

UNITED STATES PATENT OFFICE

2,166,502

METHOD OF REFINING OILS

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No Drawing. Application November 6, 1937,
Serial No. 173,197

10 Claims. (Cl. 196—34)

This invention relates to improvements in the refining of hydrocarbon mixtures such as oils, waxes, and oils rich in hydrocarbons, and is particularly concerned with the acid treatment of the more viscous fractions derived from petroleum crude oils, shale oils, coal tar oils, and the like, by distillation or treatment with solvents, such as lubricating and transformer oils, as well as with the acid treatment of long mineral oil fractions containing such viscous fractions. The initial oil mixture may be residual or distillate fractions, but is of particular advantage with the former. The initial material may be normally liquid or solid and the term "hydrocarbon mixture" is, in the present specification and claims, intended to include waxes as well as normally liquid oils containing wax. For convenience, the invention will, in this specification, be described as applied to the treatment of oils. This application is a continuation-in-part of my application Serial No. 53,585, filed December 9, 1935.

It is known to dilute lubricating and similar mineral oil fractions with low boiling normally liquid or with liquefied normally 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 settling or centrifuging. Also, the quantity separated from the main body of the treated oil with the acid sludge is frequently such as to reduce the yield of treated oil substantially below that which is theoretically possible when the quantities of actual impurities in the oil are considered. Such treatments, moreover, do not greatly improve the viscosity-temperature characteristics, as expressed, for example, by the viscosity index.

In accordance with the present invention, I have found that the separation of the acid sludge from oil can be enhanced whereby the properties and/or yield of oil is greatly improved by adding to the oil, either before or during or after contacting with the acid a diluent containing a quantity of a low-molecular weight hydrocarbon treating agent above its critical temperature. While the treating agent may be employed alone, it is greatly preferred to employ it in solution with a normal liquid diluent or solvent which is a mutual solvent for the treating agent and the oil being treated, because without such diluent it becomes necessary to employ inconveniently high pressures to dissolve in the oil a quantity

of the treating agent which is sufficient to produce the desired improvement in the separation of the sludge, particularly when the treating agent is considerably above its critical temperature. By "normal liquid" I mean a liquid which is substantially, i. e., more than about 20-40° C., below its own critical temperature.

The temperature of the process is preferably carried out at relatively low temperature, such as from about 0 to 50° C., and lower, to avoid or regulate oxidation of the oil. Higher temperatures, such as 100° C. may, however, also be employed, but it may then be desirable to use acid of lower concentrations to avoid oxidation of the oil and corrosion of the apparatus. Since, however, the removal of acid sludge can be readily achieved by my process at such elevated temperatures, and since oxidation of the oil is not always undesirable, my process is not limited to the use of low temperatures.

While the acid may be commingled with the oil either before or after the addition of the treating agent and/or the normal liquid diluent, I have found it to be more desirable to add at least the normal liquid diluent to the oil prior to the addition of the acid. This has the advantage of preventing local overheating and oxidation, and of insuring better contact between the acid and oil.

Any low-molecular weight hydrocarbon which is above its critical temperature at the temperature of the sludge separation step may be employed as the treating agent. This includes hydrocarbons containing from one to five carbon atoms in the molecule. For operations at temperatures below 50° C. methane, ethane, or a mixture of these is preferred; instead of these pure hydrocarbons, materials rich therein, such as natural gas and dry natural gas may also be used. Other examples of hydrocarbons which may be employed are: propane, normal- or isobutanes and normal- or iso-pentane. The treating agent should preferably be incapable of reacting chemically with or being chemically affected by the acid; for this reason the saturated paraffinic hydrocarbons are preferred to olefinic hydrocarbons, although the more stable olefines, such as ethylene and propylene are very suitable under most conditions. Other unsaturated hydrocarbons, while not preferred, are, however, operative to aid the precipitation of the acid sludge.

