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3,462,358
**CLAY TREATMENT OF HYDROREFINED
 CABLE OILS**

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ABSTRACT OF THE DISCLOSURE

Cable oils having ASTM D-1934 aged dissipation factors (ADF) below 0.010 are produced from severely hydrorefined 500-2000 SUS (100° F.) naphthenic oil having an ADF greater than 0.015 by contacting the hydrorefined oil at from 100-400° F. with activated adsorbent clay in an amount per barrel of oil such that from 10-90 grams of KOH would be required to neutralize the acidity of the clay.

BACKGROUND OF THE INVENTION

This invention relates to methods of producing improved cable oils, to superior cable oil compositions, and to electrical cables containing such oils.

Although some cable oils are produced by synthesis, as by the polymerization of olefins, such as octenes, butenes, and propylene, the more satisfactory cable oils are produced by refining selected fractions of naphthenic crude oils. For example, despite the very low ASTM D-1934 initial (IDF) and aged (with copper for 96 hours at 115° C.) dissipation factors (ADF) of the polybutene cable oils (ADF in the order of 0.005), they suffer from the disadvantages, when compared to refined naphthenic oils, of increased volatility, thermal instability, oxidation instability, and poor electrical properties in a closed-system oxidation test.

It has also been found that cables containing polybutene oils are not superior in electrical characteristics to cables containing refined naphthenic oils, thus, showing that a low dissipation factor is not the sole criterion for a cable oil. However, due to the market appeal of a low ADF, the petroleum refiner is actively seeking means (other than by the addition of non-hydrocarbon inhibitors) of further lowering the ADF of present naphthenic cable oils (0.04-0.10) which are conventionally refined from naphthenic distillates by solvent extraction (as with furfural) followed by treating with sulfuric acid and clay contacting. Illustrative of such processing are British Patent 526,863 and British Patent 946,540. Frequently the naphthenic distillates have been treated to remove naphthenic acids for example, as by the processes disclosed in the following U.S. Patents: 1,603,174; 2,770,580; 2,795,532; 2,966,456; and 3,080,312.

It is known to produce transformer oils, having viscosities in the range of 55-75 SUS at 100° F., by hydrogenation followed by contacting with a fuller's earth bleaching clay (e.g., see U.S. 3,252,887).

SUMMARY OF THE INVENTION

We have found that superior cable oils (having viscosi-

ties at 100° F. from 500-6000 SUS) of very low ADF can be produced from naphthenic lube oil fractions (which are, preferably, but not necessarily, caustic treated to remove naphthenic acids) by severe hydrorefining followed by clay contacting of the resulting hydrogenated naphthenic oil. Solvent extraction and H₂SO₄ treatment can be eliminated and yields are excellent. As used herein, the term "clay contacting" refers to either percolation methods or to slurry and filtration techniques. The term "hydrogenated naphthenic oil" also refers to "synthetic naphthenic oils," such as the cable oils of U.S. 3,287,259 which are obtained by hydrogenation of an aromatic oil.

In the case of the high viscosity cable oils (4000-6000 SUS at 100° F.), we have determined that a relatively inexpensive fuller's earth bleaching clay is preferred and the dosage of clay is not particularly critical. However, we have discovered, surprisingly, that with the lower viscosity cable oils (500-2000 SUS), if solvent extraction and H₂SO₄ treatment are eliminated, the more costly acid-activated adsorbent clays must be used and the dosage must be within very narrow, critical limits if one wishes to obtain a cable oil having an ADF which approaches that of the synthetic oils (below 0.010).

That is, we have discovered that a novel cable oil, with an ADF below 0.010 and which requires at least 75 hours at PFVO test conditions to reach a 6 percent power factor, can be obtained from a severely hydrorefined 500-2000 SUS naphthenic oil, having an ADF above 0.015, by contacting such oil at 100-400° F. (preferably 200-300° F.) with an adsorbent comprising an acid-activated adsorbent clay in an amount per barrel of oil such that from 10-90 grams of KOH would be required to neutralize the acidity of said acid-activated adsorbent clay.

We have further discovered that there is less variation in the ADF of these cable oils caused by the usual variations in charge stock which are encountered in continuous plant production when, in addition to the acid-activated clay, the adsorbent comprises from 5-20 lb./bbl. of a natural fuller's earth bleaching clay, such as attapulgite.

