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PREPARATION OF TRANSFORMER OILS

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4 Claims. (Cl. 208—264)

This application is a continuation-in-part of application 145,776, filed October 17, 1961, now abandoned.

This invention relates to the preparation of improved transformer oils. More specifically, this invention relates to the preparation of transformer oils which have improved non-sludging and electrical characteristics by hydrogenation of a specific hydrocarbon oil distillate.

The preparation of transformer oils for use in providing electrical insulation and conducting heat away from the transformer requires a careful and exacting procedure to provide a highly refined oil which requires a high dielectric strength, high electrical resistivity, low viscosity, low specific gravity, low pour test, non-emulsifying tendency, low evaporation rate, slow rate of sludge and/or acid development by oxidation. The processes generally used to produce transformer oils include the multi-step procedure of acid treating or solvent refining of specific hydrocarbon oil distillates followed by clay percolation. These multi-step refining procedures, especially acid treating, are expensive to operate, waste oil and are associated with corrosion and pollution problems.

It is an object of this invention to provide an economical and commercially feasible one-step process to produce improved transformer oils. A further object of this invention is to provide improved transformer oils which have the superior physical characteristics of improved electrical insulating properties, reduced sludge forming tendencies, and possess other satisfactory properties required of commercial transformer oils such as oxidation resistance, low moisture formation, low acid production and the like. These and other objects will become apparent to those skilled in the art from a consideration of the following disclosure and appended claims.

In accordance with the present invention, improved transformer oils are produced by the treatment of a hydrocarbon oil distillate having a sulfur content below about 1 weight percent, preferably below about 0.7 weight percent, a viscosity at 100° F. of between about 35 and 110 S.S.U. and a flash point of between about 200 and 350° F. with hydrogen in the presence of a hydrogenation catalyst utilizing specific reaction conditions. The starting material which is utilized in the process of this invention can be a hydrocarbon oil distillate obtained from any available crude naphthenic petroleum oil. These hydrocarbon oil distillates can be obtained by vacuum distillation or like distillation of naphthenic crude oils such as Mirando, Webster, Thompson, Gulf Coast, among others. It is essential, however, that the hydrocarbon oil distillate used as the starting material has a viscosity range at 100° F. of about 35 to about 110 S.S.U., preferably in the range of about 54 to about 64 S.S.U., a flash point in the range from about 200 to about 350° F., preferably a minimum flash point of about 270° F., and a pour point below about —50° F. One of the requirements of a suitable transformer oil is a low pour point below about —50° F. Selection of the starting hydrocarbon oil distillates containing a high content of naphthenes and some aromatics will generally provide an oil which will satisfactorily meet the low pour point requirements. These naphthenic hydrocarbon oil distillates may contain naphthenes as low as 30 volume percent to 80 percent or higher. An additional requirement of the naphthenic hydrocarbon distillate charge stock relates to the sulfur content therein. If the naphthenic hydrocarbon distillates have a sulfur content of 1 weight percent or higher, the improved transformer oil produced by the process of this invention is not obtained. If the naphthenic hydrocarbon distillates have a sulfur content below 1 weight percent, preferably below about 0.7 weight percent, an improved transformer oil is obtained utilizing the process of this invention.

The reaction conditions necessary for the production of improved transformer oils include a temperature range from about 600° F. to about 750° F. If a temperature below 600° F. or above 750° F. is employed, the resulting oil does not contain the desired improvements characteristic of an excellent transformer oil. The pressures which are employed include those above about 2000 pounds per square inch, preferably in the range from about 2000 to about 4000 pounds per square inch. Pressures above 4000 pounds per square inch can be employed but are not commercially attractive since they are costly to produce and maintain and do not result in much, if any, improvement in yields and product quality. At pressures below about 2000 pounds per square inch, improved transformer oils are not obtained. The liquid hourly space velocities which can be used range from about 0.25 to about 2.0, preferably in the range from about 0.5 to about 1.5.