The pressure must be sufficient to dissolve an effective quantity of the treating agent in the oil. The exact quantity depends upon the vis-

costly and composition of the oil, and upon the nature, concentration and temperature of the acid employed. In most cases, it is desirable to dissolve at least 0.20 gram moles of the treating agent for 100 grams of oil, and I prefer to employ at least 0.50 gram moles of the treating agent, and as much as 5.0 or more gram moles of the treating agent are suitable, although my invention is not restricted to operations between these limits. The best results are obtained when the concentration of the treating agent is within about 25% of the concentration necessary for incipient phase separation in the absence of the acid, incipient phase separation occurring when the oil is saturated with the treating agent and in a single liquid phase, but the addition of a small quantity of the treating agent will cause its separation into two phases. Concentrations above that necessary for incipient phase separation, at which the oil exists in two liquid phases, may be employed, but I prefer to operate below such concentrations. The pressures will in most cases be between 100 and 1500 lbs./sq. in. gauge. At such pressures a gas phase may be present above the solution of oil and treating agent, but the process may also be operated in the absence of a gas phase.

As pointed out heretofore, the solubility of the treating agent above its critical temperature is low and it is very desirable to enhance the solubility by employing it together with a diluent which is a normal liquid at the temperature of the treatment. The diluent will, therefore, have a higher critical temperature than the treating agent. The diluent should preferably have a relatively low internal pressure, thereby aiding the action of the treating agent, which has an internal pressure of the order of that of a gas. This diluent or mutual solvent may, for example, be a low boiling normally liquid or a liquefied normally gaseous aliphatic hydrocarbon of the type commonly known as deasphalting agents, consisting predominantly of hydrocarbons containing from two to sixteen carbon atoms, such as ethane, propane, butane, normal- and iso-butane, pentanes, heptanes, their higher homologues, gasoline, and naphtha. The corresponding olefines, and particularly the normal olefines, may also be employed, but are not preferred because of possible polymerization in the presence of acid, but can be used in certain situations. Non-hydrocarbons such as alkyl halides like propyl chloride may also be employed as diluents, either alone, or in admixture with hydrocarbons.

Good results are obtained by using a normally liquid diluent, such as isopentane. The branched chain saturated paraffinic hydrocarbons containing between four and sixteen carbon atoms, and particularly those between five and ten carbon atoms, their mixtures and fractions consisting predominantly thereof are preferred. These hydrocarbons may contain one or more tertiary or quaternary carbon atoms, or both quaternary and tertiary carbons. Specific examples are: Isopentane, 3-methyl pentane, 2,2-dimethyl-butane, 2,2,3-trimethyl butane, and 2,2,4-trimethyl pentane (iso-octane).

Whether a compound is to be employed as a treating agent or as a normal liquid diluent is determined by the temperature of operation, the treating agent being above its critical temperature, and the diluent in the normal liquid state. For example, when operating at 40° C., methane or ethane may be employed as the treating agent

and liquid propane or iso-pentane may be employed as the diluent; at 0° C., methane may be the treating agent and ethane, or propane or pentane may be the diluent.

I prefer to employ between one and six volumes of the diluent for each volume of the oil treated, although lower and higher amounts may be used. The more viscous oils generally require more diluent than the less viscous oils. All or part is preferably added to the oil prior to the addition of the acid, it being desirable that this amount be sufficient to bring the viscosity of the resulting oil solution to below 200 seconds Saybolt Universal at 100° F.

The process may be applied to treatments with any sludge forming acid, particularly the strong oxy-mineral acids, like sulfuric acid, phosphoric acid, and mixtures of acids, such as a mixture of sulfuric and acetic acids. As is understood in the art, the acid requirements vary with the viscosity and composition of the oil being treated. By way of example, it may be stated that sulfuric acid of between 85 and 100% concentration, and generally above 90% is suitable for the more viscous oils; it may be desirable to employ fuming sulfuric acid, such as 20% oleum, particularly in the refining of viscous white oils. The quantity of acid may, for example, be between five and fifty pounds of 66° Bé. acid per barrel (42 U. S. gallons) of oil. After the separation of the acid sludge, the treating agent and diluent may be separated from the oil, either before or after neutralization in the usual way, e. g., with caustic or with clay.

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 asphaltic bodies may be preliminarily precipitated by mixing the initial oil with normally gaseous hydrocarbons, or by treating the initial oil with a low-molecular weight hydrocarbon or non-hydrocarbon treating agent of the type described above under para-critical temperature conditions (i. e., at a temperature above, at, or down to about 20 to 40° C. below its critical temperature), and sufficient pressures to cause the formation of two or more liquid phases, as described in Example II. In the last named alternative, the normal liquid diluent may be present in the preliminary treatment, and one of the resulting oil fractions, as for example, the lighter liquid phase produced in the treatment may, after its separation from the other phase, be contacted with the acid.

