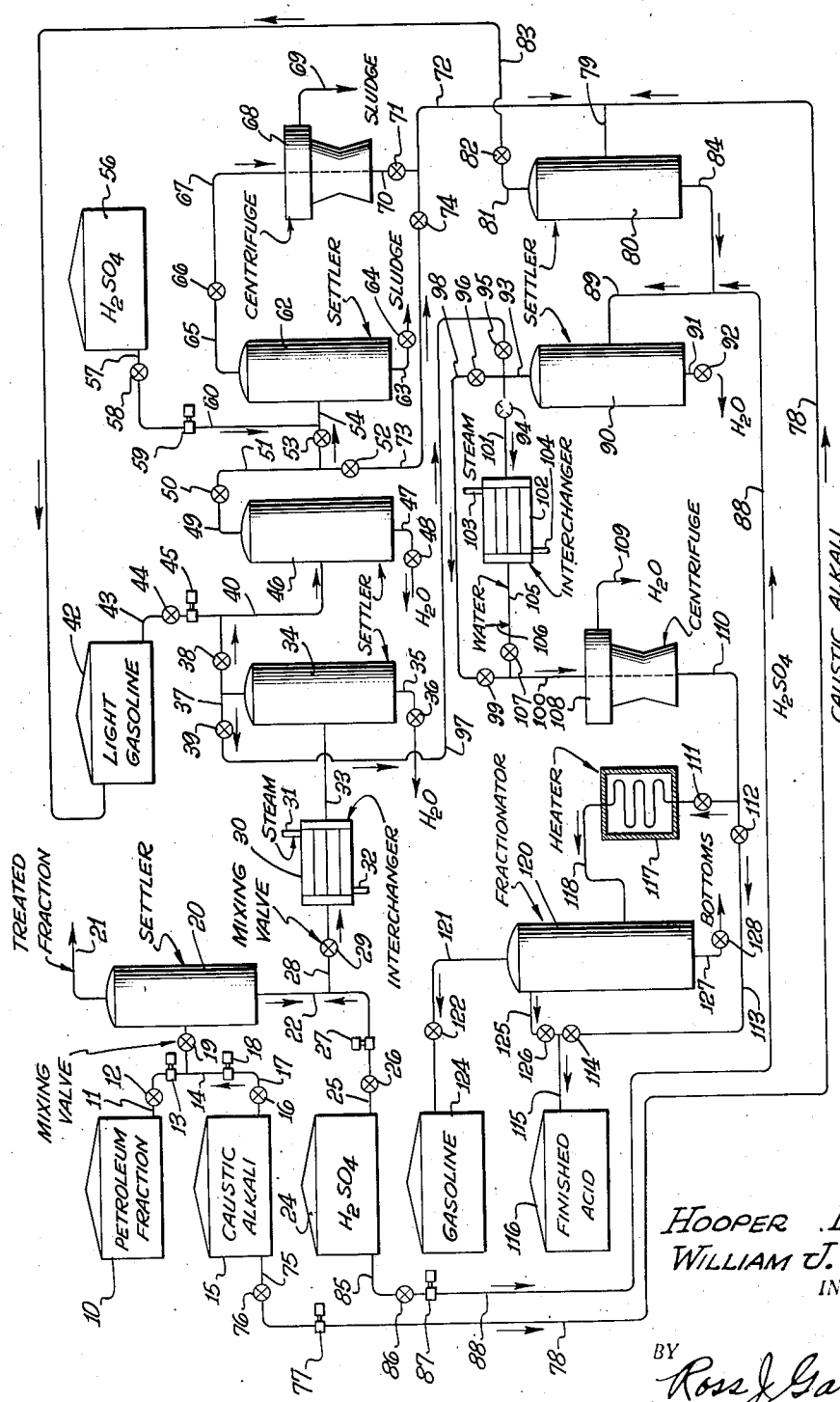
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NAPHTHENIC ACID PRODUCTION

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NAPHTHENIC ACID PRODUCTION

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This invention relates to a process for the recovery and purification of naphthenic acids.

Crude naphthenic acids obtained from alkaline sludges arising during the refining of petroleum fractions, shale oil fractions, coal tar and its fractions or obtained by synthesis such as by the oxidation of petroleum naphthenes, contain impurities which tend to detract from their commercial value. Therefore, in order to produce naphthenic acids of high market value it is necessary to remove these impurities therefrom.

