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2,963,424

**REMOVAL OF NAPHTHENIC ACIDS FROM PETROLEUM OILS AND FRACTIONS THEREOF**

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This invention relates to a method of removing and recovering acidic oxygenated compounds from hydrocarbon mixtures containing same and, more particularly, to a process whereby hydrocarbon oils are treated with strongly basic ion-exchange resins to produce products having low acid neutralization numbers. More specifically, the invention relates to the discovery that the presence of certain polar solvents increases the efficiency of strongly basic ion-exchange resins to combine with high-molecular-weight, acidic, oxygenated materials, particularly naphthenic acids in lubricating oils.

It is known that acidic oxygenated materials, such as naphthenic acids, can be neutralized and extracted from petroleum stocks by a variety of solvents. One such process is described in United States Patent 2,808,431, by W. L. Fierce. It is also known that crude naphthenic acids can be contacted with an adsorbent material, such as weakly basic ion-exchange resins, for the purpose of adsorbing a portion of the naphthenic acids thereon and subsequently desorbing the resin to produce desirable fractions of petroleum naphthenic acids. United States Patent 2,723,289 by I. W. Mills is an example of such a process.

In accordance with the present invention, it has been found that the percolation of petroleum fractions containing naphthenic acids through strongly basic exchange resins results in the removal of only a very small amount of the naphthenic acids present. The oil fractions so treated do not have a low enough neutralization number to make the process practical, especially from a commercial point of view. Also, the percolation of naphtha solutions of petroleum fractions, particularly heavy lubricating oil fractions such as lubricating oil extracts, through a strongly basic exchange resin is very inefficient and impractical. The application of weakly basic exchange resins in either of the foregoing processes is equally unsuccessful. In accordance with this invention, it has been found that if the percolation or other contacting of the petroleum fraction containing the naphthenic acids with a strongly basic exchange resin is carried out in the presence of a particular class of solvents, there results the removal of a large proportion of the naphthenic acids, and the resulting hydrocarbon material has a uniquely low neutralization number, or acid content. More particularly, the solvent used in accordance with this invention is selected from the group consisting of methyl ethyl ketone, diethyl ketone, toluene, the xylenes, ethyl benzene, acetone, dipropyl ketone, and methyl isobutyl ketone. In general, those solvents which are used in the dewaxing art and which are polar solvents appear to function to augment the naphthenic-acid-removing power of the resin.

Accordingly, it becomes a primary object of this invention to provide a process for the removal of oxygenated acidic materials from hydrocarbon mixtures containing same by treatment with a strongly basic ion-ex-

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change resin in the presence of a dewaxing solvent or one or more components of a dewaxing solvent.

Another object of the invention is to provide a process for removing naphthenic acids from petroleum fractions containing same by treatment with a strongly basic ion-exchange resin in the presence of a dewaxing solvent or one or more components of a dewaxing solvent.

Still a further object of the invention relates to a process for removing naphthenic acids from heavy lubricating oil fractions while the heavy lubricating oil fractions are dissolved in a dewaxing solvent to produce fractions which have a low acid number.

Still another object of the invention is to provide a process of producing lubricating oil fractions and/or lubricating oil solvent extracts which have low acid neutralization numbers.

These and further objects of the invention will become obvious as the description thereof proceeds.

In general, the process of this invention involves dissolving the hydrocarbon oil fraction in at least about 10% by volume of a dewaxing solvent, or one or more components of a dewaxing solvent, and treating the solution with a strongly basic ion-exchange resin, at temperatures within the range of minus 40° F. to plus 200° F. and at subatmospheric atmospheric or superatmospheric pressure, provided that the solvent does not freeze or boil under the conditions used. The resulting solution of hydrocarbon and solvent, devoid of naphthenic acids, is characterized by a low neutralization number and the hydrocarbon oil fraction may be separated from the solvent by distillation or other means. The strongly basic resin is used until its efficiency has decreased appreciably and thereafter it may be regenerated by washing with dilute caustic solution which dissolves the oxygenated acidic materials from the resin. Treatment of the resin with a low-boiling alcohol after the alkali wash is also advantageous in that it removes any deposits of sodium naphthenate which may have separated from the alkali solution due to salting-out by excess alkali. Following this, the resin is washed thoroughly with water and with the dewaxing solution, or component thereof, to complete the regeneration. It has been found that by thus regenerating strongly basic ion-exchange resins, the regenerated resin has approximately the same ability to remove naphthenic acids from petroleum fractions as does fresh resin. The resins used herein may be regenerated many times and do not appear to lose their affinity for naphthenic acids under the conditions of the instant process.

Although this process is designed to remove acidic oxygenated materials from hydrocarbon mixtures containing same, it is particularly applicable to the removal of naphthenic acids from lubricating oils and fractions, including solvent extracts from the manufacture of both neutral oils and bright stocks. The naphthenic acids found in lubricating oil and fractions thereof are generally characterized as high-molecular-weight carboxylic acids, liquid or solid in physical state, consisting mostly of alicyclic or condensed alicyclic nuclei. These naphthenic acids show little or no unsaturation and consist essentially of acids boiling above about 600° F. Naphthenic acids falling within the foregoing definition are considered in the art to offer the greatest difficulties in removal from the hydrocarbon source and purification.

