

3,252,887
ELECTRICAL INSULATING OIL
Carl J. Rizzuti, New York, N.Y., assignor to Esso Research and Engineering Company, a corporation of Delaware
No Drawing. Filed Nov. 20, 1962, Ser. No. 239,039
7 Claims. (Cl. 208-14)

This invention relates to novel oils useful as electrical insulating oils. More specifically, this invention relates to electrical insulating oils having a good oxidation resistance without an oxidation inhibitor and a good response to the addition of an oxidation inhibitor. These insulating oils are prepared by blending certain hydrofined oils in definite proportions.

GENERAL

A major factor in the market acceptance of an electrical insulating oil for use in transformers, etc., is good oxidation resistance without the use of added inhibitors. Users of insulating oils have traditionally used uninhibited insulating oils and are suspicious of insulating oils containing inhibitors unless it is known that the insulating oil itself, has a good oxidation resistance. This feeling of insulating oil users is firmly entrenched. It is due partly to a belief that an inhibitor can be destroyed in the oil or volatilized by severe heat or extreme overloads, and partly to a fear that the insulating oils made by inhibiting poor base stocks give an insufficient warning of coming breakdowns. Thus, while it is not clear how the oxidation resistance of an uninhibited insulating oil relates to its performance when fortified with an inhibitor, it is clear that in order to have a marketable product, the oil, per se, must show an excellent uninhibited oxidation resistance. It is to this end, then, that insulating oil manufacturers continually strive.

Oxidation resistance is customarily tested by the conventional Doble oxidation test for electrical insulating oils developed by the Doble Engineering Company of Belmont, Massachusetts, and is described in ASTM Standards on Electrical Insulating Liquids and Gases, D-27, December, 1959.

In the Doble oxidation test, an oil, heated to 95° C., is blown with air in the presence of coils of copper and iron wire which serve as catalysts. At periodic intervals, portions of the oil are withdrawn and examined for neutralization number, sediment or sludge formation (after 5:1 volume naphtha dilution), and interfacial tension. The times required for the formation of visible sludge, for the neutralization number to increase to 0.2 mg. of KOH per gram of oil, and for the interfacial tension to decrease below 15 dynes per centimeter are reported. A satisfactory oil must have a minimum life of at least 48 hours before reaching any of these three conditions. The interfacial tension aspect of the test is considered to be an indication of impending breakdown while the neutralization number and sludge formation aspects are more definitive. The Doble life is taken as that point (in hours) where the neutralization number reaches 0.20 or visible sludge is first noticed.

DISCOVERY

It has now been discovered that blends of two hydrofined petroleum distillates, one hydrofined at a low temperature and the other hydrofined at a high temperature, result in insulating oils having a good oxidation resistance without an oxidation inhibitor and a good response to the addition of an oxidation inhibitor, e.g., 0.3 wt. percent of 2,6-ditertiary butyl-4-methylphenol. Insulating oils prepared according to the present invention will satisfactorily pass the accepted industrial standards, e.g., some

inhibited oils have a Doble oxidation life exceeding 1000 hours.

According to this invention, the two hydrofined distillates are blended in proportions of from 40 to 95 vol. percent, e.g., 55 to 90 vol. percent of the high temperature hydrofined distillate and from 60 to 5 vol. percent, e.g., 45 to 10 vol. percent of the low temperature hydrofined distillate. Especially preferred are those blends containing from about 60 to 70 vol. percent of the high temperature hydrofined distillate.

Suitable oxidation inhibitors include polyalkyl aryl hydroxy compounds such as 2,6-ditertiary butyl-4-methylphenol, 2,4-dimethyl-6-tertiary octyl phenol, etc., as well as the various amines, e.g., diphenyl amine, phenyl-B-naphthylamine, etc. These oxidation inhibitors will generally be present in amounts of from 0.01 to 1.0 wt. percent or more.

Other additives such as metal deactivators (e.g., disalicylal-ethylene diamine), etc., may also be included in varying proportions.

