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TREATING LUBRICATING OILS

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This invention relates to the treatment of hydrocarbon lubricating oils and particularly petroleum lubricating oils by a combination process involving sulfurization and treatment with solvents in order to improve various characteristics of the oils.

It is an object of the present invention to provide a process for the production of lubricating oils having improved characteristics. One desired improved characteristic is extreme pressure properties, i. e. properties which permit the use of the oil under very high pressures such as exist for instance in gear cases. Another desired characteristic is high viscosity index. It is another object of this invention to produce a sulfurized oil in which the sulfur is held in a relatively stable form. Other and more detailed objects of my invention will become apparent as the description thereof proceeds.

The fact is well known that hydrocarbon oils will react with elemental sulfur at somewhat elevated temperatures to produce sulfurized oils. I have found that the constituents of hydrocarbon oils which react most readily with sulfur are, in general, the relatively naphthenic constituents rather than the relatively paraffinic constituents. Thus the unsulfurized constituents have a viscosity index higher than that of the original oil. By removing all or part of the sulfurized constituents by the use of solvents, an oil of improved viscosity index is produced. Since the sulfurized relatively naphthenic constituents are less similar to the relatively paraffin constituents, in terms of solubility, than are the original relatively naphthenic constituents, the separation by means of solvents is improved and the viscosity index-yield characteristics are better when solvent treating the sulfurized oil than when solvent treating the original stock. At the same time, some sulfurized materials are left in the finished oils and this produces extreme pressure properties which are highly desirable. Moreover, the sulfurized constituents which are left in the finished oil are more stable on the average than those produced by the sulfurization step alone. In other words, the solvent treatment tends to remove the less stable portion of the sulfurized constituents.

In the first step of my process I react a petroleum lubricating oil, preferably a mixed base petroleum lubricating oil stock, with an excess of sulfur at a temperature and for a time which will produce substantial sulfurization. Reaction temperatures from about 250° F. to about 550° F. can suitably be used but I prefer reaction temperatures from about 300° F. to about 400° F. The time of reaction depends upon the degree of sulfurization desired and particularly upon the reaction temperature. The higher the temperature the shorter is the required reaction time. At about 350° F. a reaction time of from 1 to 10 hours is suitable. Any type of autoclave or other reaction vessel equipped with stirring apparatus can be used. From 0.5% to 10% of sulfur, based on the weight of the oil, can be used. It is desirable to conduct the sulfurization with an inert atmosphere above the oil so as to avoid oxidation. Nitrogen or carbon dioxide can be used for this purpose. However, it is not imperative to eliminate free oxygen.

Following the sulfurization the excess sulfur, if any, is settled out and the sulfurized oil is subjected to solvent treatment. I prefer to use solvent extraction with any of the known selective solvents, such as sulfur dioxide, phenol, nitrobenzene, furfural, chloraniline, cresylic acid or beta beta' dichlordiethyl ether. The solvent extraction step is conducted in the usual manner, raffinate and extract phases are separated and the solvent is recovered from both phases. From one-half volume of solvent per volume of oil to five volumes of solvent per volume of oil can suitably be used. The temperature will, of course, depend upon the particular solvent chosen. The extract from the solvent extraction process contains the bulk of the sulfurized constituents but the raffinate likewise contains a substantial amount of sulfurized material.

As an example of my process an S. A. E. 50 Mid-Continent lubricating oil distillate was stirred with an excess of sulfur at 350° F. for 3 hours in an atmosphere of carbon dioxide. The treated oil was then solvent extracted with beta beta' dichlordiethyl ether using one volume of solvent and one volume of treated oil at 75° F. While the original distillate before sulfurization and the raffinate produced by sulfurization and solvent extraction each had a viscosity of 2740 seconds Saybolt at 100° F., the treated oil had a viscosity of 140.5 seconds Saybolt at 210° F. as compared with a viscosity of the original distillate at this temperature of only 125 seconds. Thus the viscosity index was increased from 58.5 to 78 by my process. The oil yield was 87% and the sulfur content of the raffinate was 1.4%.

Another sample of the same distillate stock was subjected to solvent extraction under conditions identical with those used in the case of

the sulfurized oil and the results were found to compare as follows:

	Viscosity index	Oil yield
		Percent
Sulfurized and solvent extracted oil	78	87
Solvent extracted oil (no sulfurization)	75	83.5

It will thus be seen that as compared with straight solvent extraction my combination process gave not only an improved yield but also an improved viscosity index. If more drastic solvent extraction conditions are used so as to reduce the yield, the viscosity index can be further improved and the sulfur content of the finished oil can be decreased.

Another experiment was conducted in which 1000 gms. of an S. A. E. 50 Mid-Continent dewaxed distillate was stirred at 350° F. for 3 hours with 40 gms. of sulfur and 1000 cc. of the sulfurization product was extracted with 1000 cc. of beta beta' dichlordiethyl ether at 75° F. The solvent was removed from the raffinate at 375° F. by stripping with carbon dioxide. This raffinate was tested for extreme pressure properties on the Timken E. P. testing machine and was found to be satisfactory at a loading of at least 15 lbs. whereas ordinary mineral oils fail at less than 10