In the course of refining crude oils, the naphthenic acids are often recovered in the form of a crude product containing from 25% to 75% oil. The market value of these acids is increased many-fold by purifying the acids through removal of the remaining oil. The instant process may be used for the purpose of removing small

amounts of naphthenic acids from hydrocarbon oils containing same, or for the purification of solutions of naphthenic acid in oil that have been obtained from various oil purification processes.

Various types of hydrocarbon oil mixtures containing acidic oxygenated materials, including naphthenic acids, may be treated in accordance with this invention. Any hydrocarbon oil fraction which can be improved by a treatment which lowers the acid neutralization number is included as a material susceptible to treatment. Lubricating oil fractions, particularly neutral oils, bright stocks, and solvent extracts from the manufacture of neutral oils and bright stocks, can be advantageously treated in ac-

pane and cresylic acid. Since solvent extraction and the solvent extracts produced thereby are well known, there is no necessity for further description for purposes of this invention. It suffices to say that one skilled in the art may have reference to one or more of the United States patents which describe in greater detail the solvent extraction process and give the characteristics of solvent extracts that may be benefited by the process of this invention.

The following table gives the physical and chemical properties of several solvent extracts and lubricating oil fractions which are illustrative of the types of material that may be treated in accordance with this invention.

TABLE I

*Characteristics of oils and extracts that may be benefited by the process of this invention*

## A. PHENOL EXTRACTS

| Name | Sample No. | API Gravity | Flash | Fire  | Vis. 100° F. | Vis. 130° F. | Vis. 210° F. | NPA Color | Pour, °F.   | Percent Sulfur | Percent C.R. | V.I. |
|------|------------|-------------|-------|-------|--------------|--------------|--------------|-----------|-------------|----------------|--------------|------|
|      | 1          | 13.3        | ----- | ----- | 340          | 138          | 46.4         | -----     | +35         | 2.45           | 0.13         | -32  |
|      | 2          | 21.8        | ----- | ----- | 94.7         | 60.3         | 37.7         | -----     | +45         | 1.48           | -----        | +33  |
|      | 3          | 14.1        | ----- | ----- | 351          | 142          | 47.1         | -----     | +40         | 2.27           | -----        | -22  |
|      | 4          | 8.4         | ----- | ----- | 1,766        | 483          | 68.8         | -----     | +40         | 3.10           | -----        | -115 |
|      | 5          | 12.1        | ----- | ----- | 901          | 301          | 61.5         | -----     | +30         | 2.48           | -----        | -16  |
|      | 6          | 11.3        | ----- | ----- | 1,672        | 483          | 71.1         | -----     | +35         | 2.65           | -----        | -73  |
|      | 7          | 10.5        | ----- | ----- | 12,676       | 2,514        | 172.1        | -----     | +60         | 2.88           | -----        | -101 |
|      | 8          | 13.7        | ----- | ----- | 25,000       | 5,400        | 355          | -----     | +80         | 2.18           | -----        | +27  |
|      | 9          | 11.1        | ----- | ----- | 23,319       | 4,750        | 282          | -----     | +55         | 2.66           | 7.2          | -40  |
|      | 10         | 15.4        | ----- | ----- | 15,000       | -----        | 285          | -----     | -----       | -----          | -----        | +39  |
|      | 11         | 12.6        | ----- | ----- | 36,410       | 4,310        | 310.1        | -----     | +80         | 2.27           | 4.7          | -1   |
|      | 12         | 14.6        | ----- | ----- | 19,500       | 4,305        | 313          | -----     | +80         | 2.2            | 4.7          | +27  |
|      | 13         | 15.4        | ----- | ----- | 32,500       | -----        | 372          | -----     | +60         | 2.33           | 4.13         | +5   |
|      | 14         | 8.6         | ----- | ----- | 145,000      | 19,000       | 616          | -----     | +70         | -----          | -----        | 0    |
|      | 15         | 13.2        | ----- | ----- | 340          | 136          | 46.3         | -----     | +30         | 2.47           | 0.14         | -34  |
|      | 16         | 14.3        | ----- | ----- | 320          | 139          | 46.9         | -----     | +40         | 2.46           | 0.2          | -5   |
|      | 17         | 11.1        | ----- | ----- | 1,189        | 369          | 63.9         | -----     | +40         | 2.65           | 0.24         | -59  |
|      | 18         | 12.1        | ----- | ----- | 911          | 304          | 60.4         | -----     | +70         | 2.58           | 0.47         | -32  |
|      | 19         | 16.9        | ----- | ----- | 9,500        | 2,551        | 237          | -----     | +100 (min.) | 1.83           | 3.03         | 50   |

