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ELECTRICAL INSULATING OILS AND METHOD FOR PRODUCING THEM

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This invention relates to improved insulating oils and more particularly to a process for preparing electrical insulating oils which are stable, non-sludging and resistant to gassing.

It is known that when hydrocarbon insulating oils are subjected to high electrical stress, they tend to decompose producing sludge and gaseous products, which may cause serious damage and eventual failure of the apparatus in which they are used. The presence of aromatic hydrocarbons in the oil tends to inhibit gassing, but they have an adverse effect in that they increase sludging. Drastic refining of highly aromatic oils in order to produce more stable electrical insulating oils results in poor yields, generally in the neighborhood of 45–55% by weight, calculated on the starting material.

It has now been found that non-gassing, sludge resistant and oxidation stable electrical insulating oils can be prepared in high yields from mineral oils having a viscosity of between 1° and 9° Engler (E) at 20° C. and preferably between 3 and 5° E at 20° C. and which are rich in aromatics and relatively high in sulfur content, namely 1% by weight or more. By aromatic rich oils it is meant that the aromatic content of the oil is 35% or more as determined by percolation over silica gel as described in the "Journal of the Institute of Petroleum," 36, 89–104 (1950).

A process for the production of a non-gassing and oxidation-stable electrical insulating mineral oil composition, which comprises:

(a) Separately (1) catalytically selectively hydrogenating a portion of an oil (A) and (2) selectively solvent extracting a portion of an oil (B), oils (A) and (B) each being mineral oils having viscosities between 1° and 9° Engler at 20° C., an aromatic content of at least 35% by weight and a sulfur content of at least 1% by weight, and

(b) Subsequently separately treating the thus-treated portions of oil (A) and of oil (B), with strong sulfuric acid, removing the sludge resulting therefrom, neutralizing the acid treated oil and thereafter treating the thus separately neutralized oils with a solid absorbent, the resulting thus completely-treated portion of oils (A) and (B) being blended in proportions of from 80 to 40 parts by weight of oil (A) and from 20 to 60 parts by weight of oil (B). Oil portions (A) and (B) should be treated separately by step (b) and not combined and thereafter processed by step (b). If the two portions (A) and (B) are treated by step (b) together, the final product will be poor and not pass the B. S. I. test.

In accordance with a preferred embodiment of the invention, an improved oil is produced by:

(a) Preparing an oil (A), starting from a mineral oil having a viscosity of between 1° and 9° E at 20° C., an

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aromatic content of at least 35% by weight and a sulfur content of at least 1% by weight, by, (1) first catalytically selectively hydrogenating this oil to a sulfur content of from 0.05–0.06% by weight, then (2) treating it with sulfuric acid or oleum, (3) separating the acid sludge, (4) neutralizing the acid oil and (5) treating it with a solid absorbent;

(b) Preparing an oil (B), starting from a mineral oil having a viscosity of between 1 and 9° E at 20° C., an aromatic content of at least 35% by weight and a sulfur content of at least 1% by weight, by (1) first extracting this oil with a selective solvent for the aromatic components of the oil to produce a raffinate with an aromatic content of not more than 25% by weight, (2) treating the raffinate obtained with concentrated sulfuric acid or oleum, (3) separating the resulting acid sludge, (4) neutralizing the acid oil obtained and, (5) treating it with a solid absorbent;

(c) Mixing 80–40 parts by weight of treated oil (A) with 20–60 parts by weight of treated oil (B).

The following detailed description of the application of the invention in separately processing the portions of oil A and of oil B, with a final blending of the thus-treated portions A and B, will give a better understanding of its practice.

PREPARATION OF OIL (A)

For preparing oil (A) the starting oil is first catalytically selectively hydrogenated to a sulfur content of 0.05–0.6% by weight, preferably 0.2–0.3% by weight, and especially approximately 0.25% by weight. By catalytic selective hydrogenation is here meant a catalytic hydrogenation under conditions in which the non-hydrocarbons present in the oil (viz. the compounds which in addition to carbon and hydrogen contain other elements such as sulfur or oxygen) are hydrogenated, but the hydrocarbons remain essentially unaffected (so that, for example, there is virtually no cracking of the oil or hydrogenation of aromatics present in the oil). Several methods are already known (see for example, Erdöl and Kohle, 6, 616–619 (1953)) for hydrogenating oils in this way, which is frequently termed hydrofining. The oil may be in either the gas or the liquid phase during the hydrogenation. In general, the selective hydrogenation is carried out at a temperature of 300° C.–400° C., a pressure of 10–200 kg. per sq. cm., a gas discharge rate of 50–5,000 liters per kg. of oil and a flow rate of the oil of 0.3–3 kg. per liter of catalyst per hour. Suitable catalysts are oxygen or sulfur-containing compounds such as oxides and sulfides of metals of groups VI and VIII of the periodic table. Mention may be made of cobalt oxide, molybdenum oxide, tungsten sulfide and nickel sulfide. The catalysts may be supported on carriers, such as active carbon, fuller's earth, kieselguhr, silica or alumina, e. g. in the form of bauxite, pumice or burnt clay. A very suitable catalyst consists of cobalt oxide and molybdenum oxide on bauxite as carrier. Suitable hydrogenation methods are described, for example, in the British patent specifications 657,521, 665,575 and 699,455.

In the catalytic selective hydrogenation, hydrogen sulfide is formed from the sulfur compounds present in the oil. A part of the hydrogen sulfide formed dissolves in the oil, and this should be removed from the oil before the treatment with concentrated sulfuric acid or oleum. This can be effected, for example, by washing the oil with a caustic alkali solution, but it is most simply carried out by blowing through the oil an inert gas such as nitrogen, if desired, at elevated temperature.

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Electrical insulating oils are often required to have a flash point which is not below a certain temperature. As a result of the catalytic selective hydrogenation, the initial boiling point of the oil is somewhat reduced. This causes a lowering of the flash point in the oil. As a result, the flash point of the final insulating oil may not satisfy the flash point requirement. If this is the case, the low-boiling compounds should be removed from the oil. This can be done in a simple way by means of distillation, preferably under reduced pressure. Distillation is carried out until the residue has the desired flash point. The removal of the low-boiling compounds is preferably carried out before the treatment with concentrated sulfuric acid or oleum.

The treatment with concentrated sulfuric acid or oleum is carried out in a manner known per se. For instance, concentrated sulfuric acid (80–100%) or oleum (to 30% SO_3) may be used in amounts of from 5–30% by weight, calculated on the oil treated, at temperatures varying from 0 to 75° C. and contact times from 5 sec. to one hour. The refining can be carried out in one or more stages and either batchwise or continuously. In batchwise refining the treatment temperature is preferably approximately 25° C., and in continuous refining preferably approximately 60° C. After the treatment with concentrated sulfuric acid or oleum, the acid sludge formed is removed from the oil.

The oil which may still contain residual acid or sulfonic acids formed during the acid treatment, is then treated with an alkaline material such as an aqueous or alcoholic solution of NaOH in order to neutralize the oil. The used alkaline material is separated from the oil, and the oil subsequently washed, if desired, e. g. with water and/or alcohol.

Finally the oil is treated with a solid adsorbent such as adsorbent earths and clay types. Suitable adsorbents are, for example, fuller's earth, bauxite and clay such as "Filtrol," whether or not activated with acid. Small quantities of alkaline material such as lime or magnesia may be added to the adsorbent. If desired, the oil may be heated during the treatment, and an inert gas such as nitrogen passed through the oil. The quantity of adsorbent used generally lies between 1 and 30% by weight, calculated on the oil treated.

When the selectively hydrogenated oil is stored for a relatively long period before the acid treatment, dark sludgy deposits may be formed in the oil. These deposits may be formed after 1–2 months, but sometimes also before or after. The formation of these deposits can be prevented by washing the oil with an alcoholic caustic alkali solution, e. g. a 4% by weight solution of NaOH in 40% by weight alcohol, after the selective hydrogenation but before storage. This treatment may also be used at the same time to remove from the oil the hydrogen sulfide formed in the catalytic selective hydrogenation and dissolved in the oil.

PREPARATION OF OIL (B)

For preparing oil (B) the same starting oil may be used as in the preparation of oil (A), or another oil, provided the starting material satisfies the foregoing requirements.

The starting material is first extracted in a manner known per se with a selective solvent for the aromatic components of the oil (e. g. liquid sulfur dioxide, furfural, phenol, nitro benzene, etc.) to produce a raffinate with an aromatic content of not more than 25% by weight and preferably no more than 15% by weight.

This raffinate is then treated with concentrated sulfuric acid or oleum and then subsequently treated as described for the preparation of oil (A).

It has already been pointed out that an advantage of the process of the invention as compared to the known processes is that a larger yield of final insulating oil is obtained. A further advantage of the process of the invention is that the insulating oils obtained have improved gassing characteristics. The process of the invention is

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of particular advantage when the starting oils have an aromatic content of 40% by weight or more, and particularly a sulfur content of 1.5% by weight or more.