The catalysts employed in the process of this invention can include any type of catalyst having hydrogenation properties. Such catalysts are known in the art. For instance, these catalysts can include oxides and sulfides of any metal of Group VI left-hand column of the Periodic System or mixtures thereof such as chromium sulfide, molybdenum sulfide, tungsten sulfide, and the like, sulfides of Group VIII of the Periodic Table or mixtures thereof such as the sulfides of iron, cobalt, nickel, platinum, palladium, rhodium, osmium, iridium, mixtures of the above sulfides of the metals of Group VI left-hand column and Group VIII such as a mixture of nickel sulfide and tungsten sulfide, tungsten sufide and cobalt sulfide, nickel sulfide and molybdenum sulfide and the like. These metals can be deposited on absorbent carriers such as alumina, silica-alumina, silica-zirconia, among others. Preferred hydrogenation catalysts include 1:1 mol ratio mixture of nickel sulfide and tungsten sulfide; tungsten sulfide; and cobalt molybdate supported or unsupported.

Pure hydrogen can be used in this process. Hydrogen of lower purity obtained by recycle from naphtha reforming or other hydrogenating processes can be used but it is recommended that the recycle hydrogen be subjected to a purification process to remove some of the undesirable impurities such as water, sulfur compounds and the like and maintain a high partial hydrogen pressure. Hydrogen can be circulated at a ratio in the range from about 500 to about 15,000 s.c.f. per barrel of charge, preferably in the range of about 1000 to about 2000 s.c.f. per barrel of charge, and if desired, higher or lower amounts can be used.

The process of this invention can be carried out in any equipment suitable for catalytic hydrogenation operations. The process may be operated batchwise. It is preferable, however, and generally more feasible to operate continuously. Accordingly, the process can be adapted to operations using a fixed bed of catalyst. Also, the process can be operated using a moving bed of catalyst, wherein the hydrocarbon flow can be concurrent or countercurrent to the catalyst flow. A fluid type of operation can also be employed.

Important advantages are apparent in using the process of this invention over the conventional acid treatment and furfural refining procedures in producing transformer oils. Of significant importance, higher yields are obtained in the process of this invention over the conventional refining procedures since the charge stock is hydrogenated and converts the undesirable material into acceptable

products thereby utilizing the entire charge stock to produce the improved transformer oil which is taken directly from the reactor without further fractionation other than removal of gases such as hydrogen and hydrogen sulfide. The acid treating and furfural refining procedure removes the undesirable material from the charge stock decreasing the yield of the resulting product and then requires an additional step of clay percolation to provide an acceptable transformer oil. Not only are higher yields obtained in less steps in this invention, but transformer oils are produced which have improved characteristics for providing more electrical insulation and reduced sludge accumulation over the conventional transformer oils. The following examples will serve to illustrate the process and improved products of the invention without limiting the same:

EXAMPLE 1

Gulf (Grade "A") coastal crude oil was distilled to obtain a transformer oil distillate having the following properties:

Gravity, °API	26.3
Pour point °F.	<—65
Flash point, °F.	285
Viscosity, S.S.U.° @ 100° F.	57.0
Color, ASTM	4½
Neutralization number, mg. KOH/gm.	0.86
Sulfur, percent wt.	0.17
Refractive index	1.49067
Molecular wt.	257

EXAMPLE 2

To compare the properties of a conventional transformer oil with a hydrogenated transformer oil, the starting material, similar to that described in Example 1, was acid treated with sulfuric acid using conventional procedures and the resulting product was percolated through clay in order to obtain transformer oil which meets standard specifications. The starting material had the following properties:

Gravity, °API	26.3
Pour point °F.	<—65
Flash point, °F.	285
Viscosity, S.S.U.° @ 100° F.	57.0
Color, ASTM	4½
Neutralization number, mg. KOH/gm.	0.86
Sulfur, percent wt.	0.17
Refractive index	1.49067
Molecular wt.	257

The refined transformer oils had the following properties:

Gravity, °API	28.0
Pour point °F.	<—65
Flash point, °F.	275
Viscosity, S.S.U.° @ 100° F.	55.0
Color, ASTM	1—
Neutralization number, mg. KOH/gm.	0.01
Sulfur, percent wt.	0.046
Refractive index	1.4848
Molecular wt.	265

EXAMPLE 3

To compare the properties of a conventional transformer oil with a hydrogenated transformer oil, the starting material, similar to that described in Example 1, above, was refined by solvent extraction with furfural using a conventional procedure and the resulting product was percolated through clay in order to obtain transformer oil which meets standard specifications. The starting material had the following properties:

Gravity, ° API	26.3
Pour point, ° F.	<—65
Flash point, ° F.	285
Viscosity, S.S.U. ° @ 100° F.	57.0

Color, ASTM	4½
Neutralization number, mg. KOH/gm.	0.86
Sulfur, percent wt.	0.17
Refractive index	1.49067
Molecular wt.	257