While my process may be applied to the acid treatment of any hydrocarbon mixtures, it is particularly useful in the treatment of the more viscous residual normally liquid oils, such as those having viscosities above 60 seconds Saybolt Universal at 210° F. It may, however, also be applied advantageously to distillate oils, and to oils having lower viscosities such as 125 seconds Saybolt Universal at 130° F., and to the treatment of waxes. In the case of waxes, it is desirable to heat the wax sufficiently to melt it and/or dissolve it in the normal liquid diluent; a normally liquid diluent is preferred in this case to a normally gaseous liquefied diluent. The process of the present invention may be applied advantageously to a wax-bearing oil, the acid treated oil, either prior to or after neutralization, being dewaxed to produce a wax having improved properties, such as color. The dewaxing may also be carried out simultaneously with the step of removing the sludge by the application of a low temperature, either before or after

mixing with the acid, but preferably after. The present process is particularly useful in the treatment of hydrocarbon oils having a viscosity greater than about 125 seconds Saybolt Universal at 130° F.

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

EXAMPLE I

A Coalinga residual oil was deasphalted with 2.05 parts by weight of liquid propane for each part of oil at 56° C. The deasphalted oil had a color on the A. S. T. M. scale of 8 diluted.

One portion of the deasphalted oil and propane was saturated with methane at 300 lbs. per sq. in. and 10.7 grams of 96% sulfuric acid for each 100 grams of oil were added, the mixture was agitated for one hour, after which the sludge formed was settled for one hour and drawn off. The solution of treated oil was drawn off through an evaporator, and the propane and methane removed. The oil was diluted with isopentane to prevent emulsification and neutralized with 20% B₂ sodium hydroxide solution.

A second portion of the oil was similarly treated with acid, but in the absence of methane; a third portion was similarly treated, but in the absence of methane or propane. All treatments save the deasphalting step were carried out at 20° C. The results are shown in Table I, yields being based on the deasphalted oil. The color was determined by the method D 155-347 of the American Society for Testing Materials. Diluted colors were determined by employing a solution of 85% kerosene and 15% oil.

Table I

Amount by weight of propane per 100 parts of oil	289	289	0
Gas used	Methane	None	None
Pressure, lbs. per sq. in.	300	120	
Yield of treated oil, percent by weight	83.4	83.4	74.6
A. S. T. M. color of treated oil	8	4-½ dil.	4-½ dil.

It will be noted that the color of the oil which was treated in accordance with the present invention, employing methane, was much lighter than the oil treated by the use of propane alone, indicating a far more complete and rapid separation of sludge.

EXAMPLE II

A Coalinga oil residue having a viscosity of about 100 seconds Saybolt Universal at 210° F. was dissolved in three parts by volume of liquid propane, and methane was pumped into the resulting solution at room temperature to cause the formation of two liquid phases. Sufficient methane was employed to cause 63% of the initial oil to be in the heavier phase, and 37% in the lighter liquid phase, and the phases were separated. The oil in the lighter phase, herein designated as the "raffinate" was used as the starting material for the acid treatment, and its properties are given in the second column of Table II.

One portion of the raffinate oil, containing 4.7 parts by volume of a mixture of propane and methane for one part of oil, the mixture consisting of 17 mol per cent of methane (being the concentration of incipient phase separation and corresponding to about 0.98 gram moles of meth-

ane to 100 grams of raffinate oil, was mixed with 10% by weight (computed on the raffinate oil) of 94% sulfuric acid at 30° C., the pressure being maintained at 635 lbs./sq. in. gauge. After stirring, the acid mixture was allowed to settle, the solution of oil in propane and methane separated from the sludge by decantation, and the propane and methane separated from the oil. The properties of the acid treated oil are given in the third column of Table II.

Two different portions of the raffinate oil were freed from the propane and methane. One of these was treated with the same quantity of 94% acid at 30° C. in the absence of a diluent, and the other was similarly acid treated in the presence of 2.5 parts by volume of isopentane. The properties of the acid treated oils are given in the fourth and fifth columns of the table.