## B. SOLVENT REFINED OILS

|                         |    |      |       |       |       |       |       |       |       |       |       |     |
|-------------------------|----|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----|
| High V.I. Br. Stock     | 20 | 26.9 | 590   | 650   | 2,450 | 938   | 155.5 | +6    | 0     | ----- | 0.71  | 100 |
| High V.I. 140 Br. Stock | 21 | 26.6 | 570   | 630   | 2,180 | 838   | 141.4 | +5    | +5    | 0.47  | 0.68  | 98  |
| High V.I. 200 Neut.     | 22 | 30.6 | 425   | 485   | 193.6 | 102   | 46.1  | 1     | 0     | 0.20  | 0.02  | 99  |
| Mid-Cont. Neutral       | 23 | 29.8 | 425   | 480   | 185.5 | 98.9  | 45.5  | ----- | 0     | ----- | 0.29  | 98  |
| Mid-Cont. Neutral       | 24 | 31.0 | 425   | ----- | 174.2 | ----- | 44.8  | ----- | +5    | 0.29  | 0.0   | 100 |
| Sinclair 120 Br. Stock  | 25 | 25.2 | 540   | 600   | 1,993 | 749   | 125.7 | +7    | +15   | 0.31  | 0.62  | 90  |
| Sinclair 200 Neut.      | 26 | 29.7 | 410   | 470   | 201   | 105   | 46    | +1½   | +10   | 0.17  | 0.01  | 91  |
| Mid-Cont. 500 Neut.     | 27 | 28.3 | 475   | 535   | 527   | 232   | 63.1  | +2½   | +10   | ----- | 0.06  | 89  |
| Mid-Cont. 120 Br. Stk.  | 28 | 27.0 | 525   | 595   | 1,731 | 668   | 121.6 | +6    | +15   | 0.17  | 0.58  | 96  |
| Mid-Cont. 150 Br. Stk.  | 29 | 27.5 | ----- | ----- | 2,420 | ----- | 148.9 | +6    | ----- | ----- | ----- | 86  |

## C. NON SOLVENT REFINED

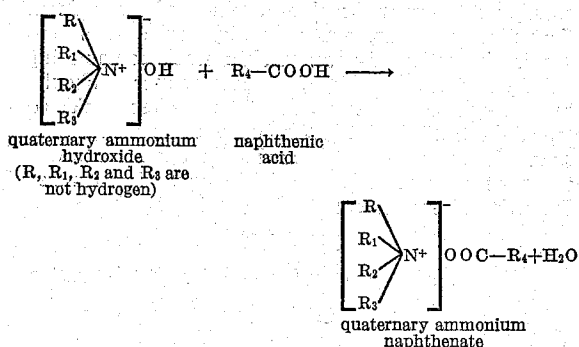
|                     |    |       |       |       |       |       |       |         |       |       |       |    |
|---------------------|----|-------|-------|-------|-------|-------|-------|---------|-------|-------|-------|----|
| Penn. 150 Neutral   | 30 | ----- | ----- | ----- | 155   | ----- | 43.0  | -----   | ----- | ----- | ----- | 87 |
| Gulf Coast Br. Stk. | 31 | 16.9  | 505   | 560   | 601.0 | 1,537 | 147.5 | +3½ dl. | +20   | 0.395 | 0.83  | 10 |
| Raw Neut. (dewaxed) | 32 | 22.4  | 435   | 500   | 356   | 159   | 51.4  | +7      | 0     | 1.23  | 0.1   | 60 |
| Mid-Cont. 200 Neut. | 33 | 26.3  | 400   | 455   | 206.6 | 104   | 45.5  | +2½     | +15   | 0.46  | 0.05  | 76 |

cordance with the instant process. The term "solvent extract" as used herein is intended to mean the extract product resulting from the treatment of lubricating oils and lubricating oil fractions with a selective solvent for the purpose of separating in the extract phase those materials which are predominantly aromatic in nature from the predominantly naphthenic and paraffinic materials which appear in the raffinate phase. Solvent extracts are produced as by-products from the solvent refining processes presently applied in the manufacture of modern lubricating oils. Various solvents are used for this purpose, including phenol, furfural, sulfur dioxide, nitrobenzene, mixtures of sulfur dioxide and nitrobenzene, mixtures of phenol and water, and the well-known Duosol solvent. This latter solvent comprises a mixture of pro-

It has been found that strongly basic ion-exchange resins of the polystyrene quaternary ammonium type and the styrene-divinylbenzene copolymer quaternary ammonium type exhibit properties which make them particularly efficient for the purposes of this invention. Examples of these resins include Amberlite IRA-400, Amberlite IRA-401, Dowex 1 and Dowex 2. The Amberlites are manufactured by the Rohm & Haas Company and the Dowex resins are produced by the Dow Chemical Company. These materials are described throughout the literature, including Kunin's text on "Ion Exchange Resins," second edition (1958), Osborn's text on "Synthetic Ion Exchangers (1956)" and the Dow Chemical Company's brochure entitled, "Dowex Fine Mesh Resins." These strongly basic exchange resins are available in

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the chloride salt form which may be converted into the active hydroxide form by treatment with sodium hydroxide solution just before use. The active hydroxide form contains strongly basic quaternary ammonium hydroxide groups on the resin surface. When an oil or oil mixture containing naphthenic acids is contacted with a mass of such active resin particles, the naphthenic acids appear to react chemically with the quaternary ammonium hydroxide group in accordance with the following illustrative equation.



