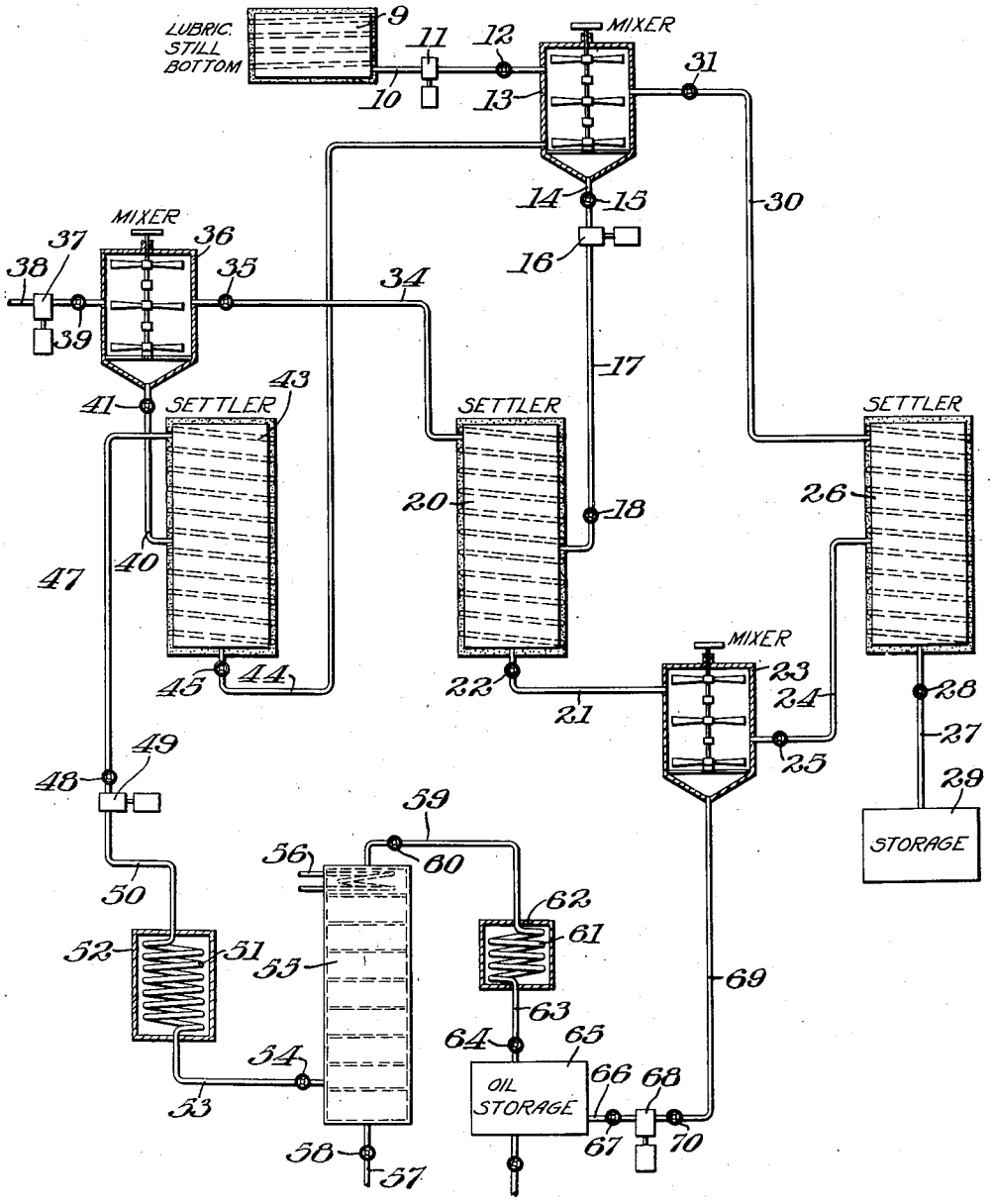
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METHOD OF RECOVERING SODIUM NAPHTHENATES FROM PETROLEUM HYDROCARBONS

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METHOD OF RECOVERING SODIUM NAPHTHENATES FROM PETROLEUM HYDROCARBONS

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This invention relates to the recovery of the cyclic acids commonly known as naphthenic acids from petroleum hydrocarbons.

