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REFINING LUBRICATING OILS

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This invention relates to a method of refining lubricating oils. More particularly, it relates to a method of improving the oxidation inhibitor susceptibility of lubricating oil fractions adapted for use as industrial oils, such as transformer oils and turbine oils.

One of the chief requirements of lubricating oils adapted for use as transformer oils and turbine oils is a high resistance to oxidation and accompanying formation of acid and sludge. High refinement of suitable lubricating oil fractions is necessary to meet this requirement. Heretofore, such refinement has been effected by subjecting a suitable lubricating oil fraction, generally after dewaxing and solvent refining, to redistillation; treating the redistilled fraction with strong sulfuric acid, such as fuming sulfuric acid; neutralizing the acid-treated oil with caustic soda; removing the oil-soluble sulfonates, formed by the sulfuric acid treatment, by extraction with a suitable solvent, such as methanol, ethanol, and the like; and then percolating the treated oil through clay. The finished oil is then inhibited with a minor amount of a suitable oxidation inhibitor, such as an alkyl phenol or an alkaline earth metal salt of a condensation product of formaldehyde and an alkyl phenol. Although this inhibited, highly refined oil adequately meets the oxidation stability requirements, the above-outlined method of refining is very costly.

It is, therefore, a principal object of the present invention to provide an improved method for refining lubricating oils. A more specific object is to provide an improved method for refining lubricating oil fractions adapted for use as turbine oils or transformer oils. A still more specific object is to provide an improved method for improving the inhibitor susceptibility of selective solvent refined lubricating oil distillates. Other objects and advantages will become apparent from the following detailed description.

It has now been found that the inhibitor susceptibility, as well as other properties, such as color, odor, and emulsion characteristics, of lubricating oils can be improved without extensive oil cracking by a method comprising contacting the oil with a substantial proportion of a solid adsorbent material at a temperature which is dependent upon the viscosity of the lubricating oil and which is expressed by the following equation:

$$T=\frac{6957}{8.97-\log_{10} V}\pm 25$$

wherein T represents the temperature expressed in degrees Rankine, and V is the viscosity of the oil at 100° F. expressed in Saybolt Universal seconds.

A preferred embodiment of the invention comprises contacting a lubricating oil fraction with a substantial proportion of a solid adsorbent material at a temperature expressed by the following equaltion:

$$T=\frac{6957}{8.97-\log_{10} V}\pm 25$$

wherein T represents the temperature in degrees Rankine,

and V is the Saybolt Universal viscosity of the oil at 100° F., and passing an inert stripping gas through the oil during the time of contact at the temperature T.

Described in greater detail, the present invention comprises mixing a suitable lubricating oil fraction, preferably a dewaxed and solvent refined distillate lubricating oil having a Saybolt Universal viscosity at 100° F. within the range of from about 35 to about 1600 seconds, and preferably within the range of from about 50 to about 600 seconds, with from about 3% to about 20%, preferably from about 5% to about 10%, by weight of the oil, of a suitable solid adsorbent material, particularly a siliceous adsorbent material, such as an active clay; heating the resulting mixture to a temperature expressed by the following equation:

$$T=\frac{6957}{8.97-\log_{10} V}\pm 25$$

wherein T represents the temperature in degrees Rankine, and V is the Saybolt Universal viscosity of the oil at 100° F.; maintaining the oil-solid adsorbent mixture at the elevated temperature for a period of time of from about 15 to about 60 minutes, passing an inert stripping gas through the mixture at a controlled rate during the time of contact at the elevated temperature to remove from about 1% to about 12%, preferably from about 2% to about 10% by weight, of undesirable light products and to minimize oxidation, and separating the treated oil from the solid adsorbent.

The finished oil, when used as a transformer or turbine oil, is then inhibited with a minor amount of suitable oxidation inhibitor. Any of the various well known agents can be used. Suitable oxidation inhibitors include: aromatic hydroxy compounds, such as the alkyl phenols, sulfur-containing organic compounds, such as phenol sulfides, thiocarbamate compounds and sulfurized oil compounds, aromatic amino compounds, such as tetramethyldiamino - diphenylmethane, phenylalphanaphthylamine and diphenylamine, and alkaline earth metal salts of condensation products of alkyl phenols and formaldehyde.