DESCRIPTION OF THE INVENTION

Commercial transformer oils (having viscosities from 55-75 SUS at 100° F.) customarily are tested by the Doble Oxidation Test for electrical insulating oils developed by the Doble Engineering Company of Belmont, Mass. This procedure has been described in ASTM Standards on Electrical Insulating Liquids and Gases, pages 307-313, December 1959, under the title "Suggested Method of Test for Oxidation Characteristics of Mineral Transformer Oil." It involves bubbling air through a known amount of the oil held at a temperature of 95° C. in the presence of copper and iron and making two types of test daily on small samples of the oil. One type of test is an acidity measurement. The other is a precipitation test in which one volume of the oil is diluted with five volumes of pentane, the mixture is allowed to stand at least eight hours, and the presence or absence of a sludge precipitate is noted.

An amplification of the Doble Oxidation Test is the so-called Power Factor Valued Oxidation (PFVO). This involves operating in the manner described above but also determining the power factor of the oil at two-hour intervals throughout the oxidation period. A curve is obtained by plotting the power factor against the oxidation time. The PFVO method is more fully described in *Journal of the Electrochemical Society*, 112, 390-395 (1965).

Although the Doble Oxidation Test is not a usual specification for cable oils, the PFVO curve of a cable oil is an indication of the quality of the oil. In particular, a good measure of oxidation stability of a cable oil is the time required, under test conditions, for the oil to reach a power factor of 6%. The longer the time required to reach a 6% power factor, the better the oil.

The PFVO continuous power factor curves (percent power factor vs. time) of the 500-2000 SUS cable oils produced by our "mixed clay contacting" are also very favorable. In particular, after 150 hours of Doble oxidation testing certain of our oils exhibit only about a 6% power factor. In contrast, the hydrorefined oils which have not been contacted with clay reach a 6% power factor in as little as 25 hours.

The base oils which are severely hydrorefined are obtained for example, by vacuum distillation of naphthenic crude oils (as in U.S. 3,184,396), especially those naphthenic crude oils wherein the 1500-3000 SUS (at 100° F.) distillate fractions have viscosity-gravity constants from 0.84 to 0.92. Preferably, the base oils should be substantially free of naphthenic acids prior to the hydrorefining (in order to reduce hydrogen consumption). Usually materials boiling below about 600° F. are removed from the hydrorefined oils, as by atmospheric distillation, prior to clay contacting. The viscosity of the base oil, or of the final hydrorefined oil, can be adjusted by the addition of other naphthenic oils of higher or lower viscosity. For example, we prefer to obtain our cable oils having viscosities at 100° F. in the range of 500-2000 SUS by blending hydrogenated oil having a viscosity from 300-600 SUS with hydrogenated oil having a viscosity from 1500-3000 SUS and then contacting the resulting blended oil with our adsorbent.

By severe hydrorefining, we refer to processes conducted in the presence of a hydrogenation catalyst at from about 500-750° F. and from 800-3000 p.s.i. of hydrogen at a fresh feed liquid hourly space velocity (LHSV) of from 0.1-8.0 (usually below 2.0), preferably conducted either in vapor phase or trickle phase. Product recycle, for example, as in U.S. 2,900,433 can be used to increase severity. Recycle liquid hourly space velocity can vary from 0 to 20; however, we prefer to operate at total liquid throughputs that obtain a greater than 25% of flooding velocity and more preferably at from 40-98% of flooding velocity.

Preferably the temperature is below that at which substantial cracking occurs, that is, no more than 20 weight percent (preferably less than 10%) of the feed stock is converted to material boiling below 300° F. Although the maximum hydrogenation temperature which will not produce substantial cracking is somewhat dependent upon the space velocity, the type of catalyst and the pressure, generally it is below 750° F. To allow a margin of safety, we prefer to operate below 700° F. At total pressures below about 2000 p.s.i. we prefer a temperature below about 650° F., since above that temperature the degradation of oil viscosity becomes large.

Typical of such severe hydrorefining methods, when conducted within the aforementioned processing conditions, are those of U.S. 2,698,614; 2,993,855; 3,012,963; 3,114,701; 3,144,404; and 3,278,420.

Typical catalysts are molybdenum oxide, nickel oxide, cobalt-molybdenum oxides, nickel-molybdenum oxides, cobalt-nickel molybdenum oxides and tungsten-nickel molybdenum oxides, preferably presulfided and on a carrier such as silica, alumina, alumina-titania and aluminosilicates (either crystalline or amorphous). Nickel sulfide, nickel-molybdenum sulfide, tungsten disulfide, nickel-tungsten sulfide and molybdenum disulfide, per se or on a carrier, can also be used as catalysts. Examples of operable catalysts are those of U.S. 2,744,052; 2,758,957; 3,053,760; 3,182,016; 3,205,165; 3,227,646; and 3,264,211.

