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METHOD OF REMOVING HIGH MOLECULAR WEIGHT NAPHTHENIC ACIDS FROM HYDROCARBON OILS

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This invention relates to a method and new solvent combination for the extraction of acidic constituents from hydrocarbon mixtures and particularly from heavy or residual lubricating oil stocks or solvent extracts from the solvent extraction of lubricating oils. The solvent combination found most suitable for this purpose comprises a mixture of methanol, a neutralizing agent and a carrier therefor with certain monohydric alcohols having 4 to 7 carbon atoms in the molecule. The acidic constituents extracted may include naphthenic acids, other organic acids, inorganic acids, esters, phenolic compounds, lactones, resins, and salts of heavy metals. A greater portion of these substances, commonly referred to as "naphthenic acids" in the lubricating oil refining art, are at least in part further characterized as high molecular weight carboxylic acids being liquid and/or solid aliphatic acids and alicyclic acids having above about 25 carbon atoms to the molecule, showing little or no unsaturation, and consisting essentially of cyclic acids and polycyclic acids. These acidic materials have boiling ranges above about 800° F. and, in general, offer difficulty in their removal and purification.

The invention relates broadly to a method and solvent composition for extracting and/or purifying these acidic materials associated with hydrocarbon mixtures regardless of the source or original acid number of the mixture treated, irrespective of the end use to which the raffinate and extract phases may be applied, and notwithstanding the chemical nature of the naphthenic acids except so far as just defined. Furthermore, the method of the invention may be applied at any desired point in the steps of refining of such hydrocarbon mixtures and is independent of the process conditions of such general refining methods, as will be described. Accordingly, although the invention and the problem solved by it will be described by reference to particular lubricating oil fractions and the reduction of the acid number thereof, the invention is not to be so limited and will find application to related arts where removal and purification of naphthenic acids is the main consideration.

In the preparation of lubricating oils from crude petroleum, it is the practice to subject both heavy and residual lubricating oil stocks to chemical and physical treatments in order to improve the viscosity characteristics, low temperature fluidity, oxidation stability, and lower the carbon residue, sulfur content, and neutralization values in order that the requirements of modern lubrication may be met by the lubricating oils. One problem that has faced the refiner of lubricating oils is the removal of acidic constituents from the heavy or residual lubricating oil stocks, as, for example, preparing such lubricating oils having low acid numbers as determined by ASTM D974–52T. As the refining operations of dewaxing, deasphalting, and solvent refining exert their influence upon the lubricating oil fractions, the acidic constituents remaining become much more difficult to remove. Refiners have in the past applied various solvent

extraction methods employing dilute aqueous alkali solutions and various organic solvents in their effort to produce lubricating oils having acceptable neutralization values. Aqueous and anhydrous ammonia solutions have been used, followed by alcohol extractions, to remove the deleterious naphthenic acids. Aqueous ammonia solutions in combination with emulsion breakers, such as methyl alcohol, ethyl alcohol, or acetone, have been applied in various continuous countercurrent extraction processes in an effort to finish lubricating oils for use with various additives that have become necessary to meet the extreme conditions in modern lubrication. In spite of the prior art efforts, in many instances the persistence of acidic constituents or naphthenic acids in finished lubricants has proved detrimental.

For instance, it is known that about 99 percent of the lower boiling naphthenic acids may be removed from light lubricating oil distillates, which may have an acid number in the range of 2 to 3, by treatment with relatively dilute aqueous alkali solutions. The treatment of a light lube distillate having an acid number of 2.75 with an equal volume of 5 percent aqueous potassium hydroxide removes about 99 percent of the naphthenic acids. Treatment of this same distillate with 1.0 N ammonium hydroxide will remove about 89 percent of the acids. Heavier lubricating oil distillates and heavy bottoms or residues aforementioned, after dewaxing or deasphalting, contain certain complex and/or high molecular weight naphthenic acids which are increasingly difficult to remove. To illustrate, a deasphalted hydrocarbon oil having an acid number of 1.75 on treatment with an equal volume of 1.0 N ammonium hydroxide results in the removal of only 23 percent of the acids. This same oil treated with a solvent comprising one part of 5.0 percent aqueous potassium hydroxide and one part of Formula 30 alcohol results in the removal of only 1.8 percent of the naphthenic acids. Treatment of this same deasphalted oil with a solvent comprising 3 parts of 1.0 N ammonium hydroxide, 2 parts of 1-butanol, and 2 parts of 2-propanol accomplishes the removal of about 76 percent of the naphthenic acids.

