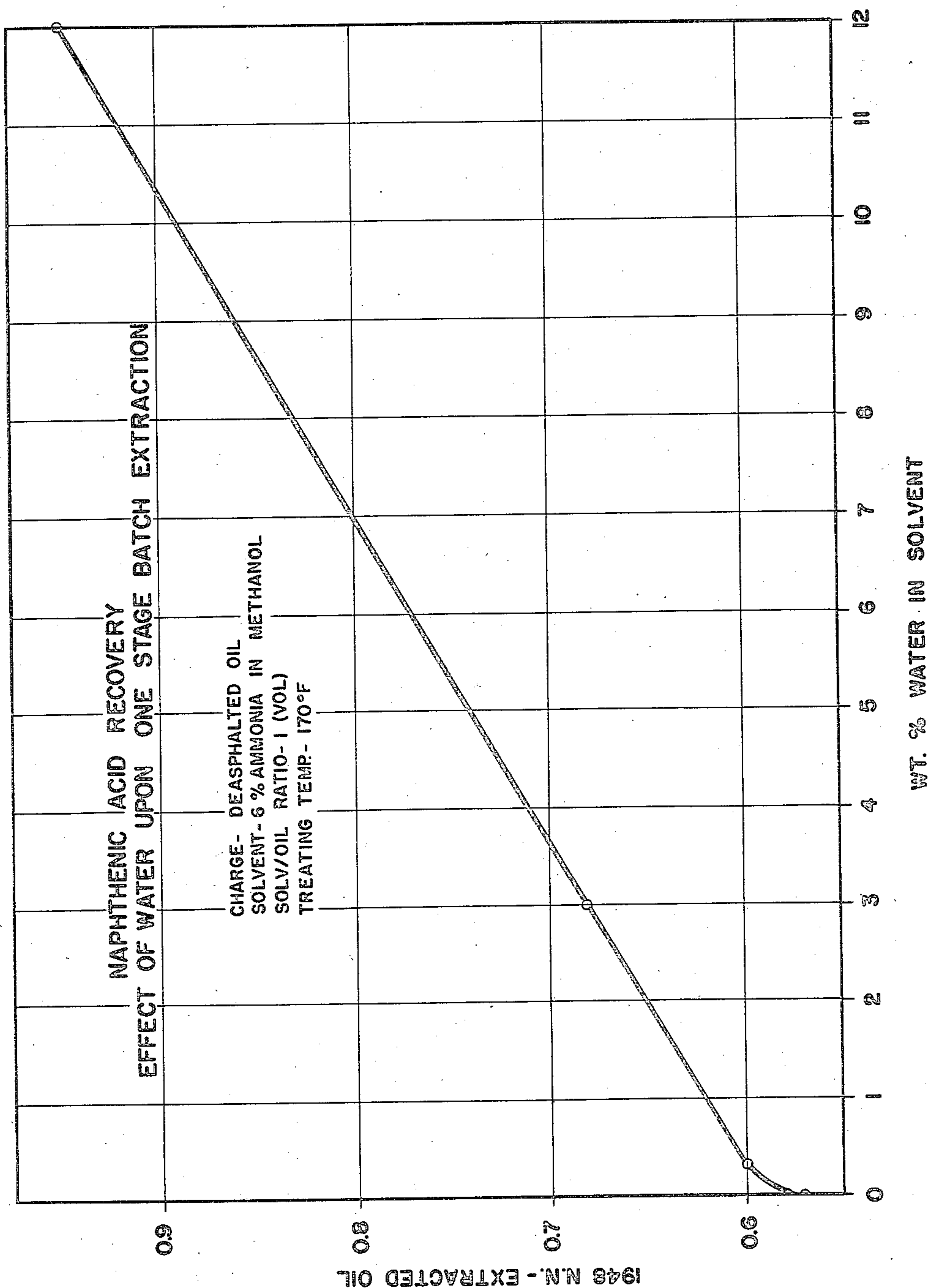


Sept. 2, 1958

W. L. FIERCE ET AL
METHOD OF REMOVING HIGH MOLECULAR WEIGHT
NAPHTHENIC ACIDS FROM HYDROCARBON OILS
Filed Feb. 6, 1956

2,850,435



INVENTORS
WILLIAM L. FIERCE
GEORGE M. LONGLAND, JR.
BY
Edward M. Long
ATTORNEY

2,850,435

METHOD OF REMOVING HIGH MOLECULAR WEIGHT NAPHTHENIC ACIDS FROM HYDROCARBON OILS

William L. Fierce, Crystal Lake, Ill., and George M. Longland, Jr., Harrisburg, Pa., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

Application February 6, 1956, Serial No. 563,470

16 Claims. (Cl. 196—41)

This invention relates to a method and a new solvent combination for the extraction of high molecular weight naphthenic acids from hydrocarbon mixtures and, particularly, from light to residual lubricating stocks or solvent extracts from the solvent extraction of lubricating oil. The acidic constituents extracted by means of this invention are broadly classifiable as naphthenic acids which, at least in part, are characterized as being high molecular weight carboxylic acids which are liquid or solids and being 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 generally boil above about 600° F. and because of their high molecular weight offer difficulty in their removal from lubricating oils for the purpose of producing finished lubricating oils of low acid number.