PREPARATION

The distillates employed in the hydrofining process should preferably be derived from naphthenic crudes. Suitable crudes are Webster, Thompson, Sugarland and Amelia. The distillates can be obtained from the naphthenic crudes by conventional atmospheric distillation and will contain from 40 to 95 vol. percent or more, e.g., 65 to 75 vol. percent naphthenes. Both distillates (both before and after hydrofining) should have a boiling point in the range of 450° to 900° F., preferably in the range of 460° to 775° F.; an API gravity in the range of 25° to 30°, preferably in the range of 26° to 28.5°; and a viscosity at 100° F. in the range of 55 to 75 SSU. By "boiling point," as used herein, it is meant that the temperature at which 5 vol. percent is first distilled off and the final boiling point will both fall within the cited temperature range.

The hydrofined oils are prepared in a conventional manner by contacting the naphthenic distillates with a hydrofining catalyst in the presence of hydrogen. The temperature of operation is important, as can be seen from Table I, infra. At the present time, it is not known why a change in the temperature of hydrofining should produce such unexpected results in both the inhibited and uninhibited Doble oxidation life. The data shown in Table I clearly demonstrate this phenomenon, however.

Table I, which follows, shows the effect of hydrofining temperature on the hydrofined product in terms of Doble oxidation stability.

TABLE I.—EFFECT OF HYDROFINING TEMPERATURE ON DOBLE OXIDATION STABILITY (UNINHIBITED)
Catalyst: Cobalt molybdate on alumina (Harshaw 0301P)
750 p.s.i.g., 2.0 v./v./hr.
450 s.c.f./bbl. H₂
1.0 lb./gal. Bennett-Clark clay @ 300° F. (contacted)

Temperature, ° F.	475	575	625	675
Sample No.	1	2	3	a 4
Hrs. to 0.2 Neut. No.	240	120	b 72	c 48
Hrs. to Trace Sludge		72	72	48
Hrs. to 15 dynes/cm. interfacial tension	240+	120+	72	48

a — 0.7 lbs./gal. clay.
b — Neut. No. 0.31 at 72 hours.
c — Neut. No. 0.81 at 48 hours.

The first distillate used in the present invention is hydrofined at a temperature, generally from 630° to 670° F., preferably from 640° to 660° F., e.g., 645° to 655° F. This results in a hydrofined oil having rather mediocre,

uninhibited oxidation resistance, but a very good response to the addition of an inhibitor. The practical upper limit to the temperature of hydrofining these naphthenic distillates appears to be about 675° F. in large scale operations. While laboratory techniques will permit higher temperatures to be used, refinery experience has revealed that thermal cracking of the feed material becomes a problem above 675° F.

The second distillate is hydrofined at a low temperature, generally from 555° to 595° F., preferably at from 565° to 585° F., e.g., 570° to 580° F. This results in a hydrofined oil having a rather poor response to the addition of an inhibitor, but a good uninhibited oxidation resistance.

During hydrofining, the feed rate is important. Best results are obtained when the feed rate is in the range of 1 to 3 volumes of feed per volume of catalyst per hour (v./v./hour). Two hundred to 900 standard cubic feet (s.c.f.) per barrel of free hydrogen are used in the hydrofining zone during the treatment of the distillates. Pressure is not critical and can be on the order of 500 to 900 p.s.i.g., e.g., 750 p.s.i.g. Any suitable hydrofining catalyst can be used such as cobalt molybdate on alumina, and the like. It is preferred to use catalysts of the type known commercially as Harshaw 0301P and Harshaw 0601P sold by the Harshaw Chemical Company, Cleveland, Ohio. This hydrofining operation is well known to those skilled in the art and involves passing the distillate, diluted with hydrogen, at the indicated feed rate and temperature, over a fixed bed of the catalyst.

The high temperature and the low temperature hydrofined distillates will most preferably boil (5 vol. percent off to final boiling point) from about 590° to 700° F., have an API gravity of from 26 to 28.5°, a viscosity at 100° F. in the range of 55 to 65 SSU, and will contain from 40 to 95 vol. percent, e.g., 65 to 75 vol. percent naphthenes.

The hydrofined distillates are then blended together after clay contacting or percolation of the individual hydrofined distillates. Alternatively, the blend itself may be treated with clay rather than first treating the individual distillates.

Clay contacting and percolation are well established petroleum processes and involve decolorizing and stabilizing the oils by contact with finely divided clays such

of 75° to 225° F. and usually from 0.4 to 1.5 lb./gal. of absorbent clay is used.

EXAMPLES

The present invention will be more clearly understood by reference to the following specific examples which include a preferred embodiment.