The resulting quaternary ammonium naphthenate salt remains on the resin surface because the naphthenate ions are held chemically by the quaternary ammonium ions forming the resin surface. In contradistinction to the foregoing action of strongly basic ion-exchange resins, particularly in the presence of polar liquids, the weakly basic ion-exchange resins contain amine groups which show a much diminished tendency to combine with naphthenic acids. Consequently, in the presence of polar solvents a large portion of the naphthenic acids remains in solution in the oil-solvent mixture, and hence is not removed by the resin. Moreover, most petroleum fractions contain trace amounts of water which hydrolyzes naphthenates of the amines, but not the quaternary ammonium naphthenates. The resin itself also usually contains a considerable amount of water, which also results in diminished naphthenic acid removal by the weakly basic resins. Traces or small quantities of water are of no importance in the removal of naphthenic acids from petroleum fractions by strongly basic ion-exchange resins of the quaternary ammonium type unless the water is present in sufficient amount to prevent contact of the oil solution with the resin surface. Accordingly, when solutions of oils dissolved in polar solvents, such as benzene, toluene or acetone, are percolated through weakly basic ion-exchange resins, essentially all of the high-boiling naphthenic acids pass through with the oil and polar solvent without appreciable adsorption on the resin surface. Even the use of a non-polar solvent, such as aliphatic naphtha, which is used to lower the viscosity and hence increase the contacting efficiency, does not sufficiently improve the affinity of weakly basic ion-exchange resins for naphthenic acids to make their use practical.

In order to illustrate the invention, the following non-limiting examples are given:

**Example 1.**—A 100 cc. burette provided with a glass stopcock was fitted in the following manner to serve as a percolation vessel: A small wad of glass wool was placed in the bottom of the burette, after which the burette was half-filled with solvent composed of 55 vol. percent toluene and 45 vol. percent methyl ethyl ketone. A strongly basic ion-exchange resin (Amberlite IRA-400), which had been treated on a Buchner funnel with six volumes of 4% sodium hydroxide solution and washed with water until the effluent had a pH of 7.0, was added

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slowly to the burette while the burette was in contact with a mechanical vibrator. The addition was stopped when the burette contained 100 cc. of the resin. The top of the burette was then attached to a reservoir by means of a rubber stopper.

A mixture of 1555 cc. of solvent (55 vol. percent toluene-45 vol. percent methyl ethyl ketone) and 545 cc. of lubricating oil extract (acid neutralization number=3.54) was poured into the reservoir and percolated through the column of resin at a rate of approximately 1 to 1.5 cc. per minute. The percolate was collected in fractions which were then stripped of solvent by distillation and the oil analyzed for acid content (acid neutralization number). The results are shown in the following table:

TABLE II

| Fraction No.      | Yield of Stripped Oil (cc.) in Fraction | Acid Neutralization Number of Stripped Oil Fraction |
|-------------------|-----------------------------------------|-----------------------------------------------------|
| Original oil..... |                                         | 3.54                                                |
| 1.....            | 20                                      | 0.02                                                |
| 2.....            | 20                                      | 0.04                                                |
| 3.....            | 20                                      | 0.05                                                |
| 4.....            | 50                                      |                                                     |
| 5.....            | 13                                      | 0.17                                                |
| 6.....            | 117                                     |                                                     |
| 7.....            | 17                                      | 0.11                                                |
| 8.....            | 118                                     |                                                     |
| 9.....            | 40                                      | 2.31                                                |
| 10.....           | 100                                     |                                                     |
| 11.....           | 30                                      | 3.07                                                |

**Example 2.**—An experiment was carried out similarly to Example 1 except that the solvent was straight V.M. & P. naphtha. Data on this percolation are as follows:

TABLE III

| Fraction No.      | Yield of Stripped Oil (cc.) in Fraction | Acid Neutralization Number of Stripped Oil Fraction |
|-------------------|-----------------------------------------|-----------------------------------------------------|
| Original oil..... |                                         | 3.54                                                |
| 1.....            | 20                                      |                                                     |
| 2.....            | 15                                      | 1.71                                                |
| 3.....            | 25                                      |                                                     |
| 4.....            | 15                                      | 2.89                                                |

**Example 3.**—An experiment was carried out similarly to Example 1 except that the solvent was straight methyl ethyl ketone. Data on the percolation are as follows:

TABLE IV

| Fraction No.      | Yield of Stripped Oil (cc.) in Fraction | Acid Neutralization Number of Stripped Oil Fraction |
|-------------------|-----------------------------------------|-----------------------------------------------------|
| Original oil..... |                                         | 3.54                                                |
| 1.....            | 19                                      | 0.13                                                |
| 2.....            | 21                                      |                                                     |
| 3.....            | 15                                      | 0.07                                                |
| 4.....            | 13                                      |                                                     |
| 5.....            | 17                                      | 0.09                                                |
| 6.....            | 21                                      |                                                     |
| 7.....            | 16                                      | 0.29                                                |
| 8.....            | 45                                      |                                                     |
| 9.....            | 20                                      | 3.36                                                |

**Example 4.**—An experiment was carried out similarly

to Example 1 except that the solvent was straight toluene. Data on the percolation are as follows:

TABLE V

| Fraction No.      | Yield of Stripped Oil (cc.) in Fraction | Acid Neutralization Number of Stripped Oil Fraction |
|-------------------|-----------------------------------------|-----------------------------------------------------|
| Original oil..... |                                         | 3.54                                                |
| 1-----            | 4                                       | 0.09                                                |
| 2-----            | 11                                      | 0.03                                                |
| 3-----            | 11.5                                    | 0.03                                                |
| 4-----            | 16.0                                    | 0.08                                                |
| 5-----            | 20.0                                    |                                                     |
| 6-----            | 12.0                                    | 0.09                                                |
| 7-----            | 20.0                                    |                                                     |
| 8-----            | 18.0                                    | 0.11                                                |
| 9-----            | 20.0                                    |                                                     |
| 10-----           | 12.5                                    | 0.06                                                |
| 11-----           | 20.0                                    |                                                     |
| 12-----           | 18.0                                    | 0.06                                                |
| 13-----           | 20.0                                    |                                                     |
| 14-----           | 17.0                                    | 0.12                                                |
| 15-----           | 20.0                                    |                                                     |
| 16-----           | 19.0                                    | 0.81                                                |
| 17-----           | 16.0                                    | 0.81                                                |
| 18-----           | 86.0                                    |                                                     |
| 19-----           | 20.0                                    | 0.95                                                |

*Example 5.*—A column of strongly basic ion-exchange resin (Amberlite IRA-400), prepared according to directions given in Example 1, was used for the removal of naphthenic acids from an extract dissolved in a mixture of toluene and methylethyl ketone until the resin had become spent and no longer removed appreciable quantities of naphthenic acids from the extract. The spent resin was washed with fresh solvent mixture to remove the entrained extract, then it was washed with 6-7 volumes of 2% sodium hydroxide solution to remove the naphthenic acids held by the resin. After the resin had been washed further with approximately 2 volumes of methanol it was washed with water until the effluent water had a pH of approximately 7.0. The resin was

ization numbers of the stripped oil fractions were in close agreement with those obtained with fresh resin.

In order to illustrate the effectiveness of Amberlite IRA-401 (a strongly basic ion-exchange resin) over Amberlite IR-4B (a weakly basic ion-exchange resin), a series of experiments was conducted in which 100-cc. portions of an oil solution containing 18.5 vol. percent of dewaxed bright stock (Acid Neutralization Number=0.21), 36.5% methyl ethyl ketone and 45.0% toluene were shaken in a batchwise operation with 10 cc. of the respective exchange resins. The Amberlite IRA-401 was activated as in Example 1 with 4% sodium hydroxide solution to convert the chloride form of the resin into the active quaternary ammonium hydroxide form before use in the series of runs. Bright stock contains high-boiling naphthenic acids which are far more difficult to remove by ordinary means than the naphthenic acids contained in neutral oils. Washing with ordinary caustic soda solution is completely ineffective for the removal of the naphthenic acids from bright stock. The results of the series of experiments are shown in Table VI:

TABLE VI

*Evaluation of anionic exchange resins (batch-treating method)*

Oil solution used:  
18.5% 150-100 dewaxed bright stock (Acid Neut. No. 0.21).  
36.5% methyl ethyl ketone.  
45.0% toluene.

| Run No. | Exchange Resin         | Acid Neut. No. of Stripped Oil | Calculated Percent Acid Removed |
|---------|------------------------|--------------------------------|---------------------------------|
| 1-----  | Amberlite IRA-401..... | 0.05                           | 76                              |
| 2-----  | Amberlite IRA-401..... | 0.05                           | 76                              |
| 3-----  | Amberlite IR-4B.....   | 0.20                           | 6                               |

The effective life of the strongly basic ion-exchange resins without regeneration is shown in Table VII:

TABLE VII

*Percolation of dewaxed bright stock and neutral oil solutions through basic exchange resins*

Solvent Used: Mixture of 55 vol. percent toluene and 45 vol. percent methyl ethyl ketone.  
Amount of Resin Used: 100 cc. (61 g.).

| Run No. | Exchange Resin | Ratio of Solvent to oil | Temp., °F. | Rate, cc./min. | Total Wgt. of Oil Passed Exclusive of Solvents (g.) | Bbls. of Oil treated per Cu. Ft. of Resin | Avg. Acid Neut. No. of total oil passed through Resin |
|---------|----------------|-------------------------|------------|----------------|-----------------------------------------------------|-------------------------------------------|-------------------------------------------------------|
|---------|----------------|-------------------------|------------|----------------|-----------------------------------------------------|-------------------------------------------|-------------------------------------------------------|

(A) Runs with 150 Vis. dewaxed bright stock (0.21 Acid Neut. No.)