Processes are known which relate to the removal of phenols from naphthenic acids after both have been liberated simultaneously from the various alkaline residues arising in the refining of petroleum fractions, however, in these processes no provisions are made for the removal of the impurties hereinafter mentioned from the phenol-free naphthenic acids.

The impurities which are oftentimes associated with the naphthenic acids and which impair their value are unsaponifiable materials such as high molecular weight hydrocarbon oils, asphalt-like substances such as bitumens, asphalt, resins, wax and wax-like bodies, and various other hydrocarbons contaminates as well as high molecular weight fatty acids and hydroxy acids. It is obvious that all of these impurities are not necessarily present in all naphthenic acids, however, in general hydrocarbon impurities are present in substantial quantities. In any event, no matter which one or ones of the particular impurities are present they will unfavorably influence the commercial desirability of the naphthenic acids.

The term "naphthenic acids" as used herein is intended to be generic and not limited to any particular kind of naphthenic acids derived from any particular crude oil or any specific methods of isolation therefrom.

Naphthenic acids are generally considered to be mono-carboxylic acids containing at least one cycloparaffin ring. However, the term as used herein is meant to include all of the naturally occurring carboxylic acids found in petroleum. This broad interpretation is employed in order to include the lower molecular weight "naphthenic acids" which are thought by some investigators to be saturated open branched chain carboxylic acids. The term "naphthenic acids" is also meant to include the synthetic oil-soluble acids produced by the oxidation of naphthenic fractions of petroleum. Such synthetic acids may be readily produced by the liquid phase oxidation of kerosene, gas oil or like fractions of petroleum with air or other oxygen-containing

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gas. The synthetic acids produced in this manner are normally liquid oil-soluble carboxylic acids. Moreover, in common with the naturally occurring naphthenic acids, the polyvalent metal soaps of these synthetic acids such as copper, lead, cobalt, manganese, iron, etc., soaps are oil-soluble.

In the conventional method of recovery of naphthenic acids from petroleum or other fractions or of the recovery of synthetic naphthenic acids from hydrocarbon oxidates the fraction or oxidate is washed with aqueous alkali metal hydroxide or carbonate, preferably sodium hydroxide or sodium carbonate, solution to extract the naphthenic acids in the form of their alkali metal soaps. These soaps are preferentially soluble in the aqueous phase and are separated from the extracted oil or oxidate by decantation. The crude naphthenic acids may be obtained from these caustic extracts by acidification with mineral acids such as sulfuric acid, hydrochloric acid and the like. Generally crude naphthenic acids recovered in this manner will contain between about 10% and about 30% by weight or more of hydrocarbon oil depending upon the molecular weight of the hydrocarbon fraction or oxidate extracted and upon conditions of the extraction such as strength of the caustic or carbonate solution, temperature and the like. The presence of hydrocarbon oil in the crude acids results from the fact that aqueous alkali metal naphthenate solutions have the ability to hold rather large proportions of oil in pseudo solution. Thus a caustic extract containing 10% to 15% by weight of sodium naphthenate may contain between about 1% and about 4% or more of hydrocarbon oil. That the oil is firmly held by the soap in a condition approaching "solution" is indicated by the fact that these soap solutions are clear and remain clear, i. e., do not separate an oily phase even upon dilution with large volumes of water. This ability of the alkali metal naphthenates to "solubilize" oil has been thought to be due to the retention of oil particles within the micelles of the soap. Further evidence of the powerful solubilizing effect of the naphthenate soaps or hydrocarbon molecules is indicated by the fact that extraction of the aqueous caustic extracts with light petroleum solvents such as naphtha and the like does not effect the removal of more than a small part of the oil.

Although extraction of the caustic extracts with light hydrocarbon solvents is not particularly efficient in removing impurities, such processes have been employed alone and in connection with other refining steps in the production of

naphthenic acids. Solvents other than petroleum solvents such as alcohols and the like have also been employed, however by such means alone it has not been possible to obtain a naphthenic acid free of hydrocarbon oil. Other methods which have been employed for the removal of the impurities described include steam distillation of the caustic extract to vaporize the hydrocarbon oil leaving an aqueous solution of soaps as a residue. This process has many disadvantages including the serious foaming of the still charge and the tendency for the sodium naphthenates to oxidize, decompose and/or polymerize during the heating period.

Another method of purification of the naphthenic acids comprises the decomposition of the soaps with a mineral acid to yield a water-soluble alkali metal salt such as sodium sulphate, sodium chloride or the like, depending upon the mineral acid employed, and the free naphthenic acids containing the above-mentioned impurities. These crude naphthenic acids are subsequently treated by extraction with a suitable solvent to effect the separation of the impurities from the acids. Solvents for this extraction are not particularly efficient and, moreover, a great deal of difficulty is generally encountered in this method of treatment due to the formation of comparatively stable emulsions in the various stages of the process. Thus in the cracking-out of the alkali soap with the mineral acid thorough agitation is necessary which often gives rise to a very stable emulsion. Similarly, the residual water remaining in the acid during subsequent stages of the treatment gives rise throughout to emulsion difficulties.

Other refining processes have included the steps of acidification of the caustic extracts, dilution of the crude acids thus obtained with light petroleum solvent, extraction of the diluted solution with caustic, separation of the aqueous soap solution, acidification of the soap solution to release the naphthenic acids and distillation of the released naphthenic acids. This process although apparently desirable in that it furnishes a de-oiling step has not been commercially feasible because of the formation of extremely stable jelly-like emulsions in the step of extracting the diluted crude naphthenic acid solution with caustic solution. Emulsions obtained in this manner have not been successfully broken with the various deemulsification agents available for such purposes and in fact the emulsions have been observed to remain stable over periods of several weeks.

It is therefore an object of this invention to separate naphthenic acid from crude naphthenic acid stocks containing any of the above named impurities, and in doing so to obtain a naphthenic acid product possessing improved characteristics with respect to color, odor, viscosity oil content and the like.

More specifically it is an object of our invention to accomplish this purification of naphthenic acids by a method which eliminates the normal emulsion difficulties incurred in such purification and at the same time effects a greater degree of purification than normally accomplished.

Other objects and advantages of our invention will become apparent to those skilled in the art as the description thereof proceeds.

We are able, by means of the process of our invention, to continuously recover and purify naphthenic acids as a result of the fact that we have discovered a method whereby it is possible

to effect such purification in the absence of emulsion difficulties. The efficiency of our process depends upon the essential elements thereof. The first of these is the cracking of the naphthenate soaps, normally resulting from the treatment of naphthenic acid-containing fractions with a caustic solution, by treatment of these soaps with a mineral acid such as sulfuric acid, hydrochloric acid or the like to yield a naphthenic acid fraction. This is a necessary element of our invention inasmuch as we have found that the treatment of the alkali metal soaps themselves by the methods described is relatively ineffectual due to the retention in the soaps of the various impurities as above pointed out. The second and related element of our invention comprises the purification of these free acids under conditions of comparatively high temperatures and pressures which has the effect of preventing the formation of emulsions during the course of the purification and at the same time providing highly efficient removal of the undesirable constituents. It is therefore, understood that both of these elements are related and in combination with each other constitute the essence of our invention.

We have found that if purification of the crude naphthenic acids is carried out at temperatures in the range of from about 150° F. to about 350° F. and at pressures in the range of about 100 pounds per square inch to about 250 pounds per square inch that emulsions are not formed in the various refining steps set forth hereinbelow. In most cases these pressures may be induced in closed systems by the temperatures employed in the operation due to the vapor pressures of water and other solvents employed but if it is desired to employ pressures in excess of the vapor pressure of the constituents at the temperatures of operation this added pressure may be created by the use of a relatively inert gas such as nitrogen or the like, or by the use of feed pumps and back-pressure valves as would be understood by those skilled in the art.

Operating under the conditions as above described we may purify the acids by various methods depending upon the degree of purity desired. The first of these methods involves the treatment of the acid fraction, obtained by acidification of the soaps, with water at the high temperatures and pressures mentioned to effect the removal therefrom of the residual mineral acid remaining after the acidification. The water and naphthenic acid phases from this treatment may be then separated by conventional means such as settling or centrifuging to yield a crude naphthenic acid containing an appreciable quantity of residual impurities. If desired, this simple water extraction may be repeated one or more times to insure the complete removal of mineral acid without danger of emulsification. This process does not effect the removal of the various hydrocarbon contaminates but results in a naphthenic acid free of mineral acid and may be simply accomplished, in the absence of emulsion difficulties, by carrying on the water extraction under the conditions of temperature and pressure disclosed.

If more complete purification is desired, another and more effective method may be employed which involves the dilution of the acids, after splitting of the alkali metal soap, with a light gasoline or naphtha fraction boiling below the boiling range of the naphthenic acids. Caustic extraction of the gasoline solution of the crude

naphthenic acids results in the removal of the naphthenic acids in the form of soaps leaving a gasoline solution of the oil or unsaponifiable material originally associated with the crude naphthenic acids. The soap phase contains small amounts of "dissolved" gasoline and extremely small proportions of the unsaponifiables originally present. The ratio of gasoline to the higher boiling unsaponifiable in the soap phase is similar to the corresponding ratio in the gasoline solution of crude acids. Acidification of these soaps with mineral acid, separating the aqueous phase containing the alkali metal salt thus formed from the released naphthenic acids and removing residual salts and mineral acids from the naphthenic acids by water washing results in the production of a naphthenic acid containing low boiling hydrocarbon impurities (gasoline solvent) which may be separated therefrom if desired by means of simple fractional distillation.

It is important that the dilution and subsequent extraction steps outlined hereabove be carried out at elevated temperatures and pressures in order to obtain highest efficiencies and more particularly to avoid the formation of stable emulsions. These operations carried out at ordinary temperatures and pressures invariably result in the formation of emulsions which fail to stratify even after long periods of settling.

A third and preferred method of purification embodies the elements of the above described method with the addition thereto of the added step of acid-treating the gasoline diluent-naphthenic acid solution to remove therefrom the resinous or asphaltic impurities in the crude naphthenic acid thereby preventing any occlusion of these impurities upon resaponification of the naphthenic acid.

The wide flexibility of our invention may be appreciated from the foregoing description of some of the methods of procedure which may be employed if the two primary elements of the invention are adhered to, namely, the splitting of the alkaline naphthenate soaps prior to purification and the operation of the subsequent purification at sufficiently high temperatures and pressures to prevent the formation of difficultly separable emulsions in the process. Over and above the flexibility permissible in the purification according to the present method other advantages accrue which serve to emphasize the novelty and effectiveness of our invention. Primary among these advantages is the ability, in the absence of emulsion difficulties, to operate the process on a continuous basis which is considerably more efficient than batch-wise methods of purification. Further, we have found that we are able to obtain acids of a higher degree of purity than are ordinarily obtainable, by the conventional purification methods.

The process of this invention may be more fully understood by reference to the accompanying drawing which not only shows the elements of the invention but further illustrates the flexibility of the process which is susceptible of considerable modification depending upon the desired grade or purity of naphthenic acid.

In the drawing the naphthenic acid-containing petroleum fraction is withdrawn from storage tank 10 by means of line 11 controlled by valve 12 and is pumped by pump 13 into manifold 14. Simultaneously caustic such as sodium hydroxide is withdrawn from storage tank 15 by means of line 16 controlled by valve 17 and is pumped by pump 18 into line 14 wherein it is intermingled with the petroleum fraction, the mixture passing through mixing valve 19 into settler 20. In this manner the naphthenic acids in the petroleum fraction are converted to their corresponding sodium soaps which settle to the bottom of settler 20 the hydrocarbon phases being removed from the upper portion of settler 20 by means of line 21. It is understood that the method of extraction is not a critical feature of our invention inasmuch as any method of recovering the naphthenic acids from fractions in which they are contained may be employed.

The crude sodium naphthenate is withdrawn from the bottom of settler 20 by means of line 22. Sulfuric acid is withdrawn from storage tank 24 by means of line 25 controlled by valve 26 and is pumped by pump 27 into line 22 wherein it contacts the crude sodium naphthenate solution, the mixture passing therefrom through line 28 and mixing valve 29 into heat interchanger 30. In the interchanger 30 the mixture is heated by means of steam or other vapor or liquids introduced into the interchanger by line 31 and removed therefrom by line 32, to a temperature in the range of about 150° F. to 350° F.

The entire operation both prior to and subsequent to the point of heating is carried out under a pressure of from 100 to 250 pounds per square inch. However, such a pressure in itself appears to be insufficient to prevent the formation of emulsions in subsequent stages of the operation but if such pressures of operation are combined with the use of relative high temperatures, the emulsion difficulties are overcome.

The mineral acid-naphthenate mixture which at this point has at least partially reacted to form sodium sulfate, water and naphthenic acids is withdrawn from the interchanger 30 by means of line 33 and is introduced into settler 34 wherein the aqueous sodium sulfate settles to the bottom and is drawn off by means of line 35 controlled by valve 36. The naphthenic acid phase is withdrawn from settler 34 by means of line 37 controlled by valves 38 and 39.