The high temperature hydrofined distillate used in the following blends was obtained by hydrofining a distillate boiling in the range of 590° to 700° F. obtained from a naphthenic crude. This crude was obtained from a pool and is believed to be predominantly Thompson, and possibly includes a small amount of Webster. The hydrofining was carried out over a cobalt molybdate catalyst sold commercially as Harshaw 0301P by the Harshaw Chemical Company. The temperature of hydrofining was 650° F. and the pressure was 750 p.s.i.g. The feed rate was 2 v./v./hr. and the hydrogen consumption rate was 450 s.c.f./bbl. The hydrofined distillate was then treated with a natural type clay (Attapulugus). 0.7 lbs. of clay per gallon of oil was used. The oil was contacted at a temperature of 300° F. for 0.5 hours. The finished oil had a boiling range of about 590° to 700° F., an API gravity of 27.3°, a viscosity at 100° F. of 58.3 SSU, and contained about 65 vol. percent naphthenes.

The low temperature hydrofined distillate used in the following blends was obtained by hydrofining the same distillate as used for the high temperature operation. The temperature of hydrofining was 575° F. and the pressure was 750 p.s.i.g. The feed rate was 2 v./v./hr. and the hydrogen consumption rate was 450 s.c.f./bbl. The hydrofined distillate was then treated with a natural type clay (Attapulugus). 0.7 lbs. of clay per gallon of oil was used. The oil was contacted at a temperature of 300° F. The finished oil had a boiling range of about 590° to 700° F., an API gravity of 27.3, a viscosity at 100° F. of 58.3 SSU, and contained about 65 vol. percent naphthenes.

These two hydrofined distillates (similar in all respects except for temperature of hydrofining) were blended in the proportions as indicated in Table II, infra. Shown in Table II are the results of the Doble oxidation test on both the uninhibited and inhibited blends of oils. The inhibited blends contained 0.3 wt. percent of 2,6-ditertiary butyl-4-methylphenol, a commercially available oxidation inhibitor.

TABLE II.—EFFECT OF BLENDING HYDROFINED DISTILLATES ON DOBLE OXIDATION STABILITY

Vol. percent hydrofined at 575° F.-----	100	75	50	35	25	0
Vol. percent hydrofined at 650° F.-----	0	25	50	65	75	100
Uninhibited:						
Hrs. to 0.2 Nent. No.-----	130	96	81	78	55	36
Hrs. to Trace Sludge-----	72	72	72	72	72	48
Hrs. to 15 dynes/cm. interfacial tension-----	96	144	144	86	60	40
Inhibited ¹ :						
Hrs. to 0.2 Nent. No.-----	432	480	416	1,204	1,344	1,515
Hrs. to Trace Sludge-----	408	480	480	1,152	1,320	1,515
Hrs. to 15 dynes/cm. interfacial tension-----	>552	>480	>552	>1,320	>1,368	>1,896

¹ 0.3 wt. % of 2,6-ditertiary butyl-4-methylphenol.

as fuller's earth or bleaching clays. Clay contacting consists of rapid batch mixing of the oil and finely ground (over 200 mesh) activated clay followed by filtration. The clay is discarded after use.

Clay percolation involves percolating the oil through a deep bed of rather coarse (30–60 mesh) clay. Percolation is allowed to continue until the color of the oil meets the specifications. The oil is removed from the percolating zone and the clay is washed with naphtha, steamed, and roasted at 1000° F. prior to reuse. The activity of the clay gradually decreases and it is eventually discarded.

The clays remove impurities from the oils and increase their oxidation stability. Suitable industrial clays useful in this invention are Bennett-Clark natural clay and Attapulugus clay. In clay contacting, usually from 0.4 to 1.5 lb./gal. of absorbent clay is contacted with the distillate oil at temperatures of about 300° F. Clay percolation is generally carried out at temperatures in the range

It is evident from the data shown in Table II that blends containing from 55 to 90 vol. percent, e.g., 60 to 70 vol. percent, of the high temperature (650° F.) hydrofined distillate have a good uninhibited oxidation resistance and a good response to the addition of an oxidation inhibitor. These properties are far superior to those one would expect from a knowledge of the properties of the individual hydrofined distillates. That is to say, that one would expect a 65/35 blend of the hydrofined distillates to have properties approximately two-thirds of the way between those of the two individual hydrofined distillates. It can be noted that the properties of a 65/35 blend as shown in Table II results in an insulating oil having substantially the better properties of both individual oils, these properties being well above the expected average.

