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METHOD OF INCREASING THE SLUDGE STABILITY OF A PETROLEUM LUBRICATING OIL DISTILLATE

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This invention relates to improvements in stable mineral oils and the method of preparing the same.

In the refining of petroleum oils, in particular, oils of the type used for such purposes as lubricating high speed spindles of knitting machinery or bearings of high speed turbines and oils used for insulating electric switches and transformers, it is frequently necessary to resort to drastic treatment with strong acids in order to reduce the sulfur content to the low maximum sulfur content required. While such treatment enables the oil to meet the sulfur specifications other properties thereof are seriously impaired. Oils so treated have unusually high oxygen absorption and are susceptible to sludging, high acidity and possible peroxide development.

Some petroleum oils, particularly certain of the low sulfur oils of the naphthenic type, become susceptible to sludging and high acidity development although subjected to only relatively light acid treatment.

Acid treated oils which develop sludge and high acidity because of the refining treatment to which they have been subjected are commonly referred to as "overtreated" oils, and as used herein the term includes any acid treated oil which is susceptible to sludging, high acidity and possible peroxide development.

In is an object of this invention to provide a method of avoiding the overtreatment of oils.

It is another object of this invention to provide a method of acid treating oils without rendering the same susceptible to sludging and high acidity development.

It is another object of the present invention to provide a method of preparing mineral oils having improved oxidation stability.

It is still another object of this invention to provide lubricants which have increased oxidation stability.

A further object of the invention is to prepare a transformer oil which has improved oxidation stability.

A further object of this invention is to provide a method of avoiding the overtreatment of electric insulating oils.

We have found that the susceptibility to sludging of a distillate due to the overtreatment thereof can be avoided or materially decreased by the addition of small amounts, for example from about 0.1% to about 5.0%, of an uncracked high sulfur residue to the distillate prior to the acid treatment of the distillate. The sulfur content of the uncracked residue may be from about 0.5% to about 7.0% and preferably from about 2.0% to about 4.0%. The residues may be the bottoms from the non-cracking distillation of high sulfur crude oils, such as Winkler crude oils or crude oils of the Winkler type.

The term "non-cracked petroleum residue" as used herein is defined as the residue resulting from the non-cracking distillation of crude petroleum or topped crude and represents about 10% to 35% of the total charge on crude distilled.

It is not possible to state definite quantities of residue which should be used since the amount required depends to a large degree upon the character of the residue; a residue representing a smaller fraction of the crude distilled will be used in lesser quantities than a residue representing a larger fraction of the crude distilled. In general, it may be stated that the amount of residue used should be that quantity which will give results comparable with that obtained using 0.1% to 5% of about 7 to about an 11 A. P. I. gravity residue having a Saybolt furol viscosity at 210° F. of about 100 seconds to about 1350 seconds, and preferably from about 0.5% to about 1% of a residue having a Saybolt furol viscosity at 210° F. from about 300 seconds to about 600 seconds.

In order that the invention may be clearly understood the same is illustrated by the following preferred embodiment thereof. A transformer oil distillate from a low sulfur naphthenic crude having the following inspection:

Gravity	A. P. I.	25.7 to 26.2
Flash	°F.	265–275
Pour	°F.	–50
Saybolt viscosity at 100° F.	seconds	51–60

was treated with one pound of 93% sulfuric acid per gallon of oil, neutralized and subsequently clay percolated to a yield of about 2000 gallon per ton of clay. This treated transformer oil distillate when tested by the Snyder Life Test had a "life" of 4 days.

The Snyder Life Test which is an index of the oxidation stability of an oil is conducted by maintaining about 500 cc. of the oil under test at a constant temperature of 120° C. Once every 24 hours a 10 cc. sample of the oil is withdrawn, cooled and centrifuged for the purpose of determining the first appearance of sludge.

The "life" of the oil is the number of days the oil can be held at a temperature of 120° C. before visible sludge is formed. The test is more

fully described in the A. S. T. M. Proceedings, vol. 24, part I, page 638 (1924).