More specifically my invention relates to a method of recovering the alkali metal salts of naphthenic acids by extracting them from the petroleum hydrocarbons with which they are associated by subjecting the mixture to an extraction with a mixture of water and a hydrocarbon oil whereby the alkali metal salts become dissolved in the water and the associated petroleum hydrocarbons become dissolved in the hydrocarbon oil, and then separating the water solution of the alkali metal naphthenates.

Naphthenic acids are present in varying quantities in a large number of crude petroleums of the naphthene base type. In the typical American crudes, only minute percentages are present in the low viscosity derivatives such as naphtha, kerosene and light lubricating oils, the preponderance of the acids being found in the viscous residua remaining after vacuum distilling the heavy lubricating oil fractions. In refinery practice, it is customary to carry out this vacuum distillation in the presence of caustic soda whereby the naphthenic acids are converted to the corresponding non-vaporizable sodium salts. The residue, therefore, which remains after the vacuum distillation has been carried to completion comprises heavy hydrocarbon oils and varying quantities of sodium naphthenates. This mixture is spoken of in refinery terminology as lubricating still bottoms.

Various methods have been proposed for the separation of the sodium naphthenates from the heavy hydrocarbon compounds with which they are associated in the lubricating still bottoms. Among these, one of the most efficient appears to be the use of alcohol for selectively dissolving the sodium naphthenates. Although this method is characterized by an exceedingly high efficiency, its application to the separation of small quantities of sodium naphthenates from large volumes of lubricating still bottoms is exceedingly costly and its use is therefore limited.

I have found that it is possible to separate the sodium naphthenates from the lubricating still bottoms by extracting the lubricating still bottoms with a mixture of water and a petroleum hydrocarbon oil at an elevated temperature and under superatmospheric pressures. If water alone is used for the extraction, it is found that exceedingly troublesome emulsions are formed which can only be broken with extreme difficulty. However, by using a mixture of water and a petroleum hydrocarbon oil, this difficulty is averted and a sharp separation between the sodium naphthenates and the hydrocarbons composing the lubricating still bottoms may be effected. This process of extracting with water and a petroleum hydrocarbon oil may be carried out in one stage or in several and, in certain operations, it may be advantageous to incorporate this treating method in a countercurrent process.

For the purpose of illustrating my invention, I have set forth a countercurrent treating process embodying my invention which will be readily understood by considering the drawing together with the accompanying description:

The apparatus consists basically of mixing devices for bringing about the proper agitation of the various aqueous and hydrocarbon solutions and pressure settling vessels wherein stratification of the oil and aqueous solutions is effected.

The mixing devices may, with advantage, consist of cylindrical structures fitted with conical bottoms which are provided in their interior with mechanical agitating devices. The pressure settling vessels may be steel receptacles or tanks constructed to withstand the pressures to which they are subjected and fitted in any advantageous manner with heating coils through which suitable heating media may be circulated. They are also provided with heat insulation to prevent the cooling of the contained liquids by radiation. In the interest of brevity, the mixing vessels will be spoken of hereafter as mixers and the pressure settling chambers as settlers.

The numeral 9 indicates a storage tank for lubricating still bottoms. This tank is preferably fited with heating coils and heat insulation to maintain the contents at elevated temperature. This is connected by the line 10 through the pump 11 and the valve 12 to a mixer 13 wherein the lubricating still bottoms are agitated with partly spent water and hydrocarbon oil from subsequent extraction steps. This mixer is in turn connected by the line 14 controlled by the valve 15 with the intake side of the pump 16. The pump may be of any suitable type capable of delivering liquid under pressures of as high as 1000 lbs. per sq. in. It discharges through the line 17 and the valve 18 into the settler 20. Herein the mixture of water and oil solutions is allowed to stratify and the lower or water layer is drawn off from the lower point of the settler 20 through the line 21 controlled by the valve 22 and delivered to the mixer 23.

In the mixer 23, the water solution is agi-

tated with fresh hydrocarbon oil which is recovered in another step of the process. The water-oil mixture is discharged through the line 24 controlled by the valve 25 into the settler 26 wherein the mixture is allowed to separate into two layers. The water layer comprising a solution of purified sodium naphthenates in water is drawn off through the bottom of the settler through the line 27 controlled by the valve 28 and delivered to a suitable storage tank 29. The hydrocarbon oil layer is drawn off from an upper point of the settler 26 through the line 30 controlled by the valve 31 and delivered into the mixer 13.

The oil layer which separates in the settler 20 is drawn off from an upper point of this vessel through the line 34 controlled by the valve 35 and is introduced into the mixer 36 wherein the oil solution is thoroughly agitated with fresh water. This water is obtained from a source (not shown) by means of the pump 37 and forced thereby under appropriate pressure through the line 38 and the valve 39 into the mixer 36.

The oil and water mixture formed in the mixer 36 is drawn off through the line 40 controlled by the valve 41 and delivered into the settler 43 wherein the separation of the oil and water occurs. The water layer is drawn off from the bottom of the settler 43 through the line 44, controlled by the valve 45, and is introduced into the mixer 13, while the oil layer is drawn off from an upper point of the settler 43 through the line 47. This line connects the settler through the valve 48 with the intake side of the pump 49 which in turn discharges through the line 50 into the heating coils 51 of the heater 52. The heated oil is discharged from the heating coil through the line 53 controlled by the expansion valve 54 into a lower point of the fractionating tower 55.

The tower 55 may be of any suitable construction and may be fitted either with bubble cap trays or with a packing of refractory contact materials. It is fitted at an upper point in the structure with a cooling coil 56 to permit of the formation of reflux for the fractionation. The bottom of the fractionating tower is provided with a drawoff line 57 controlled by the valve 58 through which the residual oil is discharged to a suitable storage tank (not shown) while the top of the tower is equipped with a vapor line 59 controlled by the valve 60 which connects the tower with the coil 61 of the condenser 62. The discharge side of the condenser coil is connected by means of the line 63 controlled by the valve 64 with the oil storage tank 65. In order to permit of the recycling of the condensed oil to the process, the storage tank 65 is fitted with a line 66 controlled by the valve 67 which connects the tank to the intake side of the pump 68. This pump in turn discharges through the line 69 and the valve 70 into the mixer 23.

In the preferred manner of practicing the invention with the apparatus shown in the drawing, lubricating still bottoms stored in the tank 9 and which, as previously described, consist of heavy residual naphthene oils together with varying proportions of sodium naphthenates, is charged by the pump 11 into the mixer 13. In the mixer, the lubricating still bottoms are agitated with partly spent water and hydrocarbon oil to effect the separation of the sodium naphthenates from the heavy oils with which they are associated. The mixture is withdrawn from the mixer 13 and by means of the pump 16 is delivered under pressure to the settler 20 wherein, under the existing temperatures and pressures, a ready stratification of the oil and water solutions takes place. The lower layer consists of a water solution of partly purified sodium naphthenates which contains suspended in it a varying proportion of heavy hydrocarbon oil which was not separated in the aforementioned extraction. The solution is drawn off from the bottom of the settler 20 through the line 21 controlled by the valve 22 and delivered into the mixer 23 where it is thoroughly agitated with a measured quantity of fresh hydrocarbon oil. The mixture is discharged into the settler 26 wherein the water solution of sodium naphthenates is separated from the hydrocarbon oil solution of the heavy oils. This water solution is drawn off through the line 27 controlled by the valve 28 and delivered into the storage tank 29, while the hydrocarbon oil containing in solution the heavy residual oils drawn off from the top of the settler 26 is delivered to the mixer 13 where it is contacted with unextracted lubricating still bottoms.