The refined transformer oils had the following properties:

Gravity, ° API	30.0
Pour point, °F.	<—65
Flash point, ° F.	280
Viscosity, S.S.U. ° @ 100° F.	55.2
Color, ASTM	1—
Neutralization number, mg. KOH/gm.	0.03
Sulfur, percent wt.	0.06
Refractive index	1.47655
Molecular wt.	285

EXAMPLE 4

A portion of the transformer oil distillate of Example 1 was hydrogenated in the presence of a nickel-tungsten sulfide catalyst having the following composition and properties:

Composition:		
Nickel	weight percent	23
Tungtsen	do	52
Sulfur	do	25
Properties:		
Pore diameter		268 A.
Pore volume	cc./g.	0.114
Density, g./cc.:		
Packed		2.00
Particle		3.50
True		5.83
Surface area	$m.^2/g.$	17

The reaction conditions were 500° F., a 0.25 liquid hourly space velocity, a hydrogen circulation ratio of 10,000 s.c.f. of hydrogen per barrel of charge stock, and a pressure of 1500 pounds per square inch. The transformer oil obtained had the following properties:

Gravity, ° API	27.7
Pour point, °F.	<—65
Flash point ° F.	290
Viscosity, S.S.U. ° @ 100° F.	58.0
Color, ASTM	1—
Neutralization number, mg. KOH/gm.	0.01
Sulfur, percent wt.	0.028
Refractive index	1.48501
Molecular wt.	240

EXAMPLE 5

A portion of the transformer oil distillate of Example 1 was hydrogenated in the presence of nickel-tungsten sulfide catalyst, described in Example 4. The reaction conditions were 650° F., a 1.0 liquid hourly space velocity, a hydrogen circulation ratio of 2000 s.c.f. of hydrogen per barrel of charge stock and a pressure of 3000 pounds per square inch. The transformer oil obtained had the following properties:

Gravity, ° API	29.1
Pour point, °F.	<—65
Flash point, ° F.	285
Viscosity, S.S.U. ° @ 100° F.	54.3
Color, ASTM	1—
Neutralization number, mg. KOH/gm.	0.01
Sulfur, percent wt.	0.008
Refractive index	1.47783
Molecular wt.	240

EXAMPLE 6

To demonstrate the effect of sulfur, a transformer oil distillate having a sulfur content of 1 weight percent was hydrogenated in the presence of a nickel-tungsten sulfide

catalyst described in Example 4. Reaction conditions were identical to the reaction conditions of Example 5; namely, 650° F., a 1.0 liquid hourly space velocity, a hydrogen circulation ratio of 2000 s.c.f. of hydrogen per barrel of charge stock and a pressure of 3000 pounds per square inch.

The naphthenic hydrocarbon distillate charge stock had the following properties:

Gravity, ° API	27.8
Pour point, ° F.	−50
Flash point ° F.	290
Viscosity, S.S.U. ° @ 100° F.	57.7
Color, ASTM	3½
Neutralization number, mg. KOH/gm.	1.60
Sulfur, percent wt.	1.0
Refractive index	1.49166

The transformer oil obtained from the hydrogenation had the following properties:

Gravity, ° API	29.1
Pour point, ° F.	<−65
Flash point, ° F.	285
Viscosity, S.S.U.° @ 100° F.	54.3
Color, ASTM	1—
Neutralization number, mg. KOH/mg.	<0.01
Sulfur, percent wt.	0.06
Refractive index	1.47803

EXAMPLE 7

The transformer oils produced in Examples 2, 3, 4 and 5 as well as the transformer oil charge stock of Example 1 were subjected to various tests to determine oxidation resistance, sludge accumulation and electrical resistivity.

The oxidation test utilized herein used the method described in ASTM Standards on Petroleum Products and Lubricants as "Test for Sludge Formation in Mineral Transformer Oil by High-Pressure Oxidation Bomb" (D 1313–54).

The sludge accumulation test utilized herein was the method described in ASTM Standards on Petroleum Products and Lubricants as "Test for Sludge Formation in Transformer Oil" (D 1314–54T).

The electrical resistivity test utilized herein is an ASTM Designation: D 1169–58, titled Standard Method of Test for Insulation-Resistivity of Electrical Insulating Oils of Petroleum Origin.