In the preferred method of operation valve 39 is closed and the naphthenic acid passes from line 37 through valve 38 into line 40. A light gasoline fraction is withdrawn from storage tank 42 by means of line 43 controlled by valve 44 and is pumped by pump 45 into line 40 and is injected together with crude naphthenic acids into settler 46. This hydrocarbon diluent may be any comparatively low boiling naphtha such as one boiling below about 350° F. and preferably below about 300° F. This low boiling naphtha has the effect upon solution of the naphthenic acids therein of diluting the impurities which are contained in the naphthenic acids. Residual water remaining with the naphthenic acids is withdrawn from the bottom of settler 46 by means of line 47 controlled by valve 48.

The naphthenic acid-light hydrocarbon solution is withdrawn from the top of settler 46 by means of line 49 controlled by valve 50 passing therethrough into line 51 controlled by valves 52 and 53. At this point alternative methods of procedure may again be followed, in one method the sulfuric acid refining of the gasoline-naphthenic acid solution is employed and in the other method the sulfuric acid refining step is bypassed. If valve 52 is closed the gasoline-naphthentic acid solution is passed through valve 53 into line 54. Sulfuric acid is withdrawn from storage tank 56 by means of line 57, controlled by valve 58 and is pumped by pump 59 through line 60 into line

54 and is passed together with the gasoline-naphthenic acid solution into settler 62. The sulfuric acid employed in the initial phase of the process to acidify the sodium naphthenate soaps and the sulfuric acid employed at this point of the operation may be of the same or different concentrations; that is, the refining process as carried out on the light hydrocarbon-naphthenic acid solution requires an acid of high concentration such as approximately 75% or higher, whereas, the acid employed in the cracking of the soaps may even be less concentrated such as in the range of 50% to 90% or higher.

In settler 62 a phase separation takes place between the sulfuric acid sludge and the hydrocarbon solution of naphthenic acids. The acid sludge phase will contain the resinous and asphaltic impurities originally contained in the naphthenic acid leaving in the gasoline solution only the high boiling hydrocarbon impurities. The acid sludge is removed from the bottom of settler 62 by means of line 63 controlled by valve 64. The acid-treated gasoline-naphthenic acid solution is withdrawn from the top of settler 62 by means of line 65 controlled by valve 66 and is passed via line 67 into centrifuge 68. In centrifuge 68 the residual sludge is separated from the hydrocarbon-naphthenic acid solution and is removed from the centrifuge by means of line 69.

The centrifuged naphthenic acid-hydrocarbon solution is withdrawn from centrifuge 68 by means of line 70 controlled by valve 71 and is passed into line 72. It is at this point in the process that the effluent from settler 46 may be introduced if it is desired to bypass the sulfuric acid refining step. This is accomplished by closing valve 53 and opening valve 52 allowing the hydrocarbon-naphthenic acid solution from settler 46 to pass via line 73 controlled by valve 74 into line 72. Irrespective of which of these streams is to be treated caustic is withdrawn from tank 15 by means of line 75 controlled by valve 76 and is pumped by pump 77 via line 78 and is commingled with the hydrocarbon-naphthenic acid solution in line 79 passing into settler 80. At this point the naphthenic acids are resaponified and the impurities retained in the soap solution constitute essentially light hydrocarbons which have replaced the major proportion of the heavier hydrocarbon impurities. The light hydrocarbon phase containing the major proportion of heavier hydrocarbon impurities originally present in the naphthentic acid is withdrawn from the top of settler 80 by means of line 81 controlled by valve 82 and is passed via line 83 back to the light gasoline storage tank 42. Because of the relatively small amount of heavier hydrocarbons in the naphthenic acid as compared to the amount of diluent employed and consequently the relatively small amount in the light diluent it may be reemployed in the process with only occasional redistillation to effect the removal of accumulated heavy hydrocarbons.

The naphthenic soaps, containing as impurities predominately light hydrocarbons are withdrawn from the bottom of settler 80 by means of line 84 and are passed into line 89. Sulfuric acid is withdrawn from storage tank 24 by means of line 85 controlled by valve 86 and is pumped by pump 87 via line 88 into line 89 mixing therein with the naphthenate soaps from settler 80. This mixture is passed into settler 90 wherein, as in settler 34, the aqueous sodium-sulfate solution separates from the naphtenic acid phase and is withdrawn from the bottom of the settler by means of line 91 controlled by valve 92.