|        |                                      |      |     |     |        |      |      |
|--------|--------------------------------------|------|-----|-----|--------|------|------|
| 1----- | Amberlite IRA-401 <sup>1</sup> ..... | 11.5 | 77  | 0.5 | 1,015  | 2.0  | 0.07 |
| 2----- | Amberlite IRA-401 <sup>1</sup> ..... | 4.4  | 77  | 0.5 | 1,456+ | 2.9+ | 0.05 |
| 3----- | Amberlite IRA-401 <sup>1</sup> ..... | 4.4  | 150 | 0.5 | 1,536  | 3.1  | 0.05 |
| 4----- | Amberlite IRA-400 <sup>2</sup> ..... | 4.4  | 77  | 0.5 | 65     | 0.1  | 0.18 |
| 5----- | Amberlite IRA-400 <sup>2</sup> ..... | 11.5 | 77  | 0.5 | 180    | 0.4  | 0.11 |
| 6----- | Amberlite IRA-400 <sup>2</sup> ..... | 11.5 | 150 | 0.5 | 251    | 0.5  | 0.11 |
| 7----- | Amberlite IRA-400 <sup>3</sup> ..... | 4.4  | 77  | 0.5 | 32     | 0.06 | 0.17 |

(B) Runs with 220 Vis. dewaxed neutral (0.17 Acid Neut. No.)

|         |                                      |     |    |     |      |      |      |
|---------|--------------------------------------|-----|----|-----|------|------|------|
| 8-----  | Amberlite IRA-400 <sup>2</sup> ..... | 4.0 | 77 | 1.0 | 507  | 1.0  | 0.04 |
| 9-----  | Amberlite IRA-400 <sup>2</sup> ..... | 4.0 | 77 | 1.0 | 564  | 1.1  | 0.05 |
| 10----- | Amberlite IRA-400 <sup>4</sup> ..... | 4.0 | 77 | 1.0 | 455+ | 0.9+ | 0.04 |

<sup>1</sup> Activated resin contained 25% water as shown by refluxing with toluene.

<sup>2</sup> Activated resin contained 16% water as shown by refluxing with toluene.

<sup>3</sup> Activated resin was heated at 220° F. for 72 hours (38% loss in weight) before use.

<sup>4</sup> Regenerated resin.

then washed with acetone and used for the removal of naphthenic acids from lubricating oil extract according to the directions given under Example 1. After removal of solvent from the percolate fractions, the acid neutral-

Another aspect of this invention is the application of the resin-treating step to a lubricating oil fraction during the process of refining while same is still in solution in the dewaxing solvent.

It is customary in the industry to manufacture lubricating oils, or lubricating oil fractions, by subjecting the oil successively to solvent extraction, solvent dewaxing and clay contacting. These processing steps are regulated so that the finished oil has an acid neutralization number not greater than 0.1 and preferably as low a value as possible. Since petroleum oils from different sources vary with respect to their content of naphthenic acids, it is sometimes difficult to obtain a finished oil having the desired neutralization number.

We have found that a large proportion of the naphthenic acids are readily removed from lubricating oils when the latter are in solution in dewaxing solvent and the solution is percolated through, or contacted with, a strongly basic ion-exchange resin. This means that the oils can be solvent-dewaxed in the normal manner and that the oil-solvent solution from the dewaxing operation can be treated with a strongly basic exchange resin, such as Amberlite IRA-401, to remove a large proportion of the naphthenic acids before the dewaxing solvent is distilled from the oil. The so-treated, solvent-free oil is then treated with clay in a conventional manner to obtain a finished lubricating oil or fraction which has a very low or negligible acid number. The addition of this extra processing step between dewaxing and clay-treating thus makes possible the production of finished lubricating oil fractions having very low acid neutralization numbers, a result which, if obtainable at all with lubricating oils from certain crude oil sources, could be effected otherwise only with great difficulty and expense.

Since it is known that solutions of lubricating oils in ordinary naphthas such as VM & P naphtha and Stoddard Solvent are not effective for efficient removal of naphthenic acids from the oil by basic ion-exchange resins, it was surprising to find that dewaxing solvent, which normally consists of a mixture of aromatic hydrocarbons and ketones, was a very great aid in the removal of naphthenic acids from the oils by strongly basic ion-exchange resins.

The effectiveness of a dewaxing solvent, composed of 55 volume percent toluene and 45 volume percent methyl ethyl ketone, in the removal of naphthenic acids from a dewaxed neutral by a strongly basic exchange resin (Amberlite IRA-400) is shown in Example 6. The use of VM & P naphtha instead of dewaxing solvent results in very little naphthenic acid removal from the lubricating oil by the strongly basic ion-exchange resin.

**Example 6.**—A 100-cc. burette provided with a glass stopcock was fitted in the following manner to serve as a percolation vessel. A small wad of glass wool was placed in the bottom of the burette, after which the burette was half-filled with solvent composed of 55 volume percent toluene and 45 volume percent methyl ethyl ketone. A strongly basic ion-exchange resin (Amberlite IRA-400), which had been treated on a Buchner funnel with six volumes of 4% sodium hydroxide solution and washed with water until the effluent had a pH of 7.0, was added slowly to the burette which was in contact with a mechanical vibrator. The addition was stopped when the burette contained 100 cc. of the resin. The top of the burette was then attached to a reservoir by means of a rubber stopper.