To the same transformer oil distillate, before acid treating, was added about 0.5% of a non-cracked residue obtained in the non-cracking distillation of Winkler crude oil. This residue had the following properties:

Gravity	A. P. I.	9.5
Flash	°F.	550–575
Furol viscosity at 210° F.	seconds	400–440

The transformer oil distillate with the added residue was treated with 1 pound of 93% sulfuric acid per gallon of oil, neutralized and subsequently percolated through granular fuller's earth to a yield of about 2000 gallon per ton of clay. When submitted to the Snyder Life Test the finished transformer oil had a "life" of 21 days showing an improvement of more than 500% over the oxidation stability of the transformer oil treated without the addition of residue.

To illustrate the effect of a small amount of residue in preventing the overtreatment of oils, the above finished oil, that is the transformer oil distillate containing 0.5% of residue was retreated with 0.5 pound of 104½% sulfuric acid, neutralized and clay treated to a yield of 2000 gallon per ton of clay. This oil had a "life" test of 19 days as compared to a "life" of 21 days of the oil before retreating and a "life" of 4 days of the distillate treated without the addition of residue. Although the oils in the last two examples were much more drastically acid-treated than the transformer oil distillate containing no residue they showed no indication of being overtreated as evidenced by the Snyder Life Test results.

While the residue may be added to the distillate without dilution the same may be blended with a light distillate in order to facilitate the handling of the residue. We have found a blend of about 53% residue and 47% of a light low cold test distillate having the following typical inspection

Gravity	A. P. I.	15.5
Flash	°F.	350
Pour	°F.	+5
Saybolt viscosity at 100° F.	seconds	3285
Saybolt viscosity at 210° F.	do	144

was suitable for this purpose. A mixture of a transformer oil distillate from naphthenic crude and about 0.7% of the above described residue blend when treated with 1 pound 93% sulfuric acid per gallon of distillate, neutralized and percolated through fuller's earth, yielding a product having a color of less than 1 N. P. A., had a "life" test of about 21 days.

While we have described our invention in connection with the treatment of transformer oil distillates the same is not limited thereto. Our invention is applicable with the same success to the treatment of spindle lubricants, turbine oils, lubricating oils requiring drastic acid treatment and white oils.

This application is a continuation-in-part of our copending application Serial 133,378, filed March 27, 1937.

We claim:

1. The method of increasing the sludge stability of a petroleum lubricating oil distillate having a Saybolt Universal viscosity greater than about 50 seconds at 100° F. and normally susceptible to sludging after sulfuric acid treatment which comprises mixing said petroleum distillate prior to treatment with sulfuric acid with from about 0.1% to about 5.0% of a heavy uncracked petroleum residue having a sulfur content from about 0.5% to about 7.0%, a Saybolt furol viscosity at 210° F. of about 100 seconds to about 1350 seconds and a gravity of about 7 A. P. I. to about 11 A. P. I. and subsequently treating said mixture with sulfuric acid.

2. The method of increasing the sludge stability of a petroleum lubricating oil distillate having a Saybolt Universal viscosity greater than about 50 seconds at 100° F. and normally susceptible to sludging after sulfuric acid treatment which comprises mixing said petroleum distillate prior to treatment with sulfuric acid with from about 0.1% to about 5.0% of a heavy uncracked petroleum residue having a sulfur content from about 2.0% to about 4.0%, a Saybolt furol viscosity at 210° F. of about 400 seconds to 440 seconds and subsequently treating said mixture with sulfuric acid.

3. The method of preparing a sludge resistant electric insulating oil which comprises mixing an electric insulating oil distillate normally susceptible to sludging after sulfuric acid treatment with about 0.1% to about 5% of an uncracked petroleum residue having a sulfur content of about 0.5% to about 7.0%, a Saybolt furol viscosity at 210° F. of about 100 seconds to about 1350 seconds and a gravity of about 7 A. P. I. to about 11 A. P. I. and subsequently treating the mixture with sulfuric acid.

4. A method of increasing the sludge stability of a petroleum lubricating oil distillate having a Saybolt viscosity greater than about 50 seconds at 100° F. and normally susceptible to sludging after sulfuric acid treatment which comprises mixing said petroleum distillate prior to treatment with sulfuric acid with from about 0.1% to about 5.0% of a heavy uncracked petroleum residue having a furol viscosity at 210° F. of approximately 400 to 440 seconds and subsequently treating said mixture with sulfuric acid.