Table II

	Raffinate oil	Acid treated oils		
		With propane and methane	Without diluent	With isopentane
Specific gravity d_{20}^{20}	0.9298	0.9238	0.9298	0.9236
Refractive index n_D^{20}	1.5160	1.5112	1.5151	1.5109
Saybolt Universal viscosity:				
At 100° F.	898	709	912	714
At 210° F.	68.3	64.6	68.8	63.7
Viscosity index	40	55	40	48.5
Color	4-D	3-½ D	4-½ D	4-D
Yield, percent	100	97	94	84

It will be noted that the yield, color, and viscosity index were each more favorable in the oil treated in accordance with the present invention than in the other treatments, the results being superior even to the treatment with isopentane which is an excellent diluent for acid treatment.

The settling rates were much higher when propane and methane were employed.

I claim as my invention:

1. The process for refining a viscous hydrocarbon mixture comprising the steps of contacting said mixture with a strong sludge-forming acid and separating the resulting sludge from the acid mixture in the presence of at least 0.20 gram moles for each 100 grams of the mixture of a low molecular weight hydrocarbon treating agent dissolved in the mixture under superatmospheric pressure at a temperature above the critical temperature of the treating agent, said quantity being sufficient to improve the separation of the sludge.

2. The process according to claim 1 in which the treating agent is methane.

3. The process according to claim 1 in which the treating agent is ethane.

4. The process for refining a viscous hydrocarbon mixture comprising the steps of diluting said mixture with a low boiling liquid hydrocarbon solvent for the mixture and for a low molecular-weight hydrocarbon treating agent, contacting the mixture with a strong sludge-forming acid and separating the resulting sludge from the acid diluted mixture in the presence of at least 0.20 gram moles for each 100 grams of the mixture of said treating agent dissolved in the mixture under superatmospheric pressure at a temperature above the critical temperature of the treating agent and substantially below the critical temperature of the liquid solvent.

5. The process according to claim 4 in which

the low boiling solvent consists predominantly of liquefied, normally gaseous aliphatic hydrocarbons.

5 6. The process according to claim 4 in which the quantity of the treating agent is below, and within 25% of, the concentration corresponding to the incipient separation of the mixture into liquid phases in the absence of the acid.

10 7. The process for refining a viscous hydrocarbon mixture comprising the steps of diluting said mixture with a low boiling liquid hydrocarbon solvent consisting predominantly of saturated aliphatic hydrocarbons having not over sixteen carbon atoms in the molecule, contacting the diluted mixture with a strong sludge forming acid, and separating the resulting sludge from the acid diluted mixture in the presence of at least 0.20 gram moles for each 100 grams of the mixture of a low molecular weight hydrocarbon treating agent dissolved in said mixture under superatmospheric pressure at a temperature above the critical temperature of the treating agent and substantially below the critical temperature of the liquid hydrocarbon solvent.

25 8. The process for refining a viscous hydrocarbon oil comprising the steps of subjecting said oil in the liquid state to the precipitating action of the quantity of low molecular weight substance at a para-critical temperature, said quantity being sufficient to cause the formation of

two liquid phases of different densities, separating said phases, commingling one of said phases with a strong sludge-forming acid, and separating the resulting sludge from the acid oil in the presence of at least 0.20 gram moles for each 100 grams of the oil of a low molecular weight hydrocarbon treating agent dissolved in said oil under superatmospheric pressure at a temperature above the critical temperature of said treating agent.

10 9. The process for refining a viscous wax-bearing hydrocarbon oil comprising the steps of diluting said oil with a low boiling liquid hydrocarbon solvent for the oil and for a low molecular weight hydrocarbon treating agent, contacting the oil with a strong sludge-forming acid, separating the resulting sludge from the acid diluted oil in the presence of at least 0.20 gram moles for each 100 grams of the oil of said treating agent dissolved in the oil under superatmospheric pressure at a temperature above the critical temperature of the treating agent and substantially below the critical temperature of the liquid solvent, said quantity being sufficient to improve the separation of the sludge, and dewaxing the oil after the acid contacting.

15 10. The process according to claim 9 in which the dewaxing is effected simultaneously with the step of separating the sludge from the acid oil.

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