A mixture composed of 20 volume percent of dewaxed neutral oil, having a S.U.S. viscosity of 200 at 100° F. and an acid neutralization number of 0.17, and 80 volume percent of dewaxing solvent of the composition mentioned above was poured into the reservoir and percolated through the column of resin at the rate of 1 to 1.5 cc. per minute. The percolate was collected in fractions which were then stripped of solvent by distillation and the oil analyzed for acid content (expressed as acid neu-

tralization number). The results are shown in the following table:

TABLE VIII

| Fraction No. | Yield of Stripped oil (cc.) in fraction | Acid neutralization number of stripped oil fraction |
|--------------|-----------------------------------------|-----------------------------------------------------|
| Original oil |                                         | 0.17                                                |
| 1            | 11                                      | 0.05                                                |
| 2            | 20                                      | 0.03                                                |
| 3            | 20                                      | 0.04                                                |
| 4            | 20                                      |                                                     |
| 5            | 20                                      | 0.03                                                |
| 6            | 20                                      |                                                     |
| 7            | 20                                      | 0.02                                                |
| 8            | 20                                      | 0.03                                                |
| 9            | 20                                      |                                                     |
| 10           | 20                                      | 0.05                                                |
| 11           | 20                                      | 0.04                                                |
| 12           | 20                                      |                                                     |
| 13           | 20                                      | 0.05                                                |
| 14           | 20                                      | 0.05                                                |
| 15           | 20                                      |                                                     |
| 16           | 20                                      | 0.05                                                |
| 17           | 20                                      | 0.04                                                |
| 18           | 20                                      | 0.04                                                |
| 19           | 20                                      | 0.05                                                |
| 20           | 20                                      | 0.05                                                |

The dewaxing solvents suitable for the purposes of this aspect of the invention are those materials used ordinarily in the dewaxing operation; therefore, no special solvent mixture is necessary for the purposes of this invention. The oil-solvent solution obtained immediately after the removal of the wax by filtration is treated with the strongly basic ion-exchange resin, either by percolation or other contacting at the prevalent temperature, after which the dewaxing solvent is removed from the oil in the usual manner. The particular dewaxing solvent composition and the conditions, such as temperature, are dictated by the requirements of the solvent dewaxing operation.

In the percolation method of operation, the hydrocarbon oil solution is passed through a bed of resin granules until the acid neutralization number of the stripped oil reaches a specified value; then the hydrocarbon oil solution stream is switched to a fresh bed of resin granules while the first bed is subjected to regeneration. In the contact method of operation, the hydrocarbon oil solution is contacted with a definite proportion of the activated resin, after which the hydrocarbon oil solution is separated by conventional means from the resin. In general, a sufficient amount of the strongly basic resin is used to accomplish complete neutralization of the acidic oxygenated compounds present in the hydrocarbon mixture being treated. Preferably, a slight excess over stoichiometric amounts of the resin, based on its basicity, are used. Usually, it is only necessary to contact each barrel of hydrocarbon mixture with about 0.3 to 2 cu. ft. of resin although smaller amounts may be used when the quantity of acidic oxygenated compounds present is small. As the content of acidic oxygenated compounds in the hydrocarbon mixture to be treated increases, the amount of resin used per unit volume or unit weight of hydrocarbon mixture must be increased. On the average, about one cubic foot of resin will satisfactorily treat two barrels of heavy oil.

The amount of non-aliphatic dewaxing solvent, or component thereof, used may vary with the physical properties of the hydrocarbon mixture and the ratios of hydrocarbon mixture to resin used. The solvent should be present in an amount sufficient to thoroughly saturate resin. In general, about 10 to 95 volume percent based on the volume of hydrocarbon mixture and solvent solution is sufficient. One function of the solvent is to reduce the viscosity of the hydrocarbon mixture so as to obtain intimate contact with the resin. Another function, in accordance with this invention, is to increase the selectivity and efficiency of the neutralization and removal of naphthenic acids.

The process may be carried out batchwise or continuously, and by percolation or other contact methods. Any known technique for bringing together a solid and a liquid in intimate contact may be employed. The temperatures of the contacting may be ambient to as high as 200° F., if desired, as long as the resin is stable at the temperature used. No particular advantage is gained in applying elevated temperatures, however, and the process reaches its maximum efficiency at about room temperature or slightly above, i.e., 65° F. to 100° F. Pressure may be applied and a system of forcing the hydrocarbon mixture through the resin bed by pressure of an inert gas may be used.

Any of the known vertical columns adapted to retain the resin as a bed through which the hydrocarbon mixture is percolated may be used. One technique that is applicable comprises intimately mixing a given volume of the hydrocarbon mixture with a granular mass of the resin and separating the liquid phase of decantation, filtration or centrifugation. Other known methods of separation may be used. The process may be made continuous by employing a column or contact chamber adapted to remove the spent or partially spent resin and adding fresh resin as needed. The efficiency of the removal of acids can be carefully followed by the neutralization-number of the product. Various diluents may be used to recover any hydrocarbon mixture retained in the resin bed. Preferably, the retained hydrocarbon mixture is washed out with small portions of a non-aliphatic dewaxing solvent.

The solvent may be introduced as a mixture with the hydrocarbon to be treated, or the solvent and hydrocarbon mixture may pass in layers or intermittently through the bed of resin. It is only essential that the solvents herein-specified be present at the time of contact of the resin with the hydrocarbon mixture. Other modifications of this aspect of the invention will become apparent to one skilled in this art.