The advantages of the process of the invention as compared to the known processes are shown by Examples I and II.

Example I

PREPARATION OF OIL A I

The starting material was a spindle oil obtained by distilling and re-distilling over lime a Venezuelan naphthenic crude oil. The spindle oil distillate had the following properties:

Viscosity	5.5° E./20° C.
Flash point (Pensky-Martens, closed)	156° C.
Sulfur content	1.76% by weight.
Aromatic content	50% by weight.

This oil was catalytically selectively hydrogenated by allowing the oil to flow in a thin layer over a catalyst bed of cobalt oxide and molybdenum oxide supported on bauxite in the form of cylindrical tablets measuring 5 x 5 mm. under the following conditions:

Temperature, ° C.	370
Hydrogen pressure, kg./sq. cm.	50
Flow rate of the oil, kg./liter, catalyst/hour	1.1
Gas discharge rate, liter/kg. oil	225

Approximately 2% by weight of the oil was lost in the catalytic selective hydrogenation.

The hydrogen sulfide dissolved in the oil was then removed by blowing with nitrogen at 60° C.–80° C.

The oil was then subjected to fractional distillation at a pressure of 20 mm. Hg until the temperature of the vapor passing over was 145° C. Approximately 6% by weight of the oil was thus removed.

The flash point of the oil was now 148° C. The sulfur content of the oil had dropped to 0.25% by weight, while the aromatic content was practically unchanged, as is shown from the very slight change in the refractive index ($n_D^{20}=1.5018$; for the starting material $n_D^{20}=1.5103$).

10% by weight of oleum (17% by weight of SO_3) was now added to the oil at a temperature of 20° C. and the mixture was then stirred for ½ hour. The acid sludge was then allowed to deposit. This was separated off and the oil was subsequently treated with a 4% solution of NaOH in 40% alcohol, and afterwards washed with dilute alcohol and water. Finally the oil was treated with 3% by weight of Filtrol for ½ hour while passing nitrogen through it.

The amount of oil obtained in this way was 79% by weight calculated on the starting material.

PREPARATION OF OIL B I

Another portion of the same starting oil was used as in the preparation of oil A I. This oil was extracted with liquid sulfur dioxide to produce a raffinate with an aromatic content of 9% by weight. The raffinate was treated with 10% by weight of oleum and then after-treated, i. e., neutralized and clay contacted as described in the preparation of oil A I.

The amount of oil obtained in this was 43.5% by weight, calculated on the starting material.

MIXING OILS A I AND B I, AND PROPERTIES OF FINAL ELECTRICAL INSULATING OIL

60 parts by weight of finished oil A I were mixed with 40 parts by weight of finished oil B I. The total yield of final electrical insulating oil was 65% by weight, calculated on the total amount of starting material.

The oxidation stability of the final oil was determined in the British Standard Specification Test for Insulating Oils (B. S. I.). According to the specification, after the conclusion of the test, the limit of the sludge formation in the oil should be 1.1% by weight and the maximum acid number of the oil 2.5 mg. of KOH/g. of oil.

The final electrical insulating oil amply satisfied this specification:

Oil	B. S. I. test	
	Sludge, percent by weight	Acid number
60% A I + 40% B I.....	0.74.....	1.7.....
B. S. I. 1.48/1951 specification limits.....	1.1 (max.).....	2.5 (max.).....

The gassing characteristics of the final oil were evaluated in the modified Pirelli apparatus (Journal of the Institute of Petroleum, 35, No. 311, pp. 735-754) at a temperature of 50° C. under a hydrogen atmosphere and at a voltage of 10 kilovolts. The amount of hydrogen which the oil adsorbs or evolves under these conditions in the course of time is measured. The hydrogen absorption or hydrogen evolution expressed in millimeters of oil pressure is plotted in a graph as a function of the time and the slope of the line thus obtained determines the gassing coefficient of the oil. For the present oil this coefficient was found to have the value of -2.8, which is very favorable.

Example II

An electrical insulating oil which satisfied the B. S. I. test was prepared by a conventional method from the same oil as was used as starting oil in Example I.

The oil was first extracted with liquid sulfur dioxide (ratio by volume of oil:SO₂=1:1.3) and the raffinate thus obtained was treated with 10% by weight of oleum and subsequently neutralized and clay-treated as described in Example I.

In the B. S. I. test the oil gave the following results:

Sludge, percent by weight.....	0.84
Acid number.....	1.4

The yield was 55% by weight, calculated on the starting material, and the gassing coefficient of the oil was positive.

Example I shows that the high yield in the process of the invention is chiefly due to the fact that in the preparation of oil A, relatively little of the starting material is lost (yield of oil A I is 79% by weight).

The improved gassing characteristics of the insulating oils of the invention are probably to be explained by the fact than in preparing oil (A) the aromatic content of the starting material is very little reduced so that the final insulating oil (despite the fact that another oil (B) with a considerably lower aromatic content is added), will have a higher aromatic content than an insulating oil prepared by the conventional method. An indication of this is that the insulating oil according to the invention has a higher refractive index than the insulating oil prepared in the conventional manner (n_D^{20} 1.4851 and 1.4784, respectively).

It is necessary to add an oil (B) to oil (A) because an oil (A) has an insufficient oxidation stability in itself. As was already observed above, in the preparation of oil (B) the starting oil is extracted in order to obtain a raffinate with an aromatic content of not more than 25% by weight, and preferably 15% by weight or less. The degree of extraction in the preparation of oil (B) affects the oxidation stability of the final insulating oil to be obtained as shown by Example III.

Example III

An oil B II was prepared from the same starting material as was used in the preparation of oil B I (see Example I). For preparing oil B II the starting material was also extracted with liquid sulfur dioxide, but less drastically than in the preparation of oil B I: the raffinate obtained had an aromatic content of 19% by weight. This raffinate was treated with 17% by weight of oleum and then aftertreated in the same way as oil B I.

Oils B I and B II both improve the oxidation stability of oil A I, but oil B I gives a greater improvement than oil B II, as is shown by the following table:

Oil	B. S. I. test	
	Sludge, percent by weight	Acid number
A I.....	1.48	1.9
60% A I + 40% B I.....	0.74	1.7
60% A I + 40% B II.....	1.0	1.9

As was already observed above, in the preparation of oil (A) the starting oil is catalytically selectively hydrogenated to a sulfur content of 0.05-0.6% by weight and preferably to 0.2-0.3% by weight. The degree of catalytic selective hydrogenation affects the oxidation stability of the final insulating oil to be obtained, as is shown by Example IV.

Example IV

The same starting material was used as in Example I.

Oils A II and A III were prepared from two portions of this starting material in the manner described in Example I for the preparation of oil A I, except that the conditions in the catalytic selective hydrogenation were somewhat modified, so that the hydrogenation products have a different sulfur content. The conditions in the catalytic selective hydrogenation were as follows:

	A II	A III
Temperature, ° C.....	375	375
Hydrogen pressure kg./sq. cm.....	50	50
Flow rate of the oil kg./liter catalyst/hour.....	0.5	2.0
Gas discharge rate, liter/kg. oil.....	260	125

The sulfur content of the oils, after blowing nitrogen therethrough and fractional distillation, was 0.05% by weight for oil A II, and 0.52% by weight for oil A III.

The oils were afterwards treated with oleum and aftertreated as described in Example I, and from each of the oils 60 parts by weight were mixed with 40 parts by weight of oil B I (see Example I). The results of the resultant mixtures in the B. S. I. test (as compared to the mixture of Example I) were:

Oil	S-content of oil (A) after sel. hydr. in percent by weight	B. S. I. test	
		Sludge, percent by weight	Acid number
60% A II + 40% B I.....	0.05	1.04	2.1
60% A I + 40% B I.....	0.25	0.74	1.7
60% A III + 40% B I.....	0.52	1.05	1.5

It is found that the mixture with oil A I amply satisfied the specification and the mixtures with oils A II and A III only just satisfied it.

The following table shows that by adding larger amounts of oil B I, the oxidation stability of oil A III may be still further improved:

Oil	B. S. I. test	
	Sludge, percent by weight	Acid number
60% A III + 40% B I.....	1.05	1.5
50% A III + 50% B I.....	0.92	1.4
40% A III + 60% B I.....	0.82	1.5

The fact that oil fractions (A) and (B) must be treated separately and not together with sulfuric acid or oleum, the acid sludge removed, the acid oil neutralized

and thereafter treated with a solid adsorbent, is illustrated by the following example.

Example IV A

The same starting material as used in Example I was hydrofined to a sulfur content of 0.23% by weight (oil X). Another portion of the same starting material was extracted to an aromatic content of 9% by weight, as described in Example I under the heading "Preparation of Oil B I" (oil Y). Oils X and Y were mixed in a weight ratio of 60:40 and the mixture was treated with 10% oleum at 20° C. and treated further as described in Example I. The final product was tested in the B. S. I. test.

Test results: 1.17% by weight of sludge, 1.8 acid number.

It has already been observed above that the high yield which can be obtained with the process of the invention is chiefly due to the fact that in the preparation of oil (A) relatively little of the starting material is lost. The yield of final insulating oil is consequently lower according as more of an oil (B) is used. Actually, the yield in the cases referred to in the above table was 65, 61 and 58% by weight respectively, calculated on the starting material. A comparison with Example II shows that the use of more than 60% by weight of an oil (B) in the mixture gives scarcely any better yield than obtained according to the conventional method.

Insulating oils prepared by the process of this invention possess satisfactory oxidation and electrical characteristics. If desired, however, minor proportions of from about 0.01% to about 1% as for example, 0.3 percent by weight, of a suitable anti-oxidant may be incorporated, such as alkyl phenols exemplified by 2,6-di-tert-butyl-4-methylphenol or 2,4-dimethyl-6-tert-butylphenol.

The good anti-oxidant sensitivity of the insulating oils of this invention is shown in Example V.

Example V

0.3% by weight of 2,6-di-tert-butyl-4-methylphenol was added as an anti-oxidant to the insulating oil described in Example I, and the oil was tested in the B. S. I. test. The results (as compared to the oil without anti-oxidant) are shown in the following table:

Oil	B. S. I. test	
	Sludge, percent by weight	Acid number
60% A I+40% B I.....	0.74	1.7
60% A I+40% B I+0.3% anti-oxidant.....	0.01	0.03

Example VI

The oxidation stability of the insulating oil of Example I was also tested in the S. E. V. test (see Zerbe's book, "Mineralöle und verwandte Produkte," p. 942). According to the specification after a test period of 7 days not more than 0.15% by weight of sludge should be formed in the oil. Moreover, the acid number of the oil after a test period of 3 days should not be more than 0.3, and after a test period of 7 days, not more than 0.4. Finally the tensile strength of the cotton threads in the oil during the test should not have decreased by more than 25% after a test period of 3 days, and by not more than 35% after a test period of 7 days.

The oil more than satisfied this specification:

	After 3 days	After 7 days
Sludge, percent by weight.....	0.01	0.05
Acid number.....	0.06	0.14
Reduction in tensile strength of threads in percent.....	10	15

Example VII

From the same starting material as used in Example I an oil A IV was prepared in the manner described for oil A I in Example I, except that in the acid refining 25% by weight of sulfuric acid of 96% was used instead of 10% by weight of oleum.

The yield of oil A IV was 78% by weight, calculated on the starting material.

70 parts by weight of oil A IV were mixed with 30 parts by weight of oil B I (see Example I). The total yield of final insulating oil was 68% by weight. The oil gave the following results in the B.S.I. test:

Oil	B. S. I. test	
	Sludge, percent by weight	Acid number
70% A IV+30% B I.....	0.95	1.1

Minor amounts of from 0.01% to 1% of still other classes of conventional additives can be incorporated in oils of this invention such as corrosion inhibitors, gas-sing inhibitors, sludge and carbon inhibitors, e. g. oil-soluble compounds capable of chelating metal ions, cyclo-alkene hydrocarbons, aromatic amines and halogenated aromatic hydrocarbons and mixtures thereof.

We claim as our invention:

1. A process for the production of a non-gassing and oxidation stable electrical insulating oil from a mineral oil containing at least 35% aromatics and 1% sulfur and having a viscosity between 1° and 9° Engler at 20° C. comprising splitting the oil into portions (A) and (B), separately treating oil portion (A) by catalytically selectively hydrogenating the oil to substantially reduce the sulfur content without essentially effecting the aromatic content of the oil and separately treating oil portion (B) with a selective aromatic solvent to obtain a raffinate fraction and subsequently treating these two oil portions (A) and (B) with sulfuric acid, removing the sludge from the acid treated oil portions (A) and (B), neutralizing the acid treated oil mixture (A) and (B) and thereafter treating the neutralized oil mixture (A) and (B) with a solid adsorbent, the treated products of oil portion (A) and oil portion (B) being blended in proportion of from 80 to 40 parts by weight of oil (A) with from 20 to 60 parts by weight of oil (B).

2. A process according to claim 1, wherein the base oil is a mineral oil having a viscosity of between 1 and 9° E. at 20° C., an aromatic content of at least 35% and a sulfur content of at least 1% by weight and wherein the sulfur content of oil (A) is reduced to about 0.2 to 0.3% by weight and the aromatic content being substantially unchanged and the oil (B) aromatic content being reduced to less than 25% by weight.

3. An electrical insulating oil prepared by the process of claim 1.

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