We prefer that such severe hydrogenation or hydrorefining be a trickle phase process at 575-625° F. and 1000-2000 p.s.i. of hydrogen using a catalyst comprising nickel and/or molybdenum sulfides on alumina or silica.

As has been noted in U.S. 2,973,315, the severity of hydrogenation can be measured by the hydrogen consumption; however, with cable oils we prefer to follow severity by observing the decrease in ultraviolet absorbency in the 260 millimicron region hereinafter sometimes referred to as "260 UVA." That is, due to hydrogenation of polycyclic aromatic hydrocarbons, the resulting hydrogenated oil will have a lower ultraviolet adsorbency in the 260 millimicron region than will the base oil before hydrogenation. Severe hydrogenation will produce a hydrorefined oil having a 260 UVA which is less than 60% of the 260 UVA of the base oil. Typically, after severe hydrogenation, the 260 mm. adsorbency is less than 10 for a 4000-6000 SUS oil, less than 8 for 900-3000 SUS oil, and less than 6 for a 300-800 SUS oil. Preferably, a severely hydrorefined naphthenic oil (at 100° F.) in the 500-2000 SUS viscosity range will have a UVA at 260 mm. of less than 7.5 and, more preferably, less than 6.0.

Preferably, in the 300-6000 SUS range, the hydrogenated oil will contain less than 0.2% of sulfur and less than 500 p.p.m. of nitrogen. The ADF of the higher viscosity (above 4000 SUS) severely hydrorefined oils will be less than 0.010 but the lower viscosity (below 1000 SUS) severely hydrorefined oils will have ADF's above 0.015, typically above 0.020, and will require no more than 30 hours under PFVO test conditions to reach a 6% power factor.

Due to differences in aromatic, sulfur and nitrogen contents of the base oils, hydrogen consumption can vary greatly; however, for severe hydrorefining of caustic treated naphthenic lube fractions hydrogen consumption is usually at least 150 s.c.f. per bbl. (excluding hydrogen which may be dissolved in the oil). Hydrogen consumption will, of course, be greater if the lube fraction is not substantially free of naphthenic acids.

In contrast, mild hydrogenation processes normally consume less than 150 s.c.f. of H₂/bbl. (unless the lube fraction has an appreciable naphthenic acid content) and are characterized by little change in polycyclic aromatic content of the oil. Mild hydrogenation is frequently termed "hydrotreating" and is usually conducted below 800 p.s.i. of hydrogen or below 500° F. Typical illustrations of mild hydrogenation treatment are found in U.S. 2,865,849; 2,921,025; 2,944,015; and 3,011,972.

Table I illustrates the difference in the reduction of UVA and in hydrogen consumption between mild hydrogenation (at 450° F. and 1000 p.s.i. of H₂) of a caustic treated naphthenic lube (which was substantially free of naphthenic acids) and severe hydrorefining at 1000 p.s.i. and 550, 600 and 650° F., respectively. Except for run No. 10, which was run at a total feed liquid hourly space velocity (LHSV) of 3.65, the total feed LHSV was 4.0. The catalyst was sulfided nickel molybdenum oxides on Al₂O₃.

TABLE I

Run No.	Temp., ° F.	Viscosity (SUS at 100° F.)		Percent decrease	UVA at 260 mm.		Percent decrease	Hydrogen Consumption, ³ s.c.f./bbl.	Wt. percent S		Nitrogen (p.p.m.)	
		Charge	Product		Charge	Product			Charge	Product	Charge	Product
1	450	107	107	0	8.1	6.0	26	80	0.23	0.16		
2	450	544	508	6.6	9.3	6.6	29	80	0.24	0.15		
3	450	2,901	2,711	6.6	10.7	9.1	15	30	0.24	0.20		
4	550	107			8.1	3.1	62	190	0.23	0.07		
5	550	2,764	2,448	11.2	11.3	6.4	43	190	0.31	0.12		
6	600	107	101	5.6	8.1	1.9	89	215	0.23	0.02	170	47
7	600	544	415	23.8	9.3	3.4	63	250	0.24	0.06	246	131
8	600	2,901	2,160	25.5	10.7	4.0	63	255	0.24	0.14	467	313
9	600	6,146	4,792	22.1	11.6	5.5	53		0.38	0.12		
10	600	2,139	3,794			3.4				0.05		
11	600	5,791	4,090	29.4	12.8	6.3	51			0.09		
12	600	5,911	4,316	26.9	13.4	6.2	46		0.38	0.13		
13	650	107	90	15.9	8.1	1.5	81	325	0.23	0.02		
14	650	544	387	28.9	9.3	2.0	78	300	0.24	0.02		
15	650	2,901			10.7	3.3	69	270	0.24	0.06		

¹ Fresh feed LHSV=0.15, all other runs at 0.5 LHSV. All runs at recycle LHSV of 3.5.