It has been found that, contrary to the teachings of the prior art, there is a distinction between the extraction efficiencies to be gained by the use of various solvent compositions to extract naphthenic acids from lubricating oil fractions. In accordance with this invention, it has been found that although ammonia alone or methyl alcohol alone or their combination with water is not a satisfactory solvent for naphthenic acids in lubricating oils, a mixture consisting of methyl alcohol and from about 5.0 to 7.0 wt. percent of ammonia in anhydrous condition, or containing no more than about 0.4 wt. percent of water, is an efficient medium for this purpose. This discovery is based on experience with a vast number of solvent combinations used to treat various lubricating oils containing naphthenic acids of different molecular sizes and under varying conditions of extraction. In addition, it has been found that the application of certain extraction conditions of temperature and pressure using anhydrous methyl alcohol and ammonia greatly increases the degree of removal of all acidic compounds present and classifiable as naphthenic acids whether the oil being treated contains a predominance of those naphthenic acids which are difficult to extract or not. The concentration of ammonia between the range of 5.0 to 7.0 wt. percent is calculated to include sufficient ammonia to at least neutralize the naphthenic acids present in the oils being treated and provide for at least some excess over stoichiometric requirements for this purpose.

The invention, therefore, has as its primary purpose that of providing a method and solvent composition for extracting naphthenic acids from hydrocarbon mixtures, particularly lubricating oil fractions and residuums.

Another purpose of the invention is to provide a solvent composition containing methyl alcohol and between about 5 to 7 wt. percent of ammonia with no more than about 0.4 wt. percent of water and preferably a solvent composition which is substantially anhydrous. 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 illustrations given are not to be construed as limita-

tions and the invention will broadly find application in related arts where the removal of naphthenic acids or similar materials from oleaginous materials, such as lubricating oils, is the main consideration.

These and other objects will become apparent as the description thereof proceeds.

The drawing is a graph showing the effect of water on the extraction efficiency of a solvent comprising 6% ammonia in methanol used to treat a deasphalted oil.

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 influences 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 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 the same distillate with 1.0 N ammonium hydroxide will remove about 89 percent of the acids. The heavier lubricating oil distillate 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 to 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 acid therein and, accordingly, it is desirable 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

was conducted which points to the fact that anhydrous ammonia-methanol solvent compositions are superior to the use of either component alone, whether or not water is present, and also superior to the expected solvent action from a combination of the two components with very small amounts of water. Most of the extractions in this series were carried out in glass separatory funnels at room temperature. The two phases were mixed thoroughly and then allowed to separate completely. The lower, solvent-rich phase was carefully withdrawn and the volumes of the two phases were noted. The naphthenic acid content of each phase was determined by the ASTM D974-52T method. The solvent was stripped from both phases to yield the extracted oil and the recovered, semi-pure naphthenic acids. In experiment 2 the solvent was anhydrous ammonia. This extraction was made in a closed Jerguson gauge at room temperature at a slightly elevated pressure.

Table I

NAPHTHENIC ACID SOLVENT EXTRACTION DATA

$$\left[\frac{\text{Solvent volume}}{\text{oil volume}} = 1, \text{ temperature} = 75^\circ \text{ F} \right]$$

Oil treated	Solvent composition (volume percent)					K ¹	Oil recovery (vol. percent)
	Ammonia	Water	Methanol	2-propanol	Butanol		
(1) Phenol extract from 85 distillate			100			0.61	94.8
(2) Phenol extract from 85 distillate	100					0.16	² 99.0
(3) Phenol extract from 85 distillate	0.25	0.75	99			5.46	93.2
(4) Phenol extract from 170 distillate	0.5	1.5	98			2.16	95.7
(5) Phenol extract from 170 distillate	1.5	4.5	94			1.07	96.2
(6) Phenol extract from 170 distillate	0.5	1.5	49	49		4.00	91.2
(7) Phenol extract from 170 distillate	0.5	1.5		98		1.59	76.0
(8) 170 distillate			100			0.48	98.9
(9) 170 distillate	0.6	2.4	97			14.1	96.6
(10) 170 distillate	0.6	2.4		97		3.09	85.7
(11) 170 distillate	0.8	18.6		80.6		10.6	97.0
(12) 170 distillate	4.0		96.0			41.0	96.5
(13) 170 distillate	0.2	0.6	99.2			9.9	96.4
(14) 170 distillate	0.4	1.2	98.4			13.1	96.2
(15) 170 distillate	0.6	1.8	97.6			13.9	96.8
(16) DAO ³	0.8	2.4	96.8			2.91	98.2
(17) DAO ³	0.8	2.4		96.8		2.10	94.4
(18) DAO ³	0.8	2.4		96.8		1.91	96.6
(19) DAO ³	0.8	2.4			96.8	2.71	86.3
(20) 80 distillate	4.0		96.0			60.0	97.0

¹ $K = \frac{\text{Concentration of acids in extract}}{\text{Concentration of acids in raffinate}}$

² Estimated.

³ Deasphalted oil was diluted with approximately 25% hexane by volume.

refining practice. Furthermore, it is desirable that the extraction 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.