Proceeding further with the refining, it is found that the acid numbers of some deasphalted products before solvent extraction may be in the order of 1.0 to 2.5. Subsequent removal of waxy hydrocarbons and resinous materials in the final stages of refining to produce finished lubricating oil blending stocks such as the bright stock aforementioned has the effect of further reduction of the acid number of values ranging from 0.3 to 1.0. Such stocks as residues, dewaxed bright stock, solvent extracts, and heavy lubricating oil distillates contain naphthenic acids of higher molecular weight or complexity which cannot be successfully removed by the application of prior art solvents. For example, treatment of a dewaxed bright stock with the ammoniacal butanol-propanol solvent aforementioned results in the extraction of only 41 percent of the acidic constituents or naphthenic acids. In many applications, heavier lubricating oil stocks exhibit instability which is traceable to the presence of the high molecular weight naphthenic acids therein and, accordingly, it is desirous that these acidic materials be further removed. The prior art methods and solvent compositions are expensive, difficult to handle, and do not in all instances accomplish the desired results with the assurance necessary for modern refining practice. Furthermore, it is desirable that the extractions be easily manipulated, produce the greatest possible reduction in acid number, and allow the purification of the naphthenic acids which in themselves represent a valuable product. Since refining methods differ greatly in their ability to remove naphthenic acids but may induce other desirable changes in

the hydrocarbon mixtures treated, it is also essential that any methods applied to meet a particular acid number requirement are easily coordinated with the established refining methods.

To the accomplishment of these and related ends, the present invention is based upon the discovery of a solvent combination which, because of the balance struck between selectivity and miscibility, not only efficiently removes high molecular weight naphthenic acids from hydrocarbon mixtures or hydrocarbon oils, but also allows for easy purification of the naphthenic acids so removed. The solvent composition found most effective in obtaining the results just discussed in accordance with this invention comprises a mixture of methyl alcohol and certain monohydric alcohols having 4 to 7 carbon atoms per molecule, optimum amounts of a neutralizing or basic agent, and a carrier therefor. The general class of alcohols found to function most effectively with methyl alcohol for this purpose may be defined as monohydric primary alcohols of 4 to 7 carbon atoms. The preferred species of C_4 to C_7 alcohols may be enumerated as n-butyl alcohol, n-amyl alcohol, iso-amyl alcohol, n-hexyl alcohol, iso-hexyl alcohol, n-heptyl alcohol, and iso-heptyl alcohol. More exactly, it has been found that mixtures comprising methyl alcohol in at least about 5 percent by volume with straight chain monohydric primary alcohols of 4 to 7 carbon atoms per molecule or branched chain monohydric primary alcohols of 5 to 7 carbon atoms per molecule as the principal organic solvent with optimum amounts of a neutralizing agent, such as ammonia or alkali metal hydroxides and low molecular weight amines, produce a solvent composition which increases the solvent efficiency, expressed in percentage of naphthenic acids extracted, by from about 10 to 40 percent over the prior art solvents. Where ammonia is used as the neutralizing agent, it is expedient to use water as the carrier therefor.

It is, therefore, a primary object of the invention to provide a process for the removal of high molecular weight acidic materials generally defined as naphthenic acids from hydrocarbon mixtures and residual lubricating oil stocks.

A second object of the invention is to provide a novel solvent combination which increases the efficiency of the extraction of high molecular weight naphthenic acids from hydrocarbon mixtures and residual lubricating oil stocks.