² Viscosity at 210° F.

³ Assuming 100% recovery of dissolved H₂.

The preferred cable oils are those obtained by our acid-activated clay treatment of hydrogenated oils having a viscosity in the range of 500–2000 SUS at 100° F., a UVA less than 6 at 260 mm. and containing only naphthenic lube fractions which have been catalytically hydrorefined at a temperature in the range from 500–750° F. at 800–3000 p.s.i. of H₂. However, our invention also encompasses the contacting, with an adsorbent comprising acid-activated clay, of blends of such a hydrorefined oil with minor quantities of synthetic "paraffin" oils which are olefin-free and/or hydrotreated oils and/or catalytically cracked oils (e.g., see U.S. 3,095,366) including cycle oils and catalyst-free bottoms and/or naphthenic oils which have been conventionally refined, as by solvent extraction and/or sulfuric acid treatment. Such blending can at times be an economical means of obtaining a desired viscosity or of adjusting the aromatic hydrocarbon content of the cable oil.

Viscosity can also be adjusted by blending two or more severely hydrorefined naphthenic oils prior to the clay contacting (e.g., the product oils of Run #7 and Run #8 of Table I can be blended to produce oils having viscosities, at 100° F., from 700–1000 SUS).

The acid-activated adsorbent clay is conventionally prepared by processes such as those disclosed in U.S. 1,397,113 and Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 4, 1949, pp. 55–57, involving, for example, sulfuric acid digestion of subbentonite (montmorillonite) clay. The acid-treated clay is usually washed with water in order to remove excess sulfuric acid and the washed clay is generally dried or calcined at elevated temperatures in order to adjust the water content of the finished clay. The dried clay can be solvent treated, if desired, to remove elemental sulfur, such as by the process of U.S. 2,949,421.

Because of differences in raw materials and process variations by manufacturers of commercial adsorbents, slight differences in the ADF of the refined oil are encountered when using various brands and grades of a given kind of adsorbent clay. However, in all cases a decided improvement results when these varied commercial adsorbents are used in accordance with the teachings of the present invention. For example, from 2–12 mg. of KOH per gram of clay can be required to neutralize the acidity of commercial acid-activated adsorbent clays by titration to pH 7—yet all such clays can advantageously be used in accordance with the present invention if used in an amount per barrel of oil such that from 10–90 grams of KOH would be required to neutralize the acidity of the clay.

Preferably, with oils of 700–1000 SUS (at 100° F.), an ADF greater than 0.015 and a 260 UVA below 6.0, the acid-activated clay is used in an amount per barrel of oil such that the acidity of the clay is equivalent to the acidity contributed by 8–12 lb. of the preferred commercially available acid-activated clays, which have acidities equivalent to 6±0.5 grams of KOH per gram of clay. This is an amount of clay per barrel of oil such that from 20–40

grams of KOH would be required to neutralize the acidity of the clay. That is, for each barrel of such a hydrorefined oil, from 36 to 48 lbs. are required for an acid-activated adsorbent clay having an acidity equivalent to 2 mg. of KOH per gram of clay. Similarly, from 4–6 lb./bbl. are required of a clay having an acidity equivalent to 12 mg. KOH/g. clay.

The clay contacting of the oil can be by the usual methods, such as by percolation of the oil through a bed of the adsorbent material at temperatures sufficiently high to allow a reasonable rate of flow through the bed or by "contact filtration" (or "slurry and filtration") in which procedure the oil is mixed with finely divided adsorbent to form a slurry and the mixture is filtered in a conventional manner. In either method the oil can be diluted with a non-reactive solvent, such as isooctane, to decrease contact time and/or to increase filtration rates.

To reduce clay consumption when contacting below about 200° F. the adsorbent admixture should be substantially free of "uncombined" water; therefore, the usual commercially available clays (which can contain large amounts of water) should be dried, as in an oven, or, preferably "activated" by such well known procedures as roasting.

It is sometimes advantageous to contact the severely hydro-refined oil with adsorbent admixtures containing, in addition to the acid-activated clay, from 10 to 50% by weight of a natural bleaching clay, such as attapulgite, and/or from 5 to 25% of bauxite or activated carbon.