The naphthenic acids are withdrawn from the settler 90 by means of line 93 controlled by valves 94, 95 and 96. It is at this point in the process that the crude naphthenic acids taken overhead from settler 34 may be introduced, thereby bypassing the treatment with light hydrocarbon, sulfuric acid refining, resaponification, and acidification of the resaponified soaps. Of this bypassing is employed the process is considerably simplified but the purity of the final product is reduced.

Two alternative procedures are again available at this stage of the operation. In the simplest of these the naphthenic acids may be passed directly through valve 96 via line 98 through valve 99 and via line 100 into centrifuge 108. Alternatively the acids may be passed through valve 94 via line 101 into interchanger 102 to increase the temperature thereof, from interchanger 102 into line 105 wherein water is introduced into the acids by means of line 106. This water-acid mixture is passed from line 105 through valve 107 into centrifuge 108. The combination of the addition of water to the acids and the heating thereof in the interchanger may be substituted by the direct addition of steam into the acid accomplishing both purposes simultaneously. The water wash at this point is designed to insure the complete removal of mineral acid employed in the resaponification.

In centrifuge 108 the acids are separated from residual water and mineral acid which are removed from the centrifuge by line 109.

The naphthenic acids are withdrawn from the centrifuge 108 by means of line 110 and may be passed directly through valve 112, line 113, valve 114, and line 115 into storage tank 116. If this procedure is employed the finished acids will contain as impurities small amounts of light hydrocarbons. However, still further purification may be effected by passing the acids from line 110 through valve 111 into preheater 117 from which they are passed via line 118 into fractionator 120. In fractionator 120 the light hydrocarbon impurities are distilled overhead being withdrawn from the fractionator by means of line 121 controlled by valve 122 and are passed into storage tank 124. Naphthenic acids, freed of the light hydrocarbon are obtained as a side cut in the distillation being withdrawn from the column by means of line 125 controlled by valve 126 passing through line 115 into a finished acid storage tank 116. The bottoms from the distillation consisting of polymeric substances and high molecular weight acidic fractions are withdrawn by means of line 127 controlled by valve 128. Alternatively this fractionation may be effected in such a manner that gasoline is obtained as the overhead distillate and the naphthenic acids as the bottoms fraction.

The following specific examples are presented to further illustrate our invention but are not to be considered as limiting the broader aspects of the invention:

Example I

A caustic extract obtained by extracting a naphthenic petroleum distillate boiling in the range of about 350 to about 600° F. and having a gravity of 31.3° API with an aqueous sodium hydroxide solution containing 2% by weight of sodium hydroxide was acidified with 80% sulfuric acid in a closed system at a pressure of 100 pounds per square inch, the mixture was heated to about

200° F. and passed into a settler maintained at the same pressure in which the crude naphthenic acids were separated from the aqueous sodium sulfate solution. The naphthenic acid phase was washed with water to remove mineral acid and again settled to separate the water. The crude acids thus produced had an acid number of about 175 mg. KOH/g.

In order to determine the quantity of oil or unsaponifiable matter associated with the naphthenic acids in the crude acid mixture, a 20-gram sample of the crude acids was converted into sodium soaps by neutralization to the phenolphthalein end point with 2% NaOH solution and the dilute soap solution thus obtained was extracted with two 50-ml. portions of ethyl ether. The ether extracted soap solution was acidified with sulfuric acid and the resulting naphthenic acids washed with water. These acids which were substantially free from unsaponifiable material had an acid number of 235 mg. KOH/g. The proportion of unsaponifiable material in the original crude acids calculated from the increase in acid number after deoiling was 25.5%.

For purposes of comparison a second 20-gram sample of the crude acids was neutralized with 2% caustic solution and the resulting dilute soap solution was extracted with two 50 ml. portions of a petroleum naphtha boiling in the range of about 150° F. to 250° F. and the extracted soap solution was acidified to obtain the naphthenic acids. These acids, after water washing to remove mineral acid and water soluble salts, had an acid number of 200 mg. KOH/g. Extraction of soap solution with the petroleum naphtha removed approximately 12.5% by weight of an unsaponifiable material or about 49% by weight of the unsaponifiable material originally present as calculated from the acid number increase obtained by ethyl ether extraction.