Having described the present invention with a certain degree of particularity, it is to be realized that various

5

modifications can be made within the spirit and scope of the invention as hereinafter claimed.

What is claimed is:

1. An oil useful as an electrical insulating oil consisting essentially of:

(a) a blend of 55 to 90 vol. percent of a high temperature hydrofined distillate hydrofined at a temperature in the range of 630° to 670° F. and boiling in the range of 450° to 900° F., and

(b) 45 to 10 vol. percent of a low temperature hydrofined distillate hydrofined at a temperature in the range of 555° to 595° F. and boiling in the range of 450° to 900° F.,

(c) said hydrofined oils being individually prepared by contacting a distillate from a naphthenic crude with a hydrofining catalyst at a feed rate of 1 to 3 v./v./hour and at a pressure of 500 to 900 p.s.i.g. in the presence of from 200 to 900 s.c.f./bbl. of hydrogen followed by treating the hydrofined distillate oils with an absorbent clay.

2. An inhibited oil useful as an electrical insulating oil comprising a major proportion of the oil as defined in claim 1 and from 0.01 to 1.0 wt. percent of an oxidation inhibitor.

3. An oil useful as an electrical insulating oil as defined in claim 1 wherein said high temperature hydrofined oil is hydrofined at a temperature of from 640° to 660° F. and said low temperature hydrofined distillate is hydrofined at a temperature of from 565° to 585° F.

4. An oil useful as an electrical insulating oil as defined in claim 3 wherein the high temperature hydrofined distillate and the low temperature hydrofined distillate boil within the range of about 590° to 700° F.

5. An oil useful as an electrical insulating oil consisting essentially of:

(a) from 60 to 70 vol. percent of a hydrofined oil hydrofined at a temperature of from 645° to 655° F., boiling in the range of about 590° to 700° F., having an API gravity of from 26 to 28.5° and a viscosity at 100° F. of from 55 to 65 SSU, and

(b) from 40 to 30 vol. percent of a hydrofined oil hydrofined at a temperature of from 570° to 580° F., boiling in the range of about 590° to 700° F., having an API gravity of from 26 to 28.5° and a viscosity at 100° F. of from 55 to 65 SSU,

6

(c) said hydrofined oils being individually prepared by contacting a distillate obtained from a naphthenic crude boiling in the range of about 590° to 700° F. with a hydrofining catalyst at a feed rate of 1 to 3 v./v./hour and at a pressure of 500 to 900 p.s.i.g. in the presence of from 200 to 900 s.c.f./bbl. of hydrogen followed by contacting the hydrofined distillate oils with from 0.4 to 1.5 lbs./gal. of an absorbent clay.

6. An oil useful as an inhibited electrical insulating oil comprising a major proportion of the insulating oil as defined in claim 5 and an oxidation inhibiting amount of 2,6-ditertiary butyl-4-methylphenol.

7. An oil useful as an electrical insulating oil which comprises:

(a) a blend of 55 to 90 volume percent of a high temperature hydrofined distillate hydrofined at a temperature of from 630° to 670° F., boiling in the range of 450° to 900° F. and having an API gravity of from 25° to 30°, and

(b) 45 to 10 vol. percent of a low temperature hydrofined distillate hydrofined at a temperature of from 555° to 595° F., boiling in the range of 450° to 900° F. and having an API gravity of from 25° to 30°,

(c) said hydrofined oils being individually prepared by contacting a distillate from a naphthenic crude with a hydrofining catalyst at a feed rate of from 1 to 3 v./v./hour and at a pressure of 500 to 900 p.s.i.g. in the presence of from 200 to 900 s.c.f./bbl. of hydrogen followed by treating the hydrofined distillate oils with an absorbent clay.

References Cited by the Examiner

UNITED STATES PATENTS

3,000,807 9/1961 Wasson et al. ----- 208—14

FOREIGN PATENTS

589,150 6/1947 Great Britain.

DELBERT E. GANTZ, *Primary Examiner.*

ALPHONSO D. SULLIVAN, *Examiner.*

H. LEVINE, *Assistant Examiner.*