Other objects and advantages of the invention will appear as the description thereof proceeds.

In order to demonstrate the invention, a series of extractions were conducted under substantially the same conditions of temperature, pressure, etc., using various solvent combinations in the treatment of a dewaxed bright stock, a material which is quite resistant to solvent treatment as a method of removal of naphthenic acids. The results are shown in the table. The solvent-to-oil ratios used in these experiments are in the order of 1:1.

Extractions of dewaxed bright stock

	Solvent Composition, Percent by Volume							Percent Acids Extracted	Distribution Coefficient of Acids	Percent Oil Loss
	NH_3	H_2O	n-Butyl Alcohol	Iso-propyl Alcohol	Methyl Alcohol	Other Alcohols				
						Type	Amount			
1*	100							3.90	0.04	<5
2	1.77	98.23						0.00	0.00	<5
3	0.89	49.11				Form. 30	50.0	8.3	0.09	<5
4	0.11	0.29	99.6					58	1.35	<5
5			100					34.2	0.52	<5
6					100			5.7	0.06	<5
7	0.11	0.29			99.6			23	0.28	<5
8	0.8	42.0	28.6	28.6				41	0.69	<5
9	0.7	41.0	33.3	25.0				33	0.50	<5
10	0.18	9.82	80	10				44	0.77	<5
11	2.7	7.3	80		10			64	1.83	<5
12	0.11	0.29	79.7		19.9			65	1.90	<5
13	0.11	0.29	59.8		39.8			62	1.61	<5
14	0.11	0.29	79.7	19.9				55.2	1.23	<5
15	0.11	0.29		79.7	19.9			45	0.82	<5
16	0.11	0.29			19.9	n-amyl	79.7	66	1.95	<5
17	0.11	0.29			19.9	n-octyl	79.7	55	1.23	**
18	0.11	0.29			19.9	tert.-butyl	79.7	41	0.69	<5
19	0.11	0.29			19.9	n-propyl	79.7	39	0.65	<5
20	0.11	0.29			19.9	n-hexyl	79.7	66	1.92	<5
21	0.11	0.29			19.9	iso-amyl	79.7	61	1.58	<5
22	0.11	0.29			19.9	2-pentanol	79.7	55	1.21	<5
23	0.11	0.29			19.9	isobutyl	79.7	53	1.13	<5
24	0.11	0.29			19.9	sec.-butyl	79.7	52	1.06	<5

*Charge stock was heavy extract from the manufacture of bright stock.
**High oil loss arising from substantial partial miscibility.

In the table, under the column headed "Other Alcohols," a number of different alcohols were tested in combination with ammonia and water with and without methyl alcohol. In experiment 3, the composition included 50 percent by volume of Formula 30 alcohol, which is 90 percent ethyl alcohol and 10 percent methyl alcohol. The asterisks in the column "Percent Oil Loss" for experiment 17 indicates greater oil loss or a reduction in selectivity beyond that tolerated for efficient extraction on a commercial basis.

The table sets forth the compositions of the various solvents employed in volume percent and shows both the percent of acids extracted and the distribution coefficient of the acids. Distribution coefficients or K values, defined as the ratio of the concentration of solute in extract to the concentration of solute in raffinate, are routinely used in extraction studies as they give a direct comparison of the various extractions regardless of any variations in the volumes of extract and raffinate. The percent of acids extracted cannot always be compared in testing various solvents unless the volume ratios of extract to raffinate are practically identical. Even starting with equal volumes of oil and solvent does not insure that the volume ratios of extract to raffinate will always be the same. Accordingly, both the "Distribution Coefficient" and "Percent Acids Extracted" have been shown in order that a more precise comparison of the results may be made. The "Percent Oil Loss" which is an indication of proper miscibility with the oil phase for the solvents tested, was less than 5 percent in every instance except experiment 17 wherein reduced selectivity was noted in the case of n-octyl alcohol in combination with methanol.

In experiment 1, the oil extracted was a high V. I. bright stock extract which is somewhat more easily treated than the dewaxed bright stock raffinate as far as the extractability of the naphthenic acid content is concerned.

However, the percent acids extracted is still far below that obtained by the preferred solvent combination. Comparison of experiments 1, 2, and 3 indicates that anhydrous ammonia, dilute ammonia, and alcoholic ammonia are quite inefficient in the extraction. Experiment 4 shows that increased efficiency is obtained with a n-butyl alcohol solution containing a certain small amount of ammonia and water.

Experiments not shown in the table indicate that low levels of water concentration could be tolerated in the solvent without adverse effects. However, in solvent combinations comprising 4 parts of butanol, 1 part methanol, and 8.7 mols of ammonia per mol of acid, when the amount of water rises above a critical concentration of about 3 to 4 percent, the napthenic acid removal decreases rapidly. With a higher ratio of butanol to methanol, as in experiment 7, more water can be tolerated. This is because the water is akin to the methanol and, as long as sufficient butanol is present, the maximum limit of water concentration is subject to some variation. Thus, where the ratio of C_4–C_7 alcohol to methyl alcohol is 4:1 or less, the water concentration in the solvent composition should not be above about 3.5 volume percent. When the ratio of C_4–C_7 alcohol is greater than 4:1, the water or carrier concentration may be greater than 3.5 volume percent and as high as about 8.0 percent. Also, the amount of ammonia, which represents the basic neutralizing agent, needed for efficient acid removal is small. About 0.1 to 2.7 volume percent of anhydrous ammonia, such amount being sufficient to react with and neutralize substantially all of the naphthenic acids, is sufficient for the extraction of deasphalted, dewaxed residual lubricating oil stocks. Additional ammonia over 2.7 volume percent produces only a slight increase in the efficiency of the acid extraction. Although ammonia is the preferred neutralizing agent for the acidic constituents present in the oil, other basic compounds may be used, such as alkalies and amines.

Experiments 5 and 6 show that alcohols alone are inefficient in acid removal. Comparison of experiments 4 and 7 indicates that even with optimum concentrations of ammonia and water, the use of n-butyl alcohol or methyl alcohol alone as the principal solvent is inefficient in acid removal. The combination of n-butyl alcohol and methyl alcohol with optimum concentrations of water and ammonia forms a superior solvent as shown by a comparison of experiments 8, 9, and 10 with experiments 11 through 15. This is best pointed out by reference to the increase in distribution coefficient obtained in experiments 11, 12, and 13. In all instances, the preferred solvents tested showed low oil loss, less than 5 percent, and phase separation was excellent.

Comparison of experiments 16 through 19 with the balance of the experiments in the table shows that n-amyl alcohol and n-butyl alcohol are superior to the isopropyl alcohol and tertiary butyl alcohol and that a higher molecular weight alcohol, such as n-octyl alcohol, is not efficient as an ingredient in the composition. From the experiments it can be seen that the extraction efficiency of n-heptyl alcohol will fall somewhere between n-hexyl alcohol and n-octyl alcohol.

In preparing compositions in accordance with this invention, it is only necessary to mix the ingredients in ratios such that the principal organic solvent comprises the mixture of methyl alcohol and the monohydric alcohol containing 4 to 7 carbon atoms per molecule along with the minor proportions of basic agent. Where ammonia is the basic agent, it is convenient to use concentrated ammonium hydroxide to incorporate the necessary amount of base in the composition since by such use the amount of water added is not excessive. The ratio concentrations of methyl alcohol to the defined group of monohydric alcohols of C_4 to C_7 carbon atoms may be within the range of 1:20 to 3:1 in the solvent combinations

of this invention. It is preferred, however, that the C_4 to C_7 alcohol be present in the greater concentration, which may be in the order of 8:1 or 4:1 and down to a lower limit of about 3:2. The preferred compositions are represented by the mixtures expressed in experiments 12, 16, 20, and 21. It is also contemplated that mixtures of various proportions of straight chain monohydric primary alcohols having 4 to 7 carbon atoms per molecule and branched chain monohydric primary alcohols having 5 to 7 carbon atoms per molecule may be used in combination with the methanol as the principal organic constituent of the solvent. Thus, the composition set forth in experiment 12 may comprise 79.7 percent of a 1:1 mixture of n-butyl alcohol and n-amyl alcohol. Other ratios of the C_4, C_5, C_6, and C_7 alcohols may be used.

