial anti-knock value which comprises distilling a naphthene base crude oil and separating therefrom a lubricating oil fraction containing a substantial amount of high boiling organic acids, subjecting the said lubricating oil fraction to vacuum distillation in the presence of caustic soda to distill off the lubricating oil constituents substantially free of organic acids, thereby producing a heavy oil residue composed of heavy hydrocarbons admixed with the sodium salts of the said high boiling organic acids, treating this still residue with mineral acid in aqueous solution in sufficient quantity to liberate the organic acids, diluting the residue mixture with recycle gas oil, formed during subsequent cracking, to increase the fluidity of the residue mixture and facilitate settling out of water and suspended salts, permitting the resulting mixture to settle to form an aqueous layer and an oily layer comprising a mixture of the heavy residual hydrocarbon oil and the organic acids, drawing off the layer of mixed residual oil and organic acids thus obtained and subjecting it to cracking under pressures of the order of 250 pounds per square inch or higher and a temperature of over 750° F. to convert the heavy hydrocarbon and acid mixture into a motor fuel having a substantial anti-knock value, fractionating the cracked products to produce motor fuel, and returning a portion of the relatively high boiling cracked products as a recycle oil for the aforesaid dilution of the acid-treated residue.

7. A process of manufacturing cracked anti-knock motor fuel from the residue formed during the distillation of naphthene base petroleum crude oil stock in the presence of alkali and containing naphthenic acids in the form of salts of the alkali, comprising treating the residue with mineral acid in aqueous solution to liberate the naphthenic acids, diluting the acidified mixture with recycle gas oil formed during cracking to facilitate settling out of water and inorganic salts, subjecting the diluted mixture to settling while maintained in a heated con-

dition to separate the water and inorganic salts, subjecting the resulting mixture of naphthenic acids and diluent oil to cracking to convert the said mixture into a motor fuel having a substantial anti-knock value, fractionating the cracked products to separate the said motor fuel, and returning a portion of the relatively high boiling cracked products as a recycle oil for the aforesaid dilution of the acid-treated residue.

8. The method of treating heavy hydrocarbon oil containing naphthenic acids and constituents suitable as lubricating oil stock for the production of substantially acid-free lubricating oil stock and a gasoline-type distillate having a high anti-knock value which comprises rendering the naphthenic acid content of such oil substantially non-volatile and distilling off the lubricating oil constituents of said oil substantially entirely free of naphthenic acids, recovering the residue containing the naphthenic compounds and heavier hydrocarbons and converting the naphthenic constituents thereof into liberated naphthenic acid, thereafter distilling said residue containing the liberated acid under cracking temperature conditions to effect the conversion of said mixture of naphthenic acids and the residual hydrocarbons into a gasoline-type distillate having a relatively high anti-knock value.

9. The method of treating heavy hydrocarbon oil containing naphthenic acids and constituents suitable as lubricating oil stock for the production of substantially acid-free lubricating oil stock and a gasoline-type distillate having a high anti-knock value which comprises rendering the naphthenic acid content of such oil substantially non-volatile and distilling off the lubricating oil constituents of said oil substantially entirely free of naphthenic acids, recovering the residue containing the naphthenic compounds and heavier hydrocarbons and converting the naphthenic constituents thereof into liberated naphthenic acids, thereafter distilling said residue containing the liberated acid under cracking temperature conditions, under a pressure of the order of 250 pounds gauge or higher and a temperature of at least 750° F., to effect the conversion of said mixture of naphthenic acids and the residual hydrocarbons into a gasoline-type distillate having a relatively high anti-knock value.

10. The method of treating heavy hydrocarbon oil containing naphthenic acids and constituents suitable as lubricating oil stock for the production of substantially acid-free lubricating oil stock and a gasoline-type distillate having a high anti-knock value which comprises rendering the naphthenic acid content of such oil substantially non-volatile and distilling off the lubricating oil constituents of said oil substantially entirely free of naphthenic acids, recovering the residue containing the naphthenic compounds and heavier hydrocarbons and converting the naphthenic constituents thereof into normal volatile naphthenic acid, diluting the said residue with a suitable clean distillate oil suitable as cracking stock, thereafter distilling said residue containing the normal acid under cracking temperature conditions to effect the conversion of said mixture of naphthenic acids and the residual hydrocarbons into a gasoline-type distillate having a relatively high anti-knock value.

11. The method of treating heavy hydrocarbon

oil containing naphthenic acids and constituents suitable as lubricating oil stock for the production of substantially acid free lubricating oil stock and a gasoline-type distillate having a high anti-knock value which comprises rendering the naphthenic acid content of such oil substantially non-volatile and distilling off the lubricating oil constituents of said oil substantially entirely free of naphthenic acids, recovering the residue containing the naphthenic compounds and heavier hydrocarbons and converting the naphthenic constituents thereof into liberated naphthenic acid, diluting said residue with a suitable clean distillate oil suitable as cracking stock, thereafter distilling said residue containing the liberated acid under cracking temperature conditions, under a pressure of the order of 250 pounds gauge or higher and a temperature of at least 750° F., to effect the conversion of said naphthenic acids and the residual hydrocarbons into a gasoline-type distillate having a relatively high anti-knock value.

12. The method of manufacturing motor fuel from naphthenic-acid constituents of petroleum, which comprises recovering from petroleum a non-aqueous mixture consisting of non-residual petroleum hydrocarbons together with free naphthenic acids in an amount constituting at least 25 per cent of the mixture, continuously heating a confined stream of said mixture to a temperature of at least 750° F., maintaining the mixture at such temperature for a sufficient period of time to effect cracking of said mixture, and cooling and fractionating the thereby cracked products to recover therefrom a fraction boiling within a motor-fuel range.

13. The method of manufacturing motor fuel from naphthenic-acid constituents of petroleum which comprises recovering from said petroleum a non-aqueous mixture consisting of non-residual petroleum hydrocarbons together with free naphthenic acids in an amount constituting at least 25 per cent of the mixture, continuously heating a confined stream of said mixture to a temperature of at least 750° F., maintaining the mixture at such temperature for a sufficient period of time to effect cracking of said mixture, cooling and fractionating the thereby cracked products to recover therefrom a fraction boiling within a motor-fuel range, and controlling the cracking of the naphthenic acids by introducing to said mixture prior to said heating step a controlled amount of relatively low-boiling hydrocarbon oil.

14. The method of converting naphthenic acids into low-boiling hydrocarbons suitable for use as motor fuel, which comprises continuously passing a confined stream of a non-aqueous mixture consisting of free naphthenic acids and non-residual hydrocarbon oil, said naphthenic acids constituting at least 25 per cent of the mixture, through a heating zone wherein said mixture is heated to a temperature of at least 750° F. to effect a thermal decomposition of said naphthenic acids to motor fuel and carbon dioxide gas, and cooling and fractionating the cracked products to separate cracked distillate boiling within a motor-fuel range from heavier products and normally gaseous materials.

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