Clay/oil contact times are conventional, usually from 2–120 minutes. Preferably, contact time is as brief as can be obtained with the available refinery equipment. Contact temperatures as high as 400° F. may be used. However, if it is desired to operate above about 350° F., it is advisable to chose those adsorbent admixtures which do not possess substantial catalytic cracking activity.

ILLUSTRATIVE EXAMPLES

In the following examples, Examples II and VIII illustrate practice of our present invention. The remaining examples are presented in order to assist in understanding the advantages of our invention.

Example I shows that when an 880 SUS naphthenic oil is severely hydrorefined and then contacted with 10, 15, or 20 lbs./bbl. of attapulgite clay, the ADF of the resulting oil is about 33 percent less than the ADF of the hydro-refined oil before clay contacting.

Example II shows that when clay contacted with 10 lbs./bbl. of an acid-activated clay, the ADF of the resulting cable oil is 61 percent less than that of the hydro-refined oil.

Example III and Example IV show that there is only a narrow range of dosage of the acid clay within which one can obtain our novel 500–2000 SUS naphthenic cable oil having an ADF below 0.010.

Examples V and VI show that increasing the clay dosage to 20 or 25 lbs./bbl. produces an oil with a higher ADF than is produced at dosages of 5 or 15 lbs./bbl. and that,

if one is not aware of the surprising results obtainable in the narrow dosage range of 8–12 lbs./bbl. of the acid-activated clay, one would be led to conclude that it would be detrimental to the ADF of the final oil to contact at greater than 5 lbs./bbl. of acid-activated clay.

Example VII shows that the adverse effect on the ADF of contacting with too large a dosage of acid-activated clay can be alleviated or mitigated by contacting with a mixture comprising an acid-activated clay and a naturally occurring bleaching clay, such as attapulgite.

Example VIII illustrates a preferred embodiment of the invention whereby a novel cable oil is produced and wherein the contacting is effected with 20 lbs./bbl. of a 1:1 weight mixture of an acid-activated clay and a naturally-occurring fuller's earth bleaching clay.

Example IX is representative of conventional cable oils prepared by solvent refining, H_2SO_4 treating and clay contacting.

Example X shows that a novel 5000 SUS cable oil having an ADF less than 0.010 can be obtained if severely hydrorefined oil is contacted with a naturally occurring bleaching earth (which is much less costly than the acid-activated clay).

Example XI shows the production of an 880 SUS cable oil, with an ADF as low as that of commercial polybutene cable oils, which is produced by sulfuric acid refining of the severely hydrorefined naphthenic oil followed by contacting with a naturally occurring fuller's earth bleaching clay. This clay contacted, sulfuric acid-refined, severely hydrorefined oil is novel and has a superior ADF in comparison with the novel, severely hydrorefined oil of Example VIII which was further refined by mixed clay contacting; however, the H_2SO_4 treated oil has the less desirable power factor after 150 hours at PFVO test conditions.

In the following examples, all ultraviolet absorbency measurements (UVA) are at 260 millimicrons and all viscosity measurements are made at 100° F. unless otherwise noted. The barrel (bbl.) refers to the usual industrial petroleum unit equal to 42 U.S. gallons.

Example I

An 880 SUS naphthenic oil, boiling mainly in the range of 630° F. to 940° F., and having an ultraviolet absorbency of 10 in the 260 millimicron region is prepared by blending 500 SUS and 2500 SUS naphthenic lube fractions, which are obtained, by the process described in U.S. 3,184,396, from a naphthenic crude blend having a viscosity-gravity-constant of 0.890. This 880 SUS oil is hydrogenated at 1000 p.s.i. of hydrogen (1200 p.s.i.g. total pressure) at 600° F., using pre-sulfided nickel-molybdenum oxides (3% NiO, 15% MoO₃) on alumina (82%) as the catalyst, until the UVA is 3.8. An overhead fraction of 3 volume percent and boiling mainly below 400° F. is removed by distillation from the hydrorefined oil in order to raise the flash point to 400° F. The ADF of this severely hydrogenated oil is 0.0180. It contains 190 p.p.m. of nitrogen. After 24 hours it has a 6 percent power factor.

This 0.018 ADF oil is heated to 220° F. and then 15 lb./bbl. of roasted attapulgite is added, with mixing, to form a clay-oil slurry.

The attapulgite used has a pH of 7.5 (in 10% aqueous suspension) and is an aluminum-magnesium silicate containing 20.1% volatile matter (i.e., removable by heating for 20 minutes at 1700° F.). When heated at 200° F. for 1 hour, the weight loss is 13.3%. The volatile-free clay analyzes 69.9% SiO₂, 12.4% Al₂O₃, 11.2% MgO, 4.1% Fe₂O₃, and 2.2% CaO. Its apparent bulk density is 32 lbs./cu. ft. and it has particles sized such that 95% will pass through a 200 mesh screen.