Another sample of the crude acids was distilled to produce an overhead amounting to 5% by weight of the crude acids of an oil having an acid number of 10 mg. KOH/g. and a bottoms fraction amounting to 95% by weight of the crude acids having an acid number of 183 mg. KOH/g.

Example II

A portion of the crude naphthenic acids described in Example I was diluted with six volumes of a petroleum naphtha boiling in the range of about 150° F. to about 250° F. and the diluted acids, under a pressure of about 100 pounds per square inch and at a temperature of about 225° F., were contacted with a dilute caustic solution containing about 2% by weight of NaOH. The resulting soap solution being maintained under a pressure of 100 pounds per square inch was heated to 225° F., acidified with 80% sulfuric acid to liberate the naphthenic acids and the mixture allowed to separate. The liberated naphthenic acids were washed with hot water to remove mineral acid and centrifuged to remove substantially all of the water. These acids had an acid number of 180 mg. KOH/g. A portion of the acids thus produced was distilled to produce as overhead distillate a naphtha fraction amounting to 21.5% by weight of the distillation charge having an acid number of 1.5 mg. KOH/g. and a bottoms fraction having an acid number of 229 mg. KOH/g. Calculations based on acid number determinations indicated that the naphthenic acids produced in this manner contained approximately 2.5% by weight of unsaponifiable matter.

Example III

A portion of the crude naphthenic acids described in Example I were diluted with six volumes of a petroleum naphtha boiling in the range of about 150° F. to 250° F. and the diluted acids, under a pressure of about 100 pounds per square inch and at a temperature of about 180° F., were contacted with 10% by weight, based on the crude naphthenic acids, of 85% of H_2SO_4 and the mixture passed to a settler where the acid sludge phase produced by the acid contacting was separated from the treated gasoline solution of acids. The treated solution was passed to a centrifuge where substantially all of the remaining sludge was removed and the centrifuged gasoline solution of treated acids at a temperature of 200° F. and under a pressure of 100 pounds per square inch was contacted with a dilute caustic solution containing about 2% by weight of NaOH to convert the acids into their sodium soaps. The resulting soap solution being maintained under a pressure of 100 pounds per square inch was heated to 225° F. and acidified with 80% sulfuric acid to liberate naphthenic acids. The liberated naphthenic acids were washed with hot water to remove mineral acid and water-soluble salts and then centrifuged to remove substantially all of the water. These naphthenic acids had an acid number of 185 mg. KOH/g. A portion of the acids thus produced was distilled to produce as overhead distillate a naphthenic fraction amounting to 21.0% by weight of the distillation charge having an acid number of 2 mg. KOH/g. and a bottoms fraction having an acid number of 234 mg. KOH/g.

In order to determine the proportion of unsaponifiable material present in the acids produced in the above process a 20-gram sample of the refined acids having an acid number of 234 mg. KOH/g. was converted into sodium naphthenate by neutralization to the phenolphthalein end point with 2% NaOH of solution and the dilute soap solution thus obtained was extracted with two 50 ml. portions of ethyl ether. The ether extracted soap solution was acidified with sulfuric acid and the resulting naphthenic acids washed with water to remove mineral acid and water soluble salts and finally dried. The purified acids had an acid number of 238 mg. KOH/g. On the basis of acid number increase the refined acids were indicated to contain 1.75% by weight of unsaponifiable material.

Having described and illustrated the essential elements of our invention and realizing that many modifications may occur to those skilled in the art without departing from the principal elements thereof which comprise essentially the recovery and purification of naphthenic acid fractions at elevated temperatures and pressures, we claim:

1. A method of recovering naphthenic acids comprising the steps of (1) contacting a petroleum fraction containing said naphthenic acids with an aqueous solution of a basic alkali metal compound thereby forming the alkali metal soap of said naphthenic acid, (2) separating the aqueous soap solution from said petroleum fraction, (3) acidifying said soap solution with a sufficient quantity of a mineral acid to convert said soap into naphthenic acids, (4) separating said naphthenic acids from the aqueous salt solution formed in the acidification step, (5) diluting said naphthenic acids with a hydrocarbon solvent,

(6) contacting said hydrocarbon solvent solution of naphthenic acid with an aqueous solution of a basic alkali metal compound thereby reforming the alkali metal soap of said naphthenic acids, (7) separating the aqueous soap solution from said petroleum fraction, (8) acidifying said soap solution with a sufficient quantity of a mineral acid to convert said soaps into naphthenic acids and (9) separating said naphthenic acids from the aqueous salt solution formed in the acidification step, said aforesaid steps 3 to 9 inclusive being effected in a continuous manner at a pressure greater than about 100 pounds per square inch and at a temperature above about 150° F.