The invention is particularly applicable to the treatment of lubricating oil raffinate fractions obtained by the selective solvent extraction, e. g., extraction with liquid sulfur dioxide, phenol, furfural, or the like, or by the Duosol process using, for example, propane and cresylic acids, or naphthenic and mixed base lubricating oil distillates, such as West Texas Ellenburger (WTE), East Texas (ET), and Mt. Poso/Coalinga lubricating oil distillates, which raffinate fractions have a total sulfur content of not greater than about 0.5% by weight. Particularly suitable lubricating oil raffinates are those having a Saybolt Universal viscosity at 100° F. within the range of from about 50 to about 300 seconds. Properties of representative suitable lubricating oil raffinates are given in Table I.

TABLE I

	60N[a]	100 WTE[b]	250 WTE[b]	100 ET[b]	250 ET[b]
API Gravity	30.2	32.6	29.7	31.6	29.3
NPA Color	1	1½	2+	1+	1½
Viscosity at 100° F. (SUS)[c]	58.5	104	239	103.7	278
Viscosity at 210° F. (SUS)[c]	34.4	40	49.8	39.5	50.3
Flash Point (° F.)	305	400	440	370	445
Pour Point (° F.)	Below −70	+5	0	0	+5
Total Sulfur (percent w.)	.09	.10	.15	.01	.13

[a] A liquid sulfur dioxide raffinate of a lubricating oil distillate obtained from a mixture of Mt. Poso and Coalinga crudes.
[b] Duosol raffinates of the corresponding lubricating oil distillates.
[c] Saybolt Universal seconds.

The solid adsorbent material employed in the treating step of the present invention is preferably a metal oxide, for example, an oxide of a metal such as silicon, aluminum, calcium, iron, copper, zinc and magnesium. Other

materials which are effective susceptibility improving agents are reduced iron and copper powder, and active carbon. The most suitable materials are certain composites of silica and alumina which include generally the active clays, such as acid activated bentonite (Filtrol), acid activated fuller's earth, naturally active fuller's earth, and similar synthetic adsorbents. When using a metal oxide such as an oxide of calcium, iron, copper, zinc or magnesium, it is preferred to use an active clay along with these materials to prevent excessive color degradation.

In the practice of the present invention, the lubricating oil fraction can be contacted with the solid adsorbent material and heated to the operating temperature in any conventional manner in various types of apparatus suited for such an operation. The operation may be a continuous or batch type of operation. It is preferred, however, to suitably mix the oil and the solid adsorbent material to obtain an oil-solid adsorbent slurry, and then pass the resulting slurry through a suitable heating device, such as a furnace to heat the slurry to the proper temperature, and to a suitable contact tank where the slurry is maintained at the elevated temperature for the desired period of time, generally a period of time of from about 15 minutes to about 60 minutes. It is preferred to pass an inert stripping gas through the slurry at a controlled rate during the period of contact at the elevated temperature to minimize oxidation and to remove the bulk of the light products. The resulting slurry is then filtered, in a suitable filter such as an Oliver Precoat Filter, or otherwise processed as by centrifugation, to separate the treated oil from the solid adsorbent material. If desired, the treated oil can then be steam stripped to remove any remaining light ends, and then passed through a blotter press to remove any remaining solids. The spent solid adsorbent material can be regenerated by burning.

The exact mechanism of improvement in inhibitor susceptibility by contacting with a solid adsorbent has not been fully determined. The exact nature of the reactions which occur during the contacting step is not fully known, but it has been found that contacting with a solid adsorbent effects the removal of sulfur compounds and it appears that there is a conversion of certain naphthenoaromatic compounds to aromatic compounds and naphthenic compounds. It is believed that the removal of sulfur compounds and naphtheno-aromatic compounds is responsible for the improvement in inhibitor susceptibility of the lubricating oil fractions.

Although it is possible to further increase the inhibitor susceptibility by increasing the contact temperature above the range defined by the above equation, it has been found that the increased contact temperatures result in extensive cracking of the lubricating oil fraction being treated as evidenced by high stripping losses during the treatment and by the lowered flash point and viscosity of the filtered product. Thus the optimum temperature range defined by the above equation is based on an optimum balance between inhibitor susceptibility improvement and extent of oil cracking.