After 20 minutes of clay/oil contact at 220° F., the clay is separated from the oil by filtration. The resulting refined cable oil has an ADF of 0.0122 (which is 32% less than that of the hydrogenated oil) and contains 123

p.p.m. of nitrogen (which is 35% less than the hydrogenated oil). The oil requires 35 hours to reach a 6% power factor.

Similar results are obtained when the clay dosage is 10 lbs./bbl. or 20 lbs./bbl.

Example II

Example I is repeated except that the adsorbent used is 10 lbs./bbl. of a sulfuric acid-activated montmorillonite clay. This acid-activated clay has an acidity equivalent to 6.31 mg. KOH per gram (pH 2.7), contains 17.8% volatiles on ignition (as measured at 1700° F.) and has a weight loss of 6.7% at 220° F. On a volatile-free basis this clay analyzes 70.9% SiO₂, 17% Al₂O₃, 3.9% Fe₂O₃, 3.2% MgO, 1.6% CaO, 1.0% Na₂O and/or K₂O and 2.0% SO₃. The apparent bulk density is 45 lbs./cu. ft. and 90% of the particles will pass through a 200 mesh screen.

The resulting refined cable oil had an ADF of 0.0070 (which is 61% less than the hydrogenated oil) and contains 69 p.p.m. of nitrogen (which is 64% less than the hydrogenated oil). The ADF of this cable oil is of the same order as those of the better polybutene oils. This cable oil is novel in that the art heretofore has not been able to produce a naphthenic cable oil having a viscosity in the range of 500–2000 SUS (and particularly in the range of 700–1000 SUS) at 100° F. and having an ADF of less than 0.010 before the addition of non-hydrocarbon oxidation inhibitors. An additional novel feature of this oil is that it possesses such unusually good oxidation stability (in the presence of copper) despite its high content (over 50 p.p.m.) of indigenous nitrogen in the form of organic nitrogen compounds. The electrical properties of this new oil are superior to those of the better of the heretofore available naphthenic cable oils, in the 700–1000 SUS viscosity range, which are obtained by conventional refining (see Example IX below) of naphthenic distillates and which contain less than 10 p.p.m. and usually less than 5 p.p.m. of indigenous nitrogen in the form of organic nitrogen compounds.

Severely hydrorefined naphthenic oils (having viscosities in the range of 35–7000 SUS at 100° F.) which are suitable bases for electrical oils of low nitrogen content (under 25 p.p.m.) can be prepared by a single stage catalytic hydrorefining process, such as that of U.S. 2,904,505 wherein the temperature is from 700–750° F., the hydrogen pressure is 1000–2000 p.s.i.g., at 0.5–2.0 LHSV and wherein less than 500 SCF of hydrogen is consumed—provided that the hydrogenation is conducted so that the 260 UVA of the feed is reduced at least 40%. In the case of transformer oils having viscosities from 40–70 SUS at 100° F., it is also important to control the hydrorefining such that the ultraviolet absorbence of the resulting hydrorefined oil in the 335 millimicron region (335 UVA) is in the range of 0.05 to 0.5.

For the production of electrical oils containing less than 10 p.p.m. of nitrogen from naphthenic or aromatic distillates, a two-stage hydrorefining process is preferred, wherein the distillate is first contacted at 550–775° F. with a sulfur-resistant catalyst and from 100–800 p.s.i. of hydrogen to produce a hydro-treated oil boiling mainly above 475° F. and having less than 20 p.p.m. of nitrogen. This low nitrogen oil is then hydrorefined under conditions such that the 335 UVA is from 0.05–0.5 and the nitrogen content is less than 10 p.p.m.

Example III

Example II is repeated except that the adsorbent is 5 lbs./bbl. of the acid-activated clay. The resulting refined oil has an ADF of 0.019 (34% less than the hydrogenated oil) and contains 106 p.p.m. of nitrogen (44% less than the hydrogenated oil). When compared with Example II this example shows that more than 5 lbs./bbl. of acid-clay is necessary if one wishes to obtain a cable oil having an ADF below 0.010.

Example IV

Example II is repeated except that the absorbent is 15 lbs./bbl. of the acid-clay. The resulting refined oil has an ADF of 0.0170 (which is only 5.5% less than the hydrogenated oil), yet the nitrogen content is only 49 p.p.m. (which is 74% less than the base oil). The higher ADF of this oil compared with that of Example II indicates that if the acid-clay dosage is too high, the electrical properties of the oil are adversely effected, probably due to the formation of corrosive sulfonates (or sulfates). Therefore, this example shows that when contacting the severely hydrogenated naphthenic oil, one must use less than 15 lbs./bbl. of the acid-clay in order to obtain a cable oil having an ADF below 0.010. By extrapolation (using the results of Examples II and III), the maximum acid-clay dosage which can be used to make a low viscosity cable oil having an ADF below 0.010 is 12 lbs./bbl. and the minimum dosage of the acid-clay is 8 lbs./bbl.

Example V

Example IV is repeated except that the clay dosage is 20 lbs./bbl. of the acid-activated clay. The resulting refined cable oil has an ADF of 0.016.

Example VI

When Example IV is repeated except that the clay dosage is 25 lbs./bbl., the resulting refined cable oil has an ADF of 0.019. This shows that too great a dosage of the acid-activated clay can cause the ADF of the resulting refined oil to be greater than the ADF of the oil before clay contacting.

Note that if the data of Example II is omitted and the oils of Examples III, IV, V, and VI are compared, it appears that 5 lbs./bbl. of the acid-clay is the maximum clay dosage which should be used in order to improve the ADF of the severely hydrorefined naphthenic oil.

Example VII

Example V is repeated except that the oil is contacted with 25 lbs./bbl. of a mixture of 20 parts by weight of the acid-activated clay and 5 parts by weight of attapulgite. The ADF of the resulting refined cable oil is 0.012.

Example VIII

Example VII is repeated except that the clay dosage is 20 lbs./bbl. of a 1:1 weight mixture of the acid-activated clay and the attapulgite. That is, the oil is treated with the equivalent of 10 lbs./bbl. of the acid-clay and 10 lbs./bbl. of attapulgite. The ADF of the resulting novel refined oil is 0.0075 and it requires over 170 hours to reach a 6% power factor. This oil is representative of a highly preferred class of novel naphthenic cable oils, having an ADF less than 0.010 before the addition of oxidation inhibitors, which can be prepared by our process and which contain more than 10 p.p.m. of nitrogen, have a 260 UVA of less than 6.0, a viscosity in the range of 700-1000 SUS, and which require at least 150 hours at PFVO test conditions to reach a 6% power factor.

Example IX

Example I is repeated except that the 880 SUS base oil is not refined by hydrogenation, but is refined by conventional extraction with furfural (15 volume percent removal) and the resulting (85%) raffinate is contacted with 40 lbs./bbl. of 99% H₂SO₄, and the resulting acidic oil neutralized and washed. This conventionally solvent-refined, H₂SO₄-treated oil is then contacted, using the procedure of Example I, with 15 lbs./bbl. of attapulgite. The resulting oil, which is representative of cable oils produced by conventional refining, has an ADF of 0.069 and contains 2 p.p.m. of nitrogen. Note that this ADF is 10 times greater than the ADF of the novel cable oil of Example II, which contains 69 p.p.m. of nitrogen.

Example X

A 5000 SUS (high viscosity) naphthenic lube fraction is obtained, by the caustic distillation process described in U.S. 3,184,396, from a naphthenic crude blend having a viscosity-gravity-constant of 0.890. This 5000 SUS oil has a UVA of 12.8 and is severely hydrogenated at 1000 p.s.i. of hydrogen and 600° F. (as in Example I) until the UVA is 6.3. The ADF of this severely hydrogenated, highly viscous cable oil is 0.0057. When contacted with 15 lbs./bbl. of attapulgite, by the procedures of Example I, the resulting refined oil has an ADF of 0.0004 and an ADF of 0.0043.

When the 0.0057 ADF hydrogenated oil of this example is treated with 20 lbs./bbl. of 99% H₂SO₄, neutralized and washed, utilizing the procedures of U.S. 2,973,317, and then contacted with 15 lbs./bbl. of attapulgite, the resulting refined oil has a higher ADF than when such H₂SO₄ treatment, neutralization and washing are omitted.

Example XI

The severely hydrogenated 0.0180 cable oil of Example I is contacted with 40 lbs./bbl. of 99% H₂SO₄, neutralized with soda ash and water-washed, utilizing the procedures of U.S. 2,973,317. The resulting H₂SO₄-treated oil is clay contacted, by the procedures of Example I, with 10 lbs./bbl. of attapulgite. The resulting novel, refined cable oil has an ADF of 0.0040 and contains 1.3 p.p.m. of nitrogen. It requires 150 hours to reach a 6% power factor.