In carrying out the method of the invention, any of the known processes of solvent treating or liquid-liquid contact may be used. Batch or countercurrent extractions and continuous extraction methods are contemplated as being within the scope of the invention. The physical conditions prevailing during the extraction are subject to some variation. Atmospheric or superatmospheric pressures may be applied and ambient temperature or elevated temperatures may be used. A preferred temperature for the extraction is about 70° F. under atmospheric pressure. All that is necessary is to contact the hydrocarbon oil to be treated with the solvent composition, allow sufficient time for intimate contact, and separate the phases. The extraction methods set forth in United States Patents 1,681,657, 2,184,928, 2,186,249, or 2,396,302 may be applied.

Hydrocarbon mixtures containing high molecular weight napthenic acids and associated acidic materials to be extracted in accordance with this invention would ordinarily have been distilled, solvent extracted for the purpose of improving the V. I., deasphalted, dewaxed, or otherwise refined. Heavy oil distillates, solvent extracts, or residues, as a preferred embodiment, may be subjected to deasphalting with a hydrocarbon solvent like propane, using a propane-to-oil ratio of 8:1 or 10:1 prior to treatment in accordance with the invention. The hydrocarbon mixture is mixed with the propane and allowed to settle at a temperature of about 120° to 130° F. The choice of treating temperature and propane-to-oil ratio depends on the degree of asphalt separation desired. The use of countercurrent contact, wherein the precipitated material from a previous treatment is washed with fresh propane, greatly increases the yield of oil. The precipitated asphalt is usually sufficiently fluid to be easily removed from the settling tank by pumping. After the asphalt is separated, the oil may be chilled to separate the wax.

A separate dewaxing step may be applied to the oil, using the centrifuging process wherein the oil is diluted with solvent, chilled to a predetermined temperature, usually about 30° to 50° F. below the desired pour point of the finished oil, and centrifuged. The solvent portion separated may be recycled. Usually about 60 to 70 percent of solvent in the final mixture is used depending on the viscosity of the oil being treated. This quantity varies with the chilling temperature, more solvent being needed for lower treating temperatures than for the higher treating temperatures because of the increased viscosity of the oil at lower temperatures. Care is exercised in controlling the rate of chilling to insure proper crystallization of the wax so that it will easily separate, especially when chilling temperatures of 0° F. are used. Various filter aids like infusorial earth, naphthalene, or anthracene may be used. Ordinarily, chlorinated solvents of high specific gravity greatly aid the separation by centrifuging. Depending on their source, heavy lubricating oil distillates are about ready for use in preparing lubricating oil compositions after thorough deasphalting, dewaxing, and clay treatment operations provided they meet neutralization number qualifications. At

this point in the refining, the process of the present invention may be applied.

With residual lubricating oil stocks, an additional step of solvent refining to remove undesirable aromatic constituents of poor viscosity characteristics may be applied. To accomplish these ends, the residual stock which may be previously deasphalted is subjected to any one of several known methods of solvent refining. The Edeleanu process using sulfur dioxide as described in Patent 911,553, with modern adaptations may be applied for this purpose. Furfuryl alcohols may be used in accordance with Patent 1,883,374 or anhydrous phenol as described in Patent 1,860,823. Other processes that may be applied are the Duosol process, the furfural process, Chlorex process employing β,β'-dichloroethyl ether, the phenol extraction process, and other solvent extraction processes which are employed to increase the viscosity index of the desired raffinate product.

As a typical example of the preparation of neutral and bright lubricating oil stocks which may be treated in accordance with this invention, a desalted crude oil is first charged to a distillation unit where straight run gasoline, two grades of naphtha, kerosene, and virgin distillate are taken off, leaving a reduced crude residue. The reduced crude is continuously charged to a vacuum distillation unit where three lubricating oil distillates are taken off as side streams, a light distillate is taken off as overhead, and a residuum is withdrawn from the bottom of the tower. This residuum may have a viscosity ranging from 100 to 1800 SUS at 210° F. This residuum is charged to a propane deasphalting unit wherein propane dissolves the desirable lubricating oil constituents and leaves the asphaltic materials as insolubles. A typical vacuum residuum charge to a propane deasphalting unit may have an API gravity of 12.9°, viscosity SUS at 210° F. of 1249, flash 585° F., fire 650° F., C. R. of 13.9 weight percent, and is black in color. The deasphalted oil may have an API gravity of 21.5° to 21.8°, viscosity SUS at 210° F. of 165–175, NPA color 6–7, flash 575° F., fire 640° F., and C. R. of 1.7–2.0. The deasphalted oil and various lubricating oil distillates from the reduced crude are separately subjected to solvent extraction for the purpose of improving the viscosity characteristics of the raffinate.

For example, an east central Texas crude oil with an API gravity of 33.1 was topped to remove such light fractions as gasoline, naphtha, kerosene, and a light lubricating distillate. The vacuum residue from this operation was a reduced crude having a viscosity of 1251 SUS at 210° F., 2.2 percent of sulfur, and an API gravity of 12.6. After propane deasphalting using a propane to oil ratio of 8:1, the bright stock oil had a viscosity of 174 SUS at 210° F. and an API gravity of 21.7. The propane to oil ratio for this step may be 10:1.

This deasphalted oil was treated with phenol, using a solvent to oil ratio of about 1:1, to produce a raffinate from which good grades of aviation lubricating oil may be produced. The extract phase, after steam distilling to remove the phenol, is available also for blending to use its solubilizing properties. Valuable naphthenic acids may be recovered from these solvent extracts by subjecting them to solvent extraction in accordance with this invention. A solvent dewaxing operation may be employed as a step in the process using MEK and toluene to remove the waxy hydrocarbons. Final finishing of the oils is accomplished by either clay contacting or percolation. The dewaxed bright stock may be treated to solvent extraction in accordance with this invention to remove acidic constituents either before or after the clay treating step. Further details of the type of procedures intended may be found in the prior art, as, for example, the article entitled "Modern manufacture of lubricating oils," by E. R. Smoley and D. Fulton, pages 594–608, Petroleum Processing, August 1947.

The dewaxed bright stock used in the experiments was obtained by subjecting a vacuum residuum to propane deasphalting, solvent refining with phenol, and solvent dewaxing in the manner just described. Typical physical properties for this bright stock are

Gravity ° API	24.
Flash	570° F.
Viscosity	3090 at 100° F., 164 at 210° F.
Pour	0° F.
Color, NPA	+8.
Neutralization number (ASTM D974–52T)	0.39.
Carbon residue	1.26.
Navy demulsibility	30+ at 130° F.
Steam emulsion number	842.
Total sulfur	0.80.
Viscosity index	90.9.

In general, the residual stocks to be treated in accordance with this invention may have a viscosity at 210° F. of about 80 to 300 SUS or higher.

Because the solvent combination described is quite volatile, the pure naphthenic acids can be separated from the extract phase by subjection to steam stripping or heating, as in a steam bath while blowing the extract with nitrogen or other inert gas. Since the extract phase containing the naphthenic acids has a strong foaming tendency when placed under vacuum it is not advisable to attempt to increase the rate of evaporation by use of reduced pressure. The solvent constituents can be condensed and recovered from the heating and agitation step for reuse in treating additional hydrocarbon mixtures.