According to a preferred embodiment of the present invention, an inert stripping gas is passed through the oil-solid adsorbent mixture at a controlled rate during the time of contact at the elevated temperature to minimize oxidation and to remove the bulk of the light products. Any inert stripping gas can be employed. Suitable stripping media include steam, nitrogen, carbon dioxide, and the like. It has been found that an added improvement in inhibitor susceptibility is obtained when the stripping is accomplished during the contacting step rather than after removal of the treated oil from the solid adsorbent material. The following example illustrates the advantage of stripping during the time of contact.

Example I

A sample of a 60 N lubricating oil raffinate, the properties of which are given in Table I, was mixed with about 7.5% by weight of Filtrol (an acid activated bentonite). The resulting mixture was heated to a temperature of about 500° F. and was maintained at this temperature for a period of about 30 minutes. The treated oil was separated from the Filtrol by filtration and then steam stripped at a temperature of about 275° F. under reduced pressure to remove about 10% by weight of light ends. The finished oil was inhibited with about 0.5% by weight of 2,6-di-tertiary butyl paracresol. The inhibited oil gave a Dornte oxidation life (in the Modified Transformer Oil Dornte Test) of about 7,000 minutes. (In the Modified Transformer Oil Dornte Test, the oil is heated in the Dornte apparatus at 250° F. in the presence of a combination copper-iron catalyst while a constant flow of minute bubbles of oxygen passes through it. The time required for 100 grams of oil to absorb 825 ml. of oxygen is reported as the life of the oil.)

Another sample of the 60 N lubricating oil raffinate was contacted with Filtrol under the same conditions given above, except that about 10% of light ends was stripped off during the contacting step, using carbon dioxide as the stripping medium. The treated oil was then removed from the Filtrol by filtration and was inhibited with about 0.5% by weight of 2,6-di-tertiary butyl paracresol. The inhibited oil had a life of about 12,000 minutes.

A sample of the untreated oil, inhibited with about 0.5% by weight of 2,6-di-tertiary butyl para-cresol, gave a Dornte life of about 3400 minutes. Thus, it is seen that by stripping during the contacting step, an improvement in inhibitor susceptibility of about 250% is obtained, whereas by stripping after the contacting step, an improvement of only about 100% is obtained.

We claim as our invention:

1. A method of producing a refined lubricating oil of improved oxidation stability which comprises contacting a selective solvent refined raffinate lubricating oil fraction having a viscosity at 100° F. within the range of from about 50 to about 300 Saybolt Universal Seconds and a flash point of from about 305° F. to about 445° F. with from about 5% to about 10% by weight, based on the oil, of a solid adsorbent consisting essentially of acid activated bentonite at a temperature substantially above the flash point of the lubricating oil fraction and expressed by the following equation:

$$T=\frac{6957}{8.97-\log_{10} V}\pm 25$$

wherein T represents the contacting temperature expressed in degrees Rankine and V is the viscosity of said lubricating oil fraction at 100° F. expressed in Saybolt Universal Seconds, for a period of time of from about 15 to about 60 minutes while passing a controlled stream of an inert stripping gas substantially uniformly through the entire oil-clay mixture during essentially the entire period of contact at said temperature T and simultaneously removing from about 2% to about 10% by weight of light ends of the oil, based on the weight of the oil fraction, in the inert gas stream, separating the treated lubricating oil fraction from the clay, and incorporating a minor oxidation-inhibiting amount of an alkylphenol oxidation inhibitor in the separated oil.

2. A method of producing a refined lubricating oil of improved oxidation stability which comprises contacting a selective solvent refined raffinate lubricating oil fraction having a viscosity at 100° F. of about 58.5 Saybolt Universal Seconds and a flash point of about 305° F., with about 7.5% by weight, based on the oil, of acid activated bentonite at a temperature of about 500° F. for a period of about 30 minutes while passing a controlled stream of carbon dioxide through the oil-clay mixture and

removing about 10% by weight of light ends of the oil, based on the weight of the oil fraction, in the carbon dioxide stream, separating the treated lubricating oil fraction from the clay, and incorporating a minor oxidation-inhibiting amount of an alkylphenol oxidation inhibitor in the separated oil.

3. A method of producing a refined lubricating oil of improved oxidation stability in accordance with claim 2, wherein the minor amount of an alkylphenol incorporated in the separated treated oil is about 0.5% by weight of 2,6-di-tertiary butyl paracresol.

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