Although the ADF of the oil of this example is better than that of the oil of Example VIII, cables made from either of these oils are identical for most commercial purposes; therefore, the process of Example VIII is greatly preferred for commercial operation since the sulfuric acid treatment is more expensive than the cost of the 10 lbs./bbl. of the acid-activated clay used in Example VIII.

Novel naphthenic cable oils having very good electrical properties are also obtained when the naphthenic distillates of the preceding examples are first treated with sulfuric acid, neutralized and washed, then severely hydrorefined (to a UVA less than 6.0) and finally clay contacted with a natural fuller's earth bleaching clay, such as attapulgite.

Electrical cables can be fabricated containing the usual oxidation inhibitors (e.g., see U.S. 3,145,258) and viscosity modifiers, such as waxes (see U.S. 2,914,429) and containing, as an insulating medium, any of the novel oils disclosed herein or mixtures of such oils. Chelating agents, such as the Schiff base additives of U.S. 3,094,583, can also be incorporated in cables containing our novel oils. Such electrical cables, containing our novel oils, possess exceptionally good aging properties.

We claim:

1. Process for producing an improved cable oil having an ASTM D-1934 aged dissipation factor (ADF) below 0.010 in the absence of added oxidation inhibitors, from a hydrogenated naphthenic oil having a viscosity in the range of 500-2000 SUS at 100° F., an ultraviolet adsorbency (UVA) less than 8 at 260 millimicrons, and having an ADF greater than 0.015, comprising contacting said oil at a temperature in the range of 100-400° F. with an adsorbent comprising an acid-activated adsorbent clay in an amount per barrel such that from 10-90 grams of KOH would be required to neutralize the acidity of said acid-activated adsorbent clay.

2. Process according to claim 1 comprising:

(a) obtaining a hydrogenated naphthenic oil with a viscosity in the range of 700-1000 SUS at 100° F., an ADF greater than 0.015, and a UVA less than 6.0 at 260 millimicrons, said oil having been catalytically hydrorefined at a temperature in the range of from 500-750° F. and at a hydrogen partial pressure from 800-3000 p.s.i.;

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(b) contacting said hydrogenated oil at a temperature in the range of 100–400° F. with an adsorbent comprising an acid-activated adsorbent clay in an amount per barrel of oil such that from 20–40 grams of KOH would be required to neutralize the acidity of said acid-activated adsorbent clay; and

(c) recovering a cable oil having an ASTM D-1934 aged dissipation factor below 0.010.

3. Process according to claim 1 wherein prior to said contacting said hydrogenated oil is blended with a minor amount of at least one oil selected from the group consisting of synthetic paraffinic cable oils, naphthenic distillates which are substantially free of naphthenic acids, hydrotreated naphthenic oils, catalytically cracked oils and solvent refined, acid-treated naphthenic oils.

4. Process according to claim 1 wherein said adsorbent comprises said acid-activated adsorbent clay and from 5–20 lbs./bbl. of a fuller's earth bleaching clay.

5. Process according to claim 2 wherein said adsorbent comprises said acid-activated adsorbent clay and from 5–20 lbs./bbl. of attapulgit.

6. Process according to claim 1 wherein said hydrogenated oil is obtained by blending hydrogenated oil having a viscosity in the range of 300–600 SUS at 100° F. with hydrogenated oil having a viscosity in the range of 1500–3000 SUS at 100° F.

7. Process according to claim 2 wherein said contacting is at a temperature in the range of 200–300° F.

8. Process according to claim 3 wherein the cable oil produced thereby has a viscosity in the range of 700–1000 SUS at 100° F.

9. A naphthenic electrical oil having a viscosity in the range of 500–2000 SUS at 100° F. and having an ADF less than 0.010 in the absence of added oxidation inhibitors and which requires at least 75 hours at PFVO test conditions to reach a 6% power factor.

10. A naphthenic cable oil according to claim 9 and

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containing more than 50 p.p.m. of indigenous nitrogen in the form of organic nitrogen compounds.

11. A naphthenic cable oil according to claim 9 which requires at least 150 hours at PFVO test conditions to reach a 6% power factor.

12. A naphthenic cable oil according to claim 10 having a 260 UVA of less than 6.0, a viscosity in the range of 700–1000 SUS at 100° F. and which requires at least 150 hours at PFVO test conditions to reach a 6% power factor.

13. An electrical cable containing as an insulating medium an oil according to claim 9.

14. An electrical cable containing as an insulating medium an oil according to claim 10.

15. An electrical cable containing as an insulating medium an oil according to claim 11.

16. An electrical cable containing as an insulating medium an oil according to claim 12.

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