The upper or oil layer which separates in the settler 20 consists of the hydrocarbon oil solution of heavy oils together with small quantities of sodium naphthenates. This solution is delivered into the mixer 36 by means of the line 34 controlled by the valve 35 wherein it is thoroughly agitated with fresh water charged into the mixer by the pump 37 through the line 38 controlled by the valve 39. The mixture of spent hydrocarbon oil and the water solution of sodium naphthenates is delivered through the line 40 controlled by the valve 41 into the settler 43 wherein stratification takes place. The water layer is drawn off from the bottom of the settler through the line 44 controlled by the valve 45 and delivered into the mixer 13. The upper layer consisting of hydrocarbon oil mixed with residual oil is drawn off from the top of the settler through the line 47 controlled by the valve 48 and delivered to the intake side of the pump 49 whereby it is charged through the line 50 into the heating coils 51 of the heater 52. In the heater the temperature of the mixture of residual oil in the hydrocarbon oil is raised to a temperature above the boiling point of the hydrocarbon oil. The mixture is discharged from the heater through the line 53 and the expansion valve 54 into the fractionating tower 55 which is maintained preferably at a pressure lower than that existing in the heating coil 51. The hydrocarbon oil is substantially vaporized and passes upwardly through the tower while the heavy unvaporized residual oil collects as a pool at the bottom of the tower and may be drawn off as desired through the line 57 controlled by the valve 58 and delivered to a suitable storage.

The vapors of the hydrocarbon oil are fractionated and a suitable vapor fraction is drawn off through the line 59 controlled by the valve 60 and delivered to the condenser 62 wherein the vapors are substantially condensed. The condensate formed in the coil 61 is drawn off through the line 63 controlled by the valve 64 and passed to the storage tank 65. A metered amount of the hydrocarbon oil is drawn off from the tank 65 to the line 66 controlled by the valve 67 and charged by means of the pump 68 through the line 69 controlled by the valve 70 to the mixer 23.

It is desirable to operate this process under pressures of from 50 to 100 lbs. per sq. in. However, the choice of the proper pressure is de-

pendent upon the quantities of sodium naphthenate present in the lubricating still bottoms, the molecular weights of the sodium naphthenates and the character of the hydrocarbon oil used as extractant. Although the above pressure range has been given as an example, the use of higher or lower pressures may be found to be advantageous.

The efficiency of the process is dependent to a large extent upon maintaining the solutions at elevated temperatures. In most operations, temperatures of from 200 to 220° F. are found to be sufficiently high but where emulsification difficulties arise it may be desirable to conduct the operations at temperatures in the neighborhood of 250° F.

The most desirable hydrocarbon extractant has been found to be a naphtha having an endpoint of approximately 400° F. However, other light distillate hydrocarbon oils, kerosene, gas oils and light lubricating oil distillates may be used successfully for dissolving the heavy hydrocarbons with which the sodium naphthenate is associated. It is not necessary that these extractants be refined and the use of untreated naphtha or kerosene distillates may also be resorted to.

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.

I claim:

1. A method of recovering purified naphthenates from alkaline distillation residues of viscous hydrocarbon oils, which comprises intimately contacting the residues while hot with water and a relatively volatile hydrocarbon oil, maintaining a substantial superatmospheric pressure on the mixture during the contacting step and then separating the aqueous solution of naphthenates from the oil mixture.

2. A method of recovering purified naphthenates from alkaline still bottoms containing a mixture of naphthenates and residual hydrocarbon oils, which comprises intimately contacting said bottoms while hot with water and a light hydrocarbon oil whereby the naphthenates are extracted by water and the residual oils by the light hydrocarbon oil, maintaining a superatmospheric pressure of at least about 50 pounds per square inch on the system to suppress the formation of emulsions and separating the aqueous solution of naphthenates from the oils.

3. A method of separating naphthenates from alkaline still bottoms produced by the distillation of viscous hydrocarbon oils in the pressure of alkali which comprises forming a mixture of the still bottoms with a light hydrocarbon oil, passing said mixture while hot countercurrent and in intimate contact with water, thereby extracting the naphthenates from the oils by the water and maintaining on the system a substantial superatmospheric pressure.

4. The process of separating sodium naphthenates from the residual oil with which they are associated in lubricating still bottoms formed by vacuum distilling lubricating oils over sodium hydroxide which comprises mixing the lubricating still bottoms with a mixture of a solvent light distillate hydrocarbon oil and water at an elevated temperature of about 200° F. and above, said solvent hydrocarbon oil being lean in residual oil and the water lean in sodium naphthenates, allowing the mixture to settle to form respectively a solvent oil solution rich in residual oil and containing a small amount of sodium naphthenates and a water solution rich in sodium naphthenates and containing a small amount of residual oil, then passing the solvent oil solution rich in residual oil countercurrently to a stream of fresh water to remove the remaining amount of sodium naphthenates whereby a water solution lean in sodium naphthenates is formed, simultaneously passing the water solution rich in scdium naphthenates countercurrently to a stream of fresh solvent oil to remove the remaining amounts of residual oil and to form the desired purified water solution of sodium naphthenates and a solvent oil solution lean in residual oil, then cylically returning the water solution lean in sodium naphthenates and the solvent oil solution lean in residual oil for mixing with the lubricating still bottoms.

5. The method described in claim 4 carried out under superatmospheric pressures.

6. The process of separating sodium naphthenates from the residual oil with which they are associated in lubricating still bottoms formed by vacuum distilling lubricating oils over sodium hydroxide which comprises mixing the lubricating still bottoms with a mixture of a solvent light distillate hydrocarbon oil and water at an elevated temperature of about 200° F. and above, said solvent hydrocarbon oil being lean in residual oil and the water lean in sodium naphthenates, allowing the mixture to settle to form respectively a solvent oil solution rich in residual oil and containing a small amount of sodium naphthenates and a water solution rich in sodium naphthenates and containing a small amount of residual oil, then passing the solvent oil solution rich in residual oil countercurrently to a stream of fresh water to remove the remaining amount of sodium naphthenates whereby a water solution lean in sodium naphthenates is formed, simultaneously passing the water solution rich in sodium naphthenates countercurrently to a stream of fresh solvent oil to remove the remaining amounts of residual oil and to form the desired purified water solution of sodium naphthenates and a solvent oil solution lean in residual oil, then cyclically returning the water solution lean in sodium naphthenates and the solvent oil solution lean in residual oil for mixing with the lubricating still bottoms while simultaneously withdrawing the solvent oil solutions of residual oil free from sodium naphthenates, heating it under superatmospheric pressure to a temperature above the boiling point of the solvent oil, expanding the heated solution into a fractionating tower wherein a substantial separation of the residual oil from the solvent oil is effected and then recycling the separated solvent oil to the process.

7. The method described in claim 6 in which the superatmospheric pressures are about 50 pounds per square inch and above.

8. The continuous method of separating sodium naphthenates from the residual oils with which they are associated in lubricating still bottoms obtained by vacuum-distilling lubricating oils over sodium hydroxide, which comprises mixing and agitating in a primary extraction zone the lubricating still bottoms with a light distillate hydrocarbon oil and water at a temperature of about 200° F. and above to form relatively partly-purified solutions of residual oil in the distillate hydrocarbon oil and sodium naphthenates in

water, extracting the partly-purified solution of residual oil in light distillate hydrocarbon oil with a further quantity of water in a secondary extraction zone, combining the resultant water extract with the solution of sodium naphthenates in water in said primary extraction zone, then extracting the combined solutions of sodium naphthenates in water with a further quantity of the light distillate hydrocarbon oil to remove any remaining residual oils whereby a substantially residual oil-free solution of sodium naphthenates in water is produced.