The comparative results of the above tests are set forth in Table I below:

Table I

	Charge Stock, Ex. 1	Acid Treatment and Percolation, Ex. 2	Furfural Refined and Clay Percolation, Ex. 3	Hydrogenated Oil, Ex. 4	Hydrogenated Oil, Ex. 5	Hydrogenated Oil, Ex. 6
Oxidation, percent wt.	0.16	0.023	0.10	0.10	0.055	0.056
Sludge Accumulation:						
Percent Wt. at 3 days	0.05	0.04	0.06	0.06	0.005	0.016
Percent Wt. at 7 days	0.11	0.08	0.15	0.04	0.006	0.025
Percent Wt. at 14 days	1.45	0.21	0.27	0.16	0.07	0.16
Resistivity, ohm-cm. $\times 10^{12}$	----------	183	513	302	1310	262

The comparative results clearly demonstrate the improved transformer oils (Example 5) obtained by the process of this invention over transformer oils refined by conventional procedures and over another transformer oil hydrogenated under milder hydrogenation conditions. The transformer oils produced by conventional methods (Examples 2 and 3) have properties which fall within the acceptable specifications of a commercial transformer oil. Comparing the results of the improved transformer oil of this invention with those of the acceptable transformer oils, it can be readily seen that the amount of undesirable sludge formed in the conventional transformer oils range from about 3 to almost 4 times greater than the transformer oils of this invention.

The resistivity of a transformer oil indicates the oil's ability to provide electrical insulation which is a primary function of a transformer oil. The transformer oil of this invention provides from about 3 to about 7 times more electrical resistivity than the conventional oils. At the same time, the improved transformer oil of this invention meets the required specification for oxidation tendencies of an excellent transformer oil and is superior in oxidation resistance over the furfural refined transformer oil.

The transformer oil of Example 4 hydrogenated under conditions outside the range of the conditions of the process provides an acceptable transformer oil according to specifications but is only superior to the conventional oils in its ability to maintain a slightly lower sludge accumulation. Comparison of the milder hydrogenated oil with the improved transformer oil of Example 5 indicates the importance of the specific reaction conditions required by the process of this invention to obtain superior transformer oils.

The transformer oil of Example 6 hydrogenated under the conditions utilized in the process of this invention but using a naphthenic hydrocarbon distillate charge stock having a sulfur content of 1 weight percent does not provide the improvements as obtained in the process of this invention which utilizes a naphthenic hydrocarbon distillate having a sulfur content below about 1 weight percent.

What is claimed is:

1. A method for producing a transformer oil of superior oxidation resistance and sludge forming characteristics which comprises employing as a hydrocarbon feed, a straight-run naphthenic hyrocarbon oil distillate fraction having a sulfur content below about 1 weight percent and a pour point below about −50° F., and subjecting said naphthenic feed to relatively severe catalytic hpdrogenating conditions including a pressure above about 2000 p.s.i.g. and a temperature in the range of from about 600 to about 750° F. to produce said transformer oil.

2. A method for producing a transformer oil which comprises relatively severely hydrogenating at a pressure above about 2000 p.s.i.g. and a temperature above about 625° F. in the presence of a strong hydrogenating catalyst, a naphthenic distillate hydrocarbon fraction having a pour point below about −50° F. and a sulfur content not substantially above about 0.7 weight percent and recovering a hydrogenated product comprising said transformer oil.

3. A method for producing a transformer oil which comprises severely hydrogenating in the presence of a strong hydrogenating catalyst, a naphthenic oil distillate fraction having a sulfur content below about 1 weight percent, a flash point between about 200° F. and about 350° F. and a pour point less than about −50° F. with hydrogen at a temperature in the range of from about 600 to about 750° F. while maintaining a pressure during said hydrogenation step above about 2000 pounds per square inch and recovering a hydrogenated product comprising said transformer oil.

4. A method for producing a transformer oil which comprises hydrogenating a naphthenic hydrocarbon oil distillate fraction having a sulfur content below about

1 weight percent and a pour point below about −50° F. in the presence of a hydrogenating catalyst at a liquid hourly space velocity from about 0.25 to about 2.0 at a pressure greater than about 2000 pounds per square inch and a temperature in the range of from about 625 to about 750° F.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,192,153 June 29, 19

Michael T. Smilski

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 26 and 45, and column 4, line 1, for "4 1/2", each occurrence, read -- 4-1/2 --; column 5, line 1: for "3 1/2" read -- 3-1/2 --; line 25, for "mg.", second occurrence, read -- gm. --.

Signed and sealed this 7th day of December 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents