

UNITED STATES PATENT OFFICE

2,111,548

METHOD OF REFINING OILS

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No Drawing. Application June 5, 1936,
Serial No. 83,695

9 Claims. (Cl. 196—40)

This invention relates to the refining of mineral oils, and is particularly concerned with an improved process for the acid treatment of the more viscous fractions derived from petroleum crude oil, shale oil, or similar sources, such as various lubricating and transformer oils. The oils may be either distillate or residual oils, although the present invention is particularly useful in overcoming difficulties encountered in the acid treatment of residual oils.

It is known to dilute lubricating and similar mineral oil fractions with low boiling or gaseous hydrocarbons during or prior to acid treatment. Difficulty is, however, often experienced in separating the acid sludge from the oil because the sludge particles are often very fluid or are too finely dispersed in the oil to be removed by ordinary means.

In accordance with the present invention I have found that the separation of the acid sludge can be greatly improved by adding a normally liquid lower branched-chain aliphatic hydrocarbon to the oil either before or during the acid treatment. These branched-chain hydrocarbons are effective in causing or aiding the formation of larger and/or harder particles of acid sludge, which are easily separated from the oil. Numerous comparative experiments have shown that these branched-chain or aliphatic iso-hydrocarbons are superior to straight-chain or normal aliphatic hydrocarbons for use as diluents for oil during acid treatment.

I may, for example, employ pure aliphatic hydrocarbons having from five to sixteen and even more carbon atoms. These hydrocarbons may contain one or more tertiary or quaternary carbon atoms, or both quaternary and tertiary carbon atoms. Specific examples of suitable hydrocarbons are: isopentane, 3-methyl-pentane, 2,2-dimethyl-butane, 2,2,3-trimethyl-butane, 2,3-dimethyl-pentane, 2-methyl-2-ethyl-butane, 2,3-dimethyl-pentane, 2,4-dimethyl-pentane, 2,2,3,3-tetramethyl-butane, 2-methyl-3-ethyl-pentane, 2-methyl-2-ethyl-pentane, 2-methyl-heptane, 2,2,4-trimethyl-pentane (iso-octane), 2-methyl-3'-metho-3-ethyl-4-methyl-pentane and 2,7-dimethyl-octane. It should be noted that the tertiary or quaternary carbon atom may be near the end or near the middle of the chain, and that when more than one tertiary or quaternary carbon atom or a tertiary and a quaternary carbon atom are present in the same molecule, they may be adjacent or separated by one or more secondary carbon atoms.

Mixtures of the above branched-chain aliphatic hydrocarbons, as well as distillation fractions rich in these hydrocarbons may also be employed. Thus, a straight run gasoline, consisting mainly of saturated hydrocarbons, or commercial hexane, commercial octane, etc., may be redistilled

under accurate fractionating conditions to produce one or more fractions substantially free from straight-chain hydrocarbons. (See Example I.) These fractions which are rich in branched-chain hydrocarbons may be used either separately or as a blend. The concentration of branched-straight-chain hydrocarbons in such a fraction or blend should preferably exceed 75% by weight.

The oil to be acid treated may, if desired, be given a preliminary refining treatment, such as an extraction with selective solvents, a dewaxing treatment, and/or asphaltenes may be preliminarily precipitated by mixing the initial oil with normally gaseous hydrocarbons, or by treating the initial oil with a low-molecular material under superatmospheric pressure at a temperature near to or above the critical temperature of the low-molecular substance. In the last named alternative, the branched-chain normally liquid hydrocarbon may be mixed with the oil prior to the treatment with the low-molecular hydrocarbon.

The acid and diluent requirements vary with the viscosity and purity of the oil being treated. Excellent results have been obtained by diluting one volume of residual oils having viscosities of over 400 sec. Say. Univ. @ 210° F. with between one and a half to four volumes of several of the above-named branched-chain hydrocarbons, although lower dilution ratios are practical when less viscous oils are treated, and even higher dilution ratios, such as one volume of oil to six volumes of diluent may be desirable in many instances. In general, it will be found desirable to dilute the oil with sufficient diluent to bring the Say. Univ. viscosity @ 100° F. to below about 200 to 500 seconds. The concentration of the acid may also be varied to suit the purity and viscosity of the oil, and may, for example, be between 85 and 100% and will generally be higher than 90% for the more viscous oils. Moreover, it may often be desirable to employ fuming sulfuric acid as, for example, 20% oleum, particularly in the refining of viscous white oils. The quantity of acid will also vary with the stock being treated, and may for example, be between five and fifty pounds of 66° Bé. sulfuric acid per barrel (42 U. S. gals.) of oil. The temperature of mixing and agitation may, for example, be between 0° C. and 60° C., but my process is not restricted to any of the preferred limits given herein.

The contacting of the acid and oil may be effected with air or with a mixing device provided with a propeller and draft tube, as is well known in the art. After the acid has been thoroughly mixed with the diluted oil the sour oil is fed into a settling tank or into a continuous settler, the decanted oil being subsequently stripped, with steam and/or vacuum if desired, to remove the diluent from the oil. Moreover, the oil may

be given a finishing treatment by contacting it with clay, preferably at an elevated temperature.

The invention may be further understood from the following examples which are, however, only for the purposes of illustrating the invention, and not for the purpose of limiting the scope of the appended claims.

Example I.—Several portions of a deasphalted Coalinga residual oil having a viscosity of over 400 sec. Say. Univ. @ 210° F. were mixed with two parts by volume of the following diluents: (a) commercial hexane; (b) a fraction distilled between 68° C. and 71° C. upon efficiently distilling commercial hexane (this cut consisted predominantly of n-hexane); (c) a fraction similarly distilled between 63° C. and 65° C. (this cut consisted predominantly of 3-methyl-pentane). Each of these diluted portions was mixed with 10% by weight of 96% sulfuric acid, and allowed to settle. The oil in the first two samples had a dark color, and very little sludge separated out, indicating that a stable suspension had been formed; a large quantity of sludge settled from the third portion, was cleared and the oil had a lighter color than the oil in the first two portions.

Example II.—Different portions of Coalinga residual oil having a viscosity of 1,266 sec. Say. Univ. @ 210° F., a viscosity index of 2, a specific gravity of 0.9779 and a refractive index

$$n_D^{20}$$

of 1.546, were diluted with various hydrocarbon diluents, treated with different quantities of 96% sulfuric acid, and desludged. The results are shown in the following table:

Diluent	Diluent: Oil ratio	Wt. percent H ₂ SO ₄	Percent yield oil	Color of oil	Wt. percent of sludge on original oil
Isopentane...	2:1	10	62	Dark green...	58
Do.....	2:1	15	55	Medium green...	80
n-Pentane...	2:1	10	74	Brown black...	38
Do.....	2:1	15	62	Brown black...	72
n-Hexane...	2:1	10	96	Brown black...	2
Do.....	2:1	15	63	Brown black...	75
Do.....	3:1	10	84	Brown black...	30
n-Heptane...	2:1	10	70	Green black...	44
Do.....	2:1	15	57	Dark green...	89
Iso-octane...	2:1	10	67	Dark green...	66
Do.....	2:1	15	54	Blue green...	87
Do.....	3:1	10	65	Light green...	65

It will be noted that in each case the color of the oils treated in the presence of the branched-chain hydrocarbon diluents was better than the color of oils treated with the same amount of acid in the presence of a straight-chain hydrocarbon diluent.

Example III.—Several portions of a Coalinga residual oil having a viscosity of 454 sec. Say. Univ. @ 210° F., a viscosity index of 30, a specific gravity of 0.9535 and a refractive index

$$n_D^{20}$$

of 1.5393, were each diluted with two parts by volume of various hydrocarbon diluents and one-half of each diluted portion was treated with 10% by weight of 96% sulfuric acid, and the other half with 15% by weight of the acid. The sludge obtained by acid treating the portions diluted with iso-pentane, iso-octane, or 2,7-dimethyloctane was non-fluid and easy to separate from the oil solution; the oils had good colors. The sludge obtained by acid treating portions diluted with n-hexane was fluid, while the sludge obtained

from the portion diluted with straight run gasoline from a Ventura crude was very fluid; both were very difficult to separate from the oil, and the oils were cloudy and had dark colors.

While my invention is particularly concerned with overcoming difficulties encountered in the acid treatment of the more viscous oils, such as those having viscosities above 100 sec. Say. Univ. @ 210° F., it is also applicable to the treatment of less viscous oils, such as, for example, those having viscosities between 125 and 200 sec. Say. Univ. @ 130° F. The designation "viscous" is, in the present specification and claims intended to designate any hydrocarbon oil having a viscosity greater than about 125 sec. Say. Univ. @ 130° F.

I claim as my invention:

1. A process for refining a viscous hydrocarbon oil comprising the step of contacting said oil with a strong sludge-forming mineral acid in the presence of a normally liquid non-viscous saturated hydrocarbon diluent consisting predominantly of branched-chain paraffinic hydrocarbons.

2. The process according to claim 1 in which the hydrocarbon diluent consists substantially of paraffinic hydrocarbons containing at least one tertiary carbon atom.

3. The process according to claim 1 in which the hydrocarbon diluent consists substantially of paraffinic hydrocarbons containing at least one quaternary carbon atom.

4. The process according to claim 1 in which the hydrocarbon diluent consists substantially of paraffinic hydrocarbons containing from five to fifteen carbon atoms.

5. A process for refining a viscous hydrocarbon oil comprising the steps of diluting said oil with a non-viscous normally liquid saturated aliphatic hydrocarbon diluent consisting predominantly of branched chain paraffinic hydrocarbons, contacting the oil with concentrated sulfuric acid to form an acid sludge, and separating the sludge from the diluted oil.

6. The process according to claim 5 in which the viscous hydrocarbon oil is a residual mineral oil having a viscosity higher than 100 sec. Say. Univ. @ 210° F.

7. In the process for refining a viscous hydrocarbon oil comprising the steps of contacting the oil with a strong sludge-forming mineral acid to form an acid sludge, and separating the sludge from the diluted oil, the step of facilitating the separation of the sludge by diluting said oil with a non-viscous normally liquid aliphatic hydrocarbon diluent containing over about 75% of branched chain paraffinic hydrocarbons.

8. In the process for refining a viscous hydrocarbon oil comprising the steps of contacting the oil with sulfuric acid to form an acid sludge, and separating the sludge from the diluted oil, the step of facilitating the separation of the sludge by diluting said oil with a non-viscous normally liquid aliphatic hydrocarbon diluent containing over about 75% of branched chain paraffinic hydrocarbons.

9. In the process for refining a viscous hydrocarbon oil comprising the steps of contacting the oil with a strong sludge-forming acid to form an acid sludge, and separating the sludge from the diluted oil, the step of facilitating the separation of the sludge by diluting said oil with a non-viscous normally liquid aliphatic hydrocarbon diluent containing over about 75% of isopentane.