9. The method as described in claim 8, carried out under superatmospheric pressure.

10. The process of preparing purified naphthenic acids which comprises extracting a crude aqueous alkaline naphthenate solution with a non-aqueous water-immiscible solvent for unsaponifiable impurities, which solvent has a distillation boiling point range lower than the boiling point range of the unsaponifiable impurities.

11. The process of preparing purified naphthenic acids which comprises extracting a crude aqueous alkaline naphthenate solution with a solvent for unsaponifiable impurities, which solvent has a distillation boiling point range lower than that of the unsaponifiable impurities, and separating the solvent from the aqueous naphthenate solution.

12. In a process of preparing purified naphthenic acids, the step of replacing the unsaponifiable matter ordinarily accompanying crude aqueous alkaline solutions of naphthenates with a volatile solvent of different boiling point range.

13. The process of preparing purified naphthenic acids which comprises extracting a crude aqueous alkaline naphthenate solution with a volatile petroleum distillate.

14. In the process of preparing purified naphthenic acids, the step which comprises extracting a crude aqueous alkaline naphthenate solution with a solvent selected from the group consisting of naphtha, kerosene, gas oil and light lubricating oil, which solvent has a distillation boiling point range lower than the boiling point range of the unsaponifiable impurities in the crude naphthenate solution.

15. In the process of preparing purified naphthenic acids, the step which comprises extracting a crude aqueous alkaline naphthenate solution containing unsaponifiable impurities with naphtha of a boiling point range having an end point of approximately 400° F.

16. In the process of preparing purified naphthenic acids, the step which comprises extracting a crude aqueous alkaline naphthenate solution at elevated temperatures of the order of 200–250° F. with a non-aqueous water immiscible solvent for unsaponifiable impurities, which solvent has a distillation boiling point range lower than the boiling point range of the unsaponifiable impurities.

17. In the process of preparing purified naphthenic acids, the step which comprises extracting a crude aqueous alkaline naphthenate solution at elevated temperatures and under superatmospheric pressure with a non-aqueous water immiscible solvent for unsaponifiable impurities, which solvent has a distillation boiling point range lower than the boiling point range of the unsaponifiable impurities, the temperature of extraction being below the boiling point range of the solvent at the pressure employed.

18. In the process of preparing purified naphthenic acids, the step which comprises extracting a crude aqueous alkaline napththenate solution at temperatures of 200–250° F. and under pressures of 50–100 pounds per square inch with a solvent selected from the group consisting of naphtha, kerosene, gas oil and light lubricating oil.

19. In the preparation of purified naphthenic acids, the method which comprises adding to an alkaline fraction of a petroleum oil, said fraction containing naphthenates and unsaponifiable oily impurities, water and a non-aqueous water-immiscible solvent for the unsaponifiable impurities, which solvent has a distillation boiling point range lower than the boiling point range of the unsaponifiable impurities, heating the said fraction with the water and solvent at elevated temperatures below the boiling point of the solvent, allowing the mix to stratify into a solvent layer containing dissolved unsaponifiable impurities and an aqueous naphthenate solution layer, and separating the said layers.

20. In the preparation of purified naphthenic acids, the method which comprises adding to an alkaline petroleum distillation residue, resulting from the distillation of a petroleum oil in the presence of caustic alkali, water and a non-aqueous water immiscible solvent for the unsaponifiable impurities, which solvent has a distillation boing point range lower than the boiling point range of the unsaponifiable impurities, heating the said mixture at elevated temperatures below the boiling point range of the said solvent and under superatmospheric pressure, allowing the mixture to stand and stratify into a solvent layer containing dissolved unsaponifiable impurities and an aqueous naphthenate solution layer, and separating the said layers.

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