Another specific application of the invention comprises the treatment of lubricating oil fractions, particularly bright stocks and residual lubricating oil stocks including solvent extracts, for the purpose of effecting reduction in the acid numbers thereof as determined by the method of ASTM D974–52T. In bright stock manufacture it is desirable that the acid number be from about 0.10 as a maximum to 0.03 or lower. At least the acid content should be reduced to the point where only very small amounts of naphthenic acids are present. For neutral lubricating oils the acid number of less than 0.05 is easily attained. Treatment of solvent extracts has for its main purpose the recovery of the high molecular weight naphthenic acids therefrom. The preferred solvent compositions represented by experiments 11, 12, 13, 16, 20, and 21 may be employed to prepare lubricating oil fractions having low acid numbers.

Although the invention has been described by reference to several specific embodiments, the only limitations attaching thereto appear in the appended claims.

What is claimed is:

1. The method of extracting acidic materials of high molecular weight from hydrocarbon mixtures comprising contacting said hydrocarbon mixtures with a solvent comprising methyl alcohol, at least one alcohol selected from the group consisting of straight chain monohydric primary alcohols having 4 to 7 carbon atoms per molecule and branched chain monohydric primary alcohols having 5 to 7 carbon atoms per molecule and mixtures thereof, and a sufficient amount of a basic agent to substantially neutralize the acid materials and recovering as the raffinate a hydrocarbon mixture substantially reduced in its content of acidic materials.

2. The method in accordance with claim 1 in which the alcohol used with methol alcohol in said solvent is a straight chain monohydric primary alcohol having 4 to 7 carbon atoms per molecule.

3. The method in accordance with claim 2 in which the alcohol used with methyl alcohol in said solvent is n-butyl alcohol.

4. The method in accordance with claim 2 in which

the alcohol used with methyl alcohol in said solvent is n-amyl alcohol.

5. The method in accordance with claim 2 in which the alcohol used with methyl alcohol in said solvent is n-hexyl alcohol.

6. The method in accordance with claim 2 in which the alcohol used with methyl alcohol in said solvent is n-heptyl alcohol.

7. The method in accordance with claim 1 in which the alcohol used with methyl alcohol in said solvent is a branched chain monohydric primary alcohol having 5 to 7 carbon atoms per molecule.

8. The method in accordance with claim 7 in which the alcohol used with methyl alcohol in said solvent is iso-amyl alcohol.

9. The method in accordance with claim 1 in which at least about 5 percent by volume of methyl alcohol is present in said solvent.

10. The method in accordance with claim 1 in which the basic agent is ammonia.

11. The method in accordance with claim 1 in which the hydrocarbon mixture being treated comprises a dewaxed and solvent refined hydrocarbon oil and the acidic materials comprise naphthenic acids boiling above about 800° F.

12. The method of treating a lubricating oil stock for the purpose of removing high molecular weight naphthenic acids therefrom to produce a raffinate having a low acid number comprising contacting said lubricating oil stock with a solvent having the following composition by volume percent:

0.11% ammonia
0.29 water
79.7 n-butyl alcohol
19.9 methyl alcohol

and separating the raffiate therefrom.

13. The method in accordance with claim 12 in which the lubricating oil stock comprises a residual stock having a viscosity at 210° F. of from about 80 to 300 SUS.

14. The method in accordance with claim 12 in which the lubricating oil stock comprises a dewaxed bright stock having an API gravity of about 24, a viscosity at 210° F. of about 164 SUS, and a neutralization number of about 0.39.

15. The method of treating a lubricating oil stock for the purpose of removing high molecular weight naphthenic acids therefrom to produce a raffinate having a low acid number comprising contacting said lubricating oil stock with a solvent having the following composition by volume percent:

0.11% ammonia
0.29 water
19.9 methyl alcohol
79.7 n-amyl alcohol

and separating the raffinate therefrom.

16. The method in accordance with claim 15 in which the lubricating oil stock comprises a residual stock having a viscosity at 210° F. of from about 80 to 300 SUS.

17. The method in accordance with claim 15 in which the lubricating oil stock comprises a dewaxed bright stock having an API gravity of about 24, a viscosity at 210° F. of about 164 SUS, and a neutralization number of about 0.39.

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