5. The method of preparing a sludge resistant electric insulating oil which comprises mixing an electric insulating oil distillate normally susceptible to sludging after sulfuric acid treatment with about 0.1% to about 5.0% of an uncracked petroleum residue having a furol viscosity at 210° F. of about 400 to about 440 seconds and subsequently treating said mixture with sulfuric acid.

6. The method of increasing the sludge stability of a petroleum distillate having a Saybolt Universal viscosity greater than about 50 seconds at 100° F. and normally susceptible to sludging after sulfuric acid treatment which comprises mixing said petroleum distillate prior to treatment with sulfuric acid with from about 0.1% to about 5.0% of an uncracked petroleum residue having a sulfur content from about 2.0% to about 4.0%, a Saybolt furol viscosity at 210° F. of about 300 seconds to about 600 seconds and subsequently drastically treating the mixture with fuming sulfuric acid.

7. The method of preparing a sludge resistant transformer oil which comprises mixing a transformer oil distillate having a gravity of about 25.7 to about 26.2 A. P. I. and a viscosity at 100° F. of about 50 to 60 seconds and which is normally susceptible to sludging after sulfuric acid treating with about 0.5% to 1.0% of an uncracked petroleum residue having a gravity of about 9.5 A. P. I. and a furol viscosity at 210° F. of about 400 to 440 seconds, treating said mixture with 1 pound of 93% sulfuric acid per gallon of oil,

neutralizing said acid treated mixture and subsequently percolating said neutralized mixture through fuller's earth to a yield of about 2000 gallons per ton.

8. The method of increasing the sludge stability of a petroleum distillate having a Saybolt Universal viscosity greater than about 50 seconds at 100° F. and normally susceptible to sludging after sulfuric acid treatment which comprises mixing said petroleum distillate prior to treatment with sulfuric acid with from about 0.1% to about 5.0% of an uncracked petroleum residue having a sulfur content from about 0.5% to about 7.0% and a gravity of about 7 A. P. I. to about 11 A. P. I.

9. The method of preparing a sludge resistant transformer oil which comprises mixing a transformer oil distillate normally susceptible to oxidation after treatment with sulfuric acid with about 0.5% to 1.0% of an uncracked petroleum residue, treating said mixture with about 1 pound of 93% sulfuric acid per gallon of oil, neutralizing said acid treated mixture and subsequently percolating said neutralized mixture through fuller's earth to about 2 N. P. A. color, said transformer oil distillate being obtained from a crude oil of the naphthenic crude type, and said uncracked residue being obtained from a crude oil of the Winkler type.

10. The method of preparing a sludge resistant transformer oil which comprises mixing a transformer oil distillate having a gravity of about 25.7 A. P. I. to about 26.2 A. P. I. and a Saybolt Universal viscosity of approximately 50 to 60 seconds at 100° F. and which is normally susceptible to sludging after sulfuric acid treating with about 0.5% to about 1.0% of an uncracked petroleum residue having a gravity of about 9.5 to 10 A. P. I., a Saybolt furol viscosity at 210° F. of approximately 400 to 440 seconds and a sulfur content of about 2.0% to about 4.0%, treating said mixture with one pound of 93% sulfuric acid per gallon of oil, neutralizing the acid treated mixture and subsequently percolating the neutralized mixture through fuller's earth to a yield of about 2000 gallons per ton.

11. The method of increasing the sludge stability of a petroleum distillate having a Saybolt viscosity greater than about 50 seconds at 100° F. and normally susceptible to sludging after sulfuric acid treatment which comprises mixing said petroleum distillate prior to treatment with sulfuric acid with from about 0.1% to about 5.0% of an uncracked petroleum residue having a furol viscosity at 210° F. of approximately 400 to 440 seconds and subsequently drastically treating said mixture with fuming sulfuric acid.

12. The method of preparing a sludge resistant transformer oil which comprises mixing a transformer oil distillate normally susceptible to oxidation after treatment with sulfuric acid with about 0.5% to about 1.0% of an uncracked petroleum residue having a sulfur content of about 0.5% to about 7.0%, treating the mixture with about one pound of 93% sulfuric acid per gallon of oil, neutralizing the acid treated mixture and subsequently percolating the neutralized mixture through fuller's earth to about 2 N. P. A. color.

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