Examples of suitable resins are strongly basic anionic exchange materials such as Rohm and Haas' Amberlite IRA-401, Amberlite IRA-400 and Amberlite IRA-410 and Dow Chemical Company's Dowex 1 and Dowex 2 (or Nalcite SAR). Such weakly basic anionic exchange resins as Rohm and Haas' Amberlite IR-4B and Amberlite IR-45 and Dow Chemical Company's Dowex 3 and Chemical Process Company's Duolite A-114, Duolite A-4 and Duolite A-7 are ineffective for use in the process of this invention. Commercially, known strongly basic anionic exchange resins and weakly basic anionic exchange resins vary greatly in their basic strength, according to the publication "Ion Exchange Resins," second edition, by Robert Kunin, Wiley and Sons, 1958.

The distinction between a weakly basic resin and a strongly basic resin is known in the art.

Acid removal by a strongly basic resin occurs through the formation of hydrolysis-resistant quaternary ammonium salts at the resin surface; even very weak acids such as boric acid and silicic acid are readily removed from various fluids by these resins. Weakly basic resins exert an action on acids which is closely allied to adsorption; most very weak acids cannot be removed in appreciable amount from fluids by this type of resin.

Amberlite IRA-400 and Amberlite IRA-410, and a more porous form of Amberlite IRA-400 called XE-75, are strongly basic anion exchange resins which are described by the manufacturer as styrene copolymers chloromethylated and aminated to quaternary ammonium derivatives. Dowex 1 and Dowex 2 are strongly basic anion exchange resins of the quaternary ammonium type, which contain styrene-divinylbenzene structural units.

What is claimed is:

1. The method of removing high-molecular-weight acidic oxygenated compounds boiling above about 600° F. from mineral lubricating oils which comprises treating said mineral lubricating oils with a strongly basic anionic

exchange resin in the presence of a solvent of the group consisting of aromatic hydrocarbon dewaxing solvents and keton dewaxing solvents and mixtures thereof.

2. The method in accordance with claim 1 in which the mineral lubricating oil is selected from the group of heavy mineral lubricating oils and solvent extracts produced in the refining of mineral lubricating oils.

3. The method in accordance with claim 2 in which the mineral lubricating oil is heavy mineral lubricating oil.

4. The method in accordance with claim 1 in which said strongly basic anionic exchange resin is selected from the group of polystyrene quaternary ammonium compounds and styrene-divinylbenzene copolymer quaternary ammonium compounds.

5. The method in accordance with claim 2 in which said mineral lubricating oil is a solvent extract produced in the refining of mineral lubricating oils.

6. The method in accordance with claim 3 in which the heavy mineral lubricating oil is a bright stock.

7. The method in accordance with claim 1 in which said solvent is a mixture of toluene and methyl ethyl ketone.

8. The method in accordance with claim 1 in which said high-molecular-weight organic acids are naphthenic acids.

9. The method of treating a mineral lubricating oil containing high-molecular-weight acidic oxygenated compounds boiling above about 600° F. which comprises passing said mineral lubricating oils into contact with a strongly basic anionic exchange resin in the presence of a solvent of the group consisting of aromatic hydrocarbon dewaxing solvents and ketone dewaxing solvents and mixtures thereof, separating a solvent solution of said mineral lubricating oil, freed of a substantial amount of said acidic oxygenated compounds, from said resin, recovering said mineral lubricating oil from said solvent and recovering said acidic oxygenated compounds from said resin.

10. The method in accordance with claim 9 in which the mineral lubricating oil is selected from the group of heavy mineral lubricating oils, and solvent extracts produced in the refining of mineral lubricating oils and said acidic oxygenated compounds are high-molecular-weight naphthenic acids.

11. The method in accordance with claim 9 in which said solvent is a mixture of toluene and methyl ethyl ketone.

12. The method in accordance with claim 9 in which said strongly basic anionic exchange resin is selected from the group of polystyrene quaternary ammonium compounds and styrene-divinylbenzene copolymer quaternary ammonium compounds.

13. The method of producing mineral lubricating oils of reduced neutralization number which comprises contacting a mineral lubricating oil that has been subjected to refining, including the step of dewaxing and dissolution in a solvent of the group consisting of aromatic hydrocarbon dewaxing solvents and ketone dewaxing solvents and mixtures thereof after the separation of wax therefrom, with a strongly basic anionic exchange resin, whereby the high-molecular-weight acidic oxygenated compounds boiling above about 600° F. therein are combined with the resin, separating said resin from said solvent mineral lubricating oil solution, and subjecting said lubricating oil to finishing treatments.

14. The method in accordance with claim 13 in which the mineral lubricating oil is a heavy mineral lubricating oil.

15. The method in accordance with claim 14 in which the heavy mineral lubricating oil is a bright stock.

16. The method in accordance with claim 13 in which said strongly basic anionic exchange resin is selected from the group of polystyrene quaternary ammonium com-

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pounds and styrene-divinylbenzene copolymer quaternary ammonium compounds.

17. The method in accordance with claim 13 in which said solvent is a mixture of toluene and methyl ethyl ketone.

18. The method in accordance with claim 13 in which said acidic oxygenated compounds are high-molecular-weight organic acids.

19. The method in accordance with claim 18 in which said high-molecular-weight organic acids are naphthenic acids.

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