2. A method of recovering naphthenic acids according to claim 1 in which steps 3 to 9 inclusive are carried out at a temperature in the range of about 150° F. to about 350° F. and at a pressure in the range of about 100 pounds to about 250 pounds per square inch.

3. A method of recovering naphthenic acids according to claim 1 in which the basic alkali metal compounds is sodium hydroxide.

4. A method of recovering naphthenic acids according to claim 1 in which the hydrocarbon solvent boils in the range of about 100° F. to about 400° F.

5. A method of recovering naphthenic acids comprising the steps of (1) contacting a petroleum fraction containing said naphthenic acids with an aqueous solution of a basic alkali metal compound thereby forming the alkali metal soap of said naphthenic acids, (2) separating the aqueous soap solution from said petroleum fraction, (3) acidifying said soap solution with a sufficient quantity of a mineral acid to convert said soaps into naphthenic acids, (4) separating said naphthenic acids from the aqueous salt solution formed in the acidification step, (5) diluting said separated naphthenic acids with a major proportion of a hydrocarbon solvent, (6) treating the resultant hydrocarbon solvent solution of naphthenic acid with sulfuric acid, (7) separating the acid sludge from said solution of naphthenic acid, (8) contacting said solution of naphthenic acid with an aqueous solution of a basic alkali metal compound thereby reforming the alkali metal soap of said naphthenic acid, (9) separating the aqueous soap solution from the hydrocarbon solvent, (10) acidifying said soap solution with a sufficient quantity of a mineral acid to convert said soaps into naphthenic acids, and (11) separating said naphthenic acids from the aqueous salt solution formed in the acidification step, said aforesaid steps 3 to 11 inclusive being effected in a continuous manner at a pressure greater than about 100 pounds per square inch and at a temperature above about 150° F.

6. A method of recovering naphthenic acids according to claim 5 in which steps 3 to 11 inclusive are carried out at a temperature in the range of about 150° F. to about 350° F. and at a pressure in the range of about 100 pounds to about 250 pounds per square inch.

7. A method of recovering naphthenic acids according to claim 5 in which the basic alkali metal salt is sodium hydroxide.

8. A method of recovering naphthenic acids according to claim 5 in which the hydrocarbon solvent boils in the range of about 100° F. to about 400° F.

9. A method of recovering naphthenic acids comprising the steps of (1) contacting a petroleum fraction containing said napthenic acids with an aqueous solution of a basic alkali metal compound thereby forming the alkali metal soap of said naphthenic acids, (2) separating the aqueous soap solution from said petroleum fraction, (3) acidifying said soap solution with a sufficient quantity of a mineral acid to convert said soaps into naphthenic acids, (4) separating said naphthenic acids from the aqueous salt solution formed in the acidification step, (5) diluting said separated naphthenic acids with a hydrocarbon solvent, (6) treating the resultant hydrocarbon solvent-naphthenic acid solution with sulfuric acid, (7) separating the acid sludge from said hydrocarbon solvent-naphthenic acid solution, (8) contacting said hydrocarbon solvent-naphthenic acid solution with an aqueous solution of a basic alkali metal compound thereby reforming the alkali metal soap of said naphthenic acid, (9) separating the aqueous soap solution from the hydrocarbon solvent, (10) acidifying said soap solution with a sufficient quantity of a mineral acid to convert said soaps into naphthenic acids, (11) separating said naphthenic acids from the aqueous salt solution formed in the acidification step, said aforesaid steps 3 to 11 inclusive being effected in a continuous manner at a pressure greater than about 100 pounds per square inch and at a temperature above about 150° F. and thereafter heating said naphthenic acids to remove therefrom residual light hydrocarbon solvent.

10. A method of recovering naphthenic acids according to claim 9 in which steps 3 to 11 inclusive are carried out at a temperature in the range of about 150° F. to about 350° F. and at a pressure in the range of about 100 pounds to about 250 pounds per square inch.

11. A method of recovering naphthenic acids according to claim 9 in which the basic alkali metal salt is sodium hydroxide.

12. A method of recovering naphthenic acids according to claim 9 in which the hydrocarbon solvent boils in the range of about 100° F. to about 400° F.

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