In order to demonstrate the present discovery of a solvent composition which strikes a balance between selectivity and miscibility whereby both low and high molecular weight naphthenic acids, the latter being ordinarily difficult to remove from lubricating oils, are effectively removed, a series of batch, equilibrium, continuous and pilot plant experiments are described.

NAPHTHENIC ACID RECOVERY—ONE STAGE TREATMENT

In order to demonstrate the effectiveness of this solvent, a series of one-stage, low temperature extractions

In general, the solvent extract from an 85 viscosity distillate or a 170 viscosity distillate is more difficult to treat than the distillate itself since the extracts contain a much higher naphthenic acid content than the original distillates. Even so, an examination of experiments 1 and 8 using 100% methanol shows that this solvent is unsatisfactory. Ammonia alone (experiment 2) gives even more unsatisfactory results in comparison with methanol (experiment 1) on the same type of oil. Experiment 3 shows that 0.25% ammonia, 0.75% water and 99% methanol gives an increased K value, or extraction efficiency, but the oil recovery is lowered and consequently the purity of the acids extracted is diminished. Comparison of experiments 4, 6 and 7 shows that replacement of part of the methanol in the solvent with 2-propanol increased the extraction efficiency but again lowered the purity of the acids, whereupon replacement of all of the methanol with 2-propanol (experiment 7) reduced both the extraction efficiency and acid purity.

Considering next the experiments 8 through 15 on the treatment of 170 vis distillate lubricating oil fractions, it is seen that the highest extraction efficiency without appreciable sacrifice of naphthenic acid purity or oil loss

was obtained in experiment 12 using 4.0% ammonia with 96.0% methanol. In experiment 10 the change from methanol to 2-propanol greatly reduced the extraction efficiency and lowered the naphthenic acid purity from that obtained in experiment 9, using the same amounts of water and ammonia in each case. Increasing the ammonia and water content of the 2-propanol solvent in experiment 11 did not recover the lost efficiency but did increase the product purity. According to experiments 13, 14, and 15, increase in water content with increase in ammonia content, using methanol, had very little effect on the naphthenic acid purity and seemed to favorably influence the extraction efficiency; but, leaving the water out entirely (experiment 12) gave a tremendous increase in extraction efficiency with little or no loss in naphthenic acid purity.

The naphthenic acids present in lubricating oil fractions of Mid-Continent origin will vary in molecular weight from about 350 to 550. The ease of extraction decreases with increase in molecular weight of the acids, depending on the concentration of the naphthenic acids in the oil being treated. This is demonstrated in part by comparison of experiment 20 with experiment 12 (Table I). The 80 vis. distillate contains naphthenic acids varying in molecular weight from 352 to 363. The 170 vis. distillate contains naphthenic acids of molecular weight

equipped with supplementary heaters. All components charged to and taken from the bombs were carefully weighed both in the charge or product container used in the transfer and in the bombs. The volumes were also recorded to serve as another check on the weights. The oil-acid mixture was charged first, after which the bomb and solvent were chilled to prevent ammonia loss during solvent addition. After the charge had been added, the bomb was placed in the bath for an hour with vigorous shaking each five minutes, after which it was inverted and placed in the bath with the inlet valve and line submerged for a half hour settling period. Following this settling period, the lower oil phase was carefully withdrawn, first into a beaker, and later as the interface approached, into a graduated cylinder. The bomb was then returned to the bath for another half hour period to prevent contamination of the acid phase with oil clinging to the sides of the vessel. A small amount of acid phase was then withdrawn into the graduated cylinder and the remainder charged to a glass distillation flask. Weights and volumes were recorded for each phase after which the solvent was stripped from the samples in the beaker and distillation flask. Neutralization values, in accordance with ASTM Method D974-53T (1948 N. N.), were used as a measure of acid content of the charge and products. The results are shown in Table II.

Table II
SUMMARY OF DATA FROM EQUILIBRIUM EXPERIMENTS
NAPHTHENIC ACID EXTRACTION FROM DEASPHALTED OIL

Exp. No.	Charge oil ¹		Solvent					Treating temp. (° F.)	Oil phase			Acid phase	
	1948 N. N.	Weight (gm.)	Weight percent ammonia	Weight percent methanol	Weight percent water	Weight percent 1-butanol	Total weight (grams)		Weight percent sol.	1948 N. N. rec. oil	Weight percent sol.	1948 N. N. rec. acid	Weight (gm.) acid
21.....	1.51	237.0	5.9	94.1	-----	-----	108.1	170	5.4	0.76	94.9	34.2	4.7
22.....	1.51	122.0	5.9	94.1	-----	-----	212.1	170	3.0	0.46	97.8	26.9	4.4
23.....	1.51	184.2	5.9	94.1	-----	-----	166.6	170	4.3	0.58	97.0	37.3	3.5
24.....	1.48	184.0	9.8	91.2	-----	-----	157.2	170	3.6	0.65	96.9	36.0	4.4
25.....	1.52	187.7	2.1	97.9	-----	-----	160.0	170	2.3	0.66	97.1	35.8	4.5
26.....	1.52	188.6	8.0	92.0	-----	-----	163.4	195	6.0	0.67	97.3	38.4	4.0
27.....	1.51	184.8	5.8	94.2	-----	-----	158.4	140	4.6	0.64	95.5	24.0	6.8
28.....	1.5	184.5	9.8	70.2	-----	-----	154.8	140	2.9	0.81	96.7	27.0	4.7
29.....	0.20	181.9	5.9	94.1	-----	-----	166.1	170	2.4	0.18	96.5	0.83	5.6
30.....	0.30	116.7	6.2	93.8	-----	-----	119.2	170	6.5	0.20	97.3	2.95	2.7
31.....	0.20	184.4	9.8	91.2	-----	-----	167.0	170	2.6	0.18	98.5	8.01	2.3
32.....	0.20	182.6	2.1	97.9	-----	-----	158.8	170	2.5	0.18	97.4	2.69	4.0
33.....	0.20	183.5	8.0	92.0	-----	-----	162.0	195	0.9	0.18	98.3	4.66	2.5
34.....	0.19	190.2	6.1	93.9	-----	-----	160.0	140	4.0	0.19	96.8	2.23	4.9
35.....	0.19	183.1	9.8	90.2	-----	-----	156.2	140	7.0	0.19	97.3	2.6	3.5
36.....	1.51	187.3	5.9	91.1	3.0	-----	162.4	170	3.6	0.68	97.5	40.6	3.9
37.....	1.51	181.0	5.9	82.1	12.0	-----	167.0	170	3.3	0.95	97.8	27.7	3.8
38.....	1.52	284.9	5.7	94.0	0.3	-----	158.1	170	2.8	0.60	97.8	46.1	3.2
39.....	0.20	184.9	4.8	75.6	-----	19.6	165.4	170	3.6	0.18	98.3	3.90	2.5
40.....	1.52	185.2	5.8	18.8	-----	75.4	161.2	170	15.8	0.64	82.5	6.49	25.0
41.....	35.8	194.6	6.0	94.0	-----	-----	162.2	170	7.67	13.3	69.12	78.2	63.8
42.....	55.4	188.3	5.9	94.1	-----	-----	157.7	170	14.7	24.6	48.3	61.3	144.4

¹ Charge oils with 1948 neut. nos. of about 1.5 were ordinary DAO. Other charge oils were prepared by addition or substitution of pilot plant naphthenic acids or extracted oils.

around 427. Substantially complete removal of naphthenic acids of low molecular weight is effected in one stage treatment of the 80 vis distillate as compared with the 170 vis. distillate. Experiments 16 through 19 represent the results obtained in treating a deasphalted oil (diluted with 25 vol. percent of hexane to reduce the viscosity). K values of about 2.0 to 3.0 are considered excellent for this type of oil, but the phase separation was slow and the neutralization value of the finished oil did not meet standard requirements. This was attributed to the presence of the 2.4% of water in the solvent composition as will be demonstrated.

NAPHTHENIC ACID RECOVERY—EQUILIBRIUM DATA

In this series of experiments, stainless steel bombs, approximately 2 inches in diameter and 1 ft. in length, and having a capacity of 500 ml., were used. The bombs were immersed in a 10-gallon Reid vapor pressure bath

In experiments 23, 22 and 21 at 170° F. the effect of varying the solvent/oil ratio was studied. It can be seen that the neutralization number reduction of the oil was directly proportional to the ratio, while the purity and yield of the recovered acids were roughly inversely proportional to the ratio. Experiments 23, 24 and 25 indicate the effect of varying the ammonia concentration in the solvent. The neutralization number reduction of the oil was better with 5.9 wt. percent ammonia than with either 9.8 or 2.1 wt. percent. Yet it should be noted that the extraction was quite efficient at all three ammonia levels. Experiments 26, 27 and 28 show the effects of carrying out the extractions at temperatures other than 170° F. The results at 140 and 195° F. were inferior to those obtained at 170° F. A comparison of experiments 27 and 28 indicates that better results are obtained with 5.8% ammonia in the solvent than with 9.8%. This tends to bear out the results obtained at 170° F. in experiments 23 and 24.

In experiments 29, 30, 31, 32, 33, 34 and 35 the charge oil was a previously extracted deasphalted oil. The results indicate that it is quite difficult to reduce the neutralization number of the oil below about 0.18 in any stage extraction regardless of the conditions used. The effect of water upon the extraction of naphthenic acids is clearly brought out by experiments 36, 37 and 38, of Table II. These data are presented graphically in Figure I. Small amounts of water up to about 0.4 wt. percent can be tolerated. However, the extraction efficiency quickly drops off as the water content of the solvent is increased. Experiments 39 and 40 indicate that some 1-butanol can be tolerated in the solvent. However, as the amount increases the selectivity of the solvent decreases with a lessening in neutralization number reduction and a decrease in the purity of the recovered naphthenic acids. Experiments 41 and 42 indicate that effective extractions of deasphalted oil can be made even when excessive amounts of acids are present.

The equilibrium experiments were designed to study the effects of the following variables: temperature, ammonia, concentration, solvent/oil ratio, water concentration, and the use of alcohols other than methanol. It was found that the most efficient solvent is one composed of 6% by wt. of ammonia in methanol. Any increase or decrease in the ammonia percentage or addition of water or butanol to the solvent caused a marked decrease in extraction efficiency. Using a weight relationship of about 42.1 gms. of deasphalted oil to 38.1 gms. of solvent, containing 6.2% by wt. of ammonia and 93.8% by wt. of methanol, at 170° F. produced the greatest reduction in naphthenic acid content for deasphalted oil containing those acids most difficult to extract. Obviously, the acid purity can be increased by re-extraction, using a continuous tower operation. Acid purities of 80% or higher are predictable.

Specific information as to the effect of various variables upon the extraction of deasphalted oil is contained in Table II.

In order to demonstrate the superiority of the anhydrous ammonia-methanol solvent in treating all types of distillates, a series of equilibrium experiments were conducted like those shown in Table II using various distillate oils either in their pristine condition or with added quantities of naphthenic acids obtained from pilot plant extractions of other distillates. These experiments were all conducted using a solvent comprising 6.1% by wt. of ammonia and 93.9% by wt. of methanol. The results which are shown in Table III indicate that this solvent is highly effective for the extraction of naphthenic acids from the distillate oils.

Table III

SUMMARY OF DATA FROM EQUILIBRIUM EXPERIMENTS
NAPHTHENIC ACID EXTRACTION FROM LUBE DISTILLATES

Exp. No.	Charge oil			Solvent, total weight (grams)	Treating temp. (° F.)	Oil phase		Acid phase		
	Stock	1948 N. N.	Weight (gm.)			Weight percent solvent	1948 N. N. recovered oil	Weight percent solvent	1948 N. N. rec. acid	Weight (gm.) acid
43	80 vis. dist.	2.58	192.4	79.6	140	1.7	0.22	88.6	50.3	9.1
44	80 vis. dist.	31.9	196.8	77.6	140	3.8	5.95	53.3	94.8	58.0
45	80 vis. dist.	17.4	188.5	78.9	140	2.5	2.10	71.6	104.0	27.6
46	170 vis. dist.	2.91	193.8	80.4	150	1.9	0.44	89.2	55.9	8.7
47	170 vis. dist.	40.0	194.9	79.9	150	5.5	10.4	43.0	72.6	89.1
48	170 vis. dist.	18.4	191.6	78.9	150	3.0	3.32	68.4	94.7	31.8
49	350 vis. dist.	2.91	191.3	80.4	160	4.1	1.02	88.6	47.0	8.2
50	350 vis. dist.	36.6	194.5	79.7	160	9.0	16.9	45.9	63.7	68.7
51	350 vis. dist.	16.6	191.8	80.0	160	3.9	6.02	71.6	81.2	26.4

The properties of the naphthenic acids in a semi-pure state obtained from these various distillates, and from 150 vis. bright stock for comparison, are given in Table IV. The values for Neutralization Number and molecular weight were obtained from the pure acids.

Table IV

PROPERTIES OF NAPHTHENIC ACIDS (SEMI-PURE)

Source	80 dist.	170 dist.	350 dist.	150 br. st.
API gravity	11.9	13.1	12.6	13.0
Vis. at 210° F. (sec.)	103.5	148.2	289.1	479.2
Neut. No. (1948)	119.6	110.2	102.5	65.3
Percent unsaponifiable	22.7	16.1	16.9	36.8
Percent naphthenic acids	77.3	83.9	83.1	63.2
Neut. No. of pure acids	155	131	123	103
Mol. weight of pure acids	363	427	455	543

ASTM DISTILLATION

Source	Initial	5%	10%	40%	50%	90%	EP
80 dist.	658	682	695	-----	709	727	755
170 dist.	690	720	730	-----	795	835	860
350 dist.	705	760	800	-----	885	925	945
150 br. stk.	870	920	950	1,085	-----	-----	-----

It is preferable to carry out the extractions at temperatures sufficiently elevated to preclude any necessity for diluents, but if low treating temperatures (80–110° F.) are used, dilution of the oil to be treated with hexane or carbon tetrachloride to reduce its viscosity gives improved results. The lubricating oil fractions used in the experiments were of Mid-Continent origin. The term 80 Dist. means that the distillate oil has a viscosity of 80 SUS at 100° F. The same connotation applies to the terms 170 Dist. and 350 Dist. The viscosity of the bright stock is measured at 210° F., i. e., 150 SUS bright stock at 210° F. This bright stock was derived from the deasphalted oil used in the previous experiments by dewaxing, which step is unnecessary before the naphthenic acids can be fractionated therefrom.

The process and solvent composition of this invention is particularly applicable to continuous extraction techniques whereby the oil to be treated is passed into the top of an extraction tower wherein it meets the stream of upwardly flowing solvent. The extract solution is taken off at the top of the tower and the raffinate solution is drawn off from the bottom thereof. To demonstrate this aspect of the invention, a series of experiments was conducted in a pilot plant designed to carry out continuous counter-current solvent extraction. Since the details of such processes are well known in the art, only a general description of the apparatus is necessary to describe the experiments, the results of which are shown in Table V.

In carrying out these continuous counter-current extraction experiments, a treating tower consisting of twenty-

three feet of three-inch, stainless steel pipe packed with one-half-inch Berl saddles was used. The tower had enlarged settling sections at the top and bottom. The tower was equipped with an extract solution overflow line connected to the top, a charge oil line entering just below

the top settling section, a methanol-ammonia solvent line entering about three feet from the bottom and a raffinate line leading from the bottom to a pump. A sight glass was installed near the top of the lower settling zone for observation and control of the oil-solvent interface. Hot water circulation through four jackets surrounding the tower was used to control the temperature. The tower pressure was maintained by a Grove regulator installed in the extract overflow line. A nitrogen system was ar-

recovered methanol was returned through a cooler to methanol storage. Extracted acids from the solvent in the methanol recovery tower were drained directly from the drier reboiler. Sampling lines were provided for the raffinate and extract phases and the recirculating methanol stream before and after ammonia addition. A record was kept of the oil feed rate, the solvent feed rate, the temperature and pressure, and an exact analysis of the products made as seen in Table V.

NAPHTHENIC ACID EXTRACTION—PILOT PLANT

Run No.	Charge oil		Treating conditions						Products		
	Stock	Acid No.	Oil rate, cc./min.	Solvent rate, cc./min.	Solvent/oil ratio	Mols NH ₃ per mol acid	Temp., ° F.	Pressure, p.s.i.g.	Yield of oil	Acid No. oil	Acid No. naph. acids
52	80 dist.	2.7	150	30	0.2	10	140	20	96.1	0.03	64
53	80 dist.	2.7	150	15	0.1	10	140	20	97.0	0.06	72
54	80 dist.	2.7	150	7.5	0.05	10	140	30	96.7	0.30	78
55	80 dist.	2.7	200	7.5	0.038	10	140	30	96.3	0.45	78
56	80 dist.	2.7	200	100	0.50	25	140	15	96.0	0.03	115
57	170 dist.	3.0	150	15	0.1	9	140	30	96.0	0.55	80
58	170 dist.	3.0	150	30	0.2	9	140	30	96.5	0.40	76
59	170 dist.	2.9	150	38	0.25	15	150	40	97.5	0.14	110
60	170 dist.	2.9	150	100	0.67	35	150	40	100.3	0.03	107
61	350 dist.	2.9	100	50	0.50	30	145	40	97.0	0.52	96
62	350 dist.	2.9	100	100	1.0	50	150	15	99.5	0.06	102
63	350 dist.	2.9	100	50	0.50	30	160	40	98.9	0.34	-----
64	350 dist.	2.9	100	100	1.0	100	160	40	96.5	0.28	-----
65	350 dist.	2.9	75	150	2.0	180	160	40	96.8	0.05	-----
66	350 dist.	2.9	125	125	1.0	80	160	40	-----	0.03	-----
67	350 dist.	2.9	125	125	1.0	50	160	40	-----	0.03	76
68	350 dist.	2.9	100	50	0.50	30	175	40	97.0	0.41	-----
69	350 dist.	2.9	100	100	1.0	65	175	40	96.8	0.11	-----
70	DAO	1.6	100	25	0.25	20	170	25	97.8	0.57	-----
71	DAO	1.6	100	50	0.5	10	150	25	97.9	0.70	-----
72	DAO	1.6	100	50	0.5	10	170	25	97.2	0.60	77
73	DAO	1.6	100	50	0.5	30	170	25	97.3	0.48	74
74	DAO	1.6	100	50	0.5	30	180	30	-----	0.40	74
75	DAO	1.6	100	50	0.5	10	180	30	-----	0.60	74
76	DAO	1.6	100	50	0.5	10	180	25	99.7	0.63	77
77	DAO	1.6	100	50	0.5	14	195	40	-----	0.75	71
78	DAO	1.6	100	50	0.5	23	195	40	-----	0.52	71
79	DAO	1.6	100	100	1.0	30	170	25	97.8	0.38	-----
80	DAO	1.6	100	100	1.0	80	170	25	98.8	-----	74
81	DAO	1.6	100	100	1.0	120	170	40	-----	0.39	70
82	DAO	1.6	50	50	1.0	160	170	40	-----	0.34	-----
83	DAO	1.6	50	100	2.0	320	140	40	-----	0.23	-----
84	DAO	1.6	75	150	2.0	240	170	40	97.3	0.20	-----
85	DAO	1.6	50	100	2.0	240	170	40	98.9	0.29	-----
86	DAO	1.6	50	100	2.0	240	170	40	96.6	0.17	-----
87	DAO	1.5	50	100	2.0	40	170	40	97.0	0.50	-----
88	DAO	1.5	50	100	2.0	100	170	40	98.3	0.23	-----
89	DAO	1.5	75	150	2.0	200	170	40	99.8	0.17-0.23	68

ranged to supply nitrogen to the overflow line, if needed, to maintain tower pressure during transition periods.

The oil to be treated was withdrawn from a charge tank and proceeded through a metering tank, a rotameter, an electrically heated line and a steam heater to the top of the tower. After passing through the tower, the oil or raffinate was withdrawn from the bottom, and pumped by a metering pump through a rotameter to a separate heater and stripper, consisting of a three-inch column containing fifteen inches of open flash-zone above a five foot section packed with $\frac{3}{8} \times \frac{3}{8}$ inch Raschig rings, wherein traces of methanol were removed. The stripper was fully jacketed for 125-pound steam and equipped with additional electrical heat to maintain a temperature of about 320° F. Nitrogen was used as the stripping medium. Methanol was pumped through a metering tank and the charge heater to the treating tower. The ammonia was passed from a cylinder, through a pressure regulator, rotameter and needle valve to enter the methanol line between the methanol rotameter and heater. After passing through the tower, the acid-containing solvent flowed overhead through a Grove regulator and a steam heater to an acid recovery tower which consisted of ten feet of four-inch stainless pipe, packed with $\frac{1}{2} \times \frac{1}{2}$ inch Raschig rings, and a reboiler. Heat was supplied to the recovery tower by steam in the feed heater and reboiler, and through one-half-inch tubing wound around the column. A temperature of about 270° F. was maintained in the reboiler and feed zone. Nitrogen was also used as the stripping medium in the methanol recovery tower. The

A portion of the treated deasphalted oil from experiment 74 was finished to a 0° F. pour, 90 VI bright stock by batch phenol extraction, dewaxing with methyl ethyl ketone, and clay contacting. A refined raffinate, 160 SUS at 210° F., 90 VI and having an acid number of 0.22, a dewaxed bright stock, 160 SUS at 210° F., 90 VI, and having an acid number of 0.28, and a finished bright stock, 160 SUS at 210° F., 90 VI, treated with 10#/bbl. of Filtrol X-466, and having an acid number of 0.16, were obtained. The phenol extract from this treatment had an acid number of 0.85.

As shown in Table V, solvent/oil ratios as low as from 0.1 to 0.2 can reduce the neutralization number of 80 distillate to well below 0.1. For the heavier oil stocks higher solvent/oil ratios are required for maximum acid removal. The ratios required range up to a value of about 2.0 for deasphalted oil. The amount of ammonia required for maximum acid removal depends upon the oil stock being extracted. Runs Nos. 52, 60, 67 and 86 show that the amount in terms of mols NH₃ per mol acid ranges from a low of 10 for 80 distillate to a high of 240 for deasphalted oil.

Several related advantages come from the application of the instant process to lubricate oils. It is possible to produce marketable naphthenic acids of relatively high purity in amounts equal to about 2% of the oil treated. There is a pronounced reduction in corrosion in the phenol extraction unit used in conjunction with the naphthenic acid extraction. A sizable reduction in clay treatment requirements for finishing the lubricating

stocks to the required neutralization number specifications is gained.

The experiments have shown that the process is particularly applicable to continuous counter-current extraction of naphthenic acids from lubricating oil fractions. In such counter-current extraction processes, when applied to distillate lubricating oils, the invention is practiced by treating the oil with a solvent comprising substantially anhydrous methanol and ammonia at a temperature of about 140 to 175° F. using from about 9 to 180 mols of ammonia per mol of naphthenic acid in the oil and a solvent-to-oil ratio of about 0.038 to 2.0 and continuously separating a raffinate oil having a reduced naphthenic acid content. In applying the technique of continuous counter-current solvent extraction to deasphalted oils from which bright stocks are obtained, the invention is practiced by treating the oil with a solvent comprising substantially anhydrous methanol and ammonia at a temperature of about 140° to 195° F. using about 10 to 320 mols of ammonia in the solvent per mol of naphthenic acid in the oil and a solvent-to-oil ratio of about 0.5 to 2.0.

What is claimed is:

1. The process for the extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined lubricating oils which comprises treating of said lubricating oils with a solvent consisting of anhydrous methanol containing between about 1 to 15% by weight of ammonia, based on the amount of methanol, at temperatures ranging from 80° to 200° F. under pressures of from about atmospheric to 150 pounds per square inch, and recovering as the oil phase a lubricating oil substantially devoid of naphthenic acids.
2. The process for the extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined lubricating oils which comprises treating said lubricating oils with a solvent consisting of methanol with about 5% to 7% by weight of ammonia and containing not more than about 0.40% by weight of water, said amounts of ammonia and water being based on the amount of methanol, said treatment taking place at temperatures ranging from about 140° to 195° F. and under pressures ranging from about 15 to 40 pounds per square inch, and recovering as the oil phase a lubricating oil substantially devoid of naphthenic acids.
3. In the process for the extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined lubricating oils to obtain products substantially devoid of naphthenic acids, the improvement comprising treating said lubricating oils to solvent extraction using low solvent to oil ratios in the order of about 0.2 to 2.0 at temperatures of from 140° to 195° F. under pressures of from 15 to 40 pounds per square inch, and employing as the solvent a composition consisting of methanol containing between about 5% to 7% of ammonia, based on the amount of said methanol.
4. In the process for the extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined lubricating oils, the improvement comprising treating said lubricating oils to solvent extraction using low solvent to oil ratios in the order of 0.2 to 2.0, temperatures of from 140° to 195° F. under pressures of from 15 to 40 pounds per square inch, and employing as the solvent a composition consisting of methanol containing between about 5% to 7% by weight of ammonia, no more than about 0.40% by weight of water, said amounts of ammonia and water being based on the amount of methanol.
5. The process for the continuous counter-current extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined distillate lubricating oils which comprises treating said oil with a solvent comprising substantially anhydrous methanol and ammonia at a temperature of about 140° to 175° F., the mols of ammonia in said solvent per mol of naphthenic

acid in said oil ranging from about 9 to 180 and the solvent-to-oil ratios being from about 0.04 to 2.0, and continuously separating a raffinate oil having a reduced content of naphthenic acids.

6. The process in accordance with claim 5 in which the oil being treated is a refined lubricating oil distillate having a viscosity of about 80 SUS at 100° F. and an acid number of about 2.7.

7. The process in accordance with claim 5 in which the oil being treated is a refined lubricating oil distillate having a viscosity of about 170 SUS at 100° F. and an acid number of about 3.0.

8. The process in accordance with claim 5 in which the oil being treated is a refined lubricating oil distillate having a viscosity of about 350 SUS at 100° F. and an acid number of about 2.9.

9. The process for the continuous counter-current extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined deasphalted lubricating oils which comprises treating said oil with a solvent comprising substantially anhydrous methanol and ammonia at a temperature of about 140° to 195° F., the mols of ammonia in said solvent per mol of naphthenic acid in said oil ranging from about 10 to 320 and the solvent-to-oil ratios being from about 0.5 to 2.0 and continuously separating a raffinate oil having a reduced content of naphthenic acids.

10. The process in accordance with claim 9 in which the oil being treated is a refined deasphalted oil having an acid number of about 1.6.

11. The process of removing high molecular weight naphthenic acids from refined lubricating oil distillates having viscosities at 100° F. of from about 80 SUS to 170 SUS which comprises treating said distillates with a solvent consisting of anhydrous methanol containing between about 5% to 7% by wt. of ammonia, at temperatures ranging from 140° to 150° F. using pressures of from 15 to 40 pounds per square inch and solvent-to-oil ratio of between about 0.2 to 0.5.

12. In a continuous process for solvent extracting high molecular weight naphthenic acids boiling above about 600° F. from refined lubricating oils which comprises continuously passing a lubricating oil stream into counter-current contact with a solvent stream to separate a solvent phase and an oil phase, the improvement comprising introducing as the solvent a mixture of anhydrous methanol and ammonia in proportions such that the total solvent-to-oil ratio does not exceed about 2.0 and the mols of ammonia per mol of naphthenic acid present in said oil is below 240, said contact taking place at about 140° F. to 190° F. and separating an oil phase having a substantially reduced acid number and a solvent phase of naphthenic acids.

13. In the process for the continuous counter-current extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined distillate lubricating oils having viscosities of about 80 SUS at 100° F. wherein the oil is contacted with a solvent and an extract phase and raffinate oil phase are continuously separated, the improvement comprising treating said oil with a solvent comprising a substantially anhydrous mixture of methanol and ammonia, using a solvent-to-oil ratio of about 0.20, at a temperature of about 140° F., and adjusting the amount of ammonia in said solvent so that about 10 mols of ammonia per mol of naphthenic acid in said oil are present and recovering as the raffinate an oil having an acid number of about 0.03.

14. In the process for the continuous counter-current extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined distillate lubricating oils having viscosities of about 170 SUS at 100° F. wherein the oil is contacted with a solvent and an extract phase and a raffinate oil phase are continuously separated, the improvement comprising treating said oil with a solvent comprising a substantially anhydrous mix-

13

ture of methanol and ammonia, using a solvent-to-oil ratio of about 0.7, at a temperature of about 150° F., and adjusting the amount of ammonia in said solvent so that about 35 mols of ammonia per mol of naphthenic acid in said oil are present and recovering as the raffinate an oil having an acid number of about 0.03.

15. In the process for the continuous counter-current extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined distillate lubricating oils having viscosities of about 350 SUS at 100° F. wherein the oil is contacted with a solvent and an extract phase and raffinate oil phase are continuously separated, the improvement comprising treating said oils with a solvent comprising a substantially anhydrous mixture of methanol and ammonia, using a solvent-to-oil ratio of about 1.0, at a temperature of about 160° F., and adjusting the amount of ammonia in said solvent so that about 50 to 80 mols of ammonia per mol of naphthenic acid are present in said oil and recovering as the raffinate an oil having an acid number of about 0.03.

16. In the process for the continuous counter-current extraction of high molecular weight naphthenic acids boiling above about 600° F. from refined deasphalted

14

lubricating oils having viscosities of about 150 SUS at 210° F. wherein the oil is contacted with a solvent and an extract phase and a raffinate phase are continuously separated, the improvement comprising treating said oils with a solvent comprising a substantially anhydrous mixture of methanol and ammonia, using a solvent-to-oil ratio of about 2.0, at a temperature of about 170° F., and adjusting the amount of ammonia in said solvent so that about 200 mols of ammonia per mol of naphthenic acid in said oil are present and recovering as the raffinate an oil having an acid number of about 0.17 to 0.23.

References Cited in the file of this patent

UNITED STATES PATENTS

1,163,025	Mann et al. _____	Dec. 7, 1915
2,424,158	Fuqua et al. _____	July 15, 1947
2,616,830	Pratt _____	Nov. 4, 1952
2,769,768	Fierce et al. _____	Nov. 6, 1956

FOREIGN PATENTS

116,418	Great Britain _____	June 13, 1918
245,633	Great Britain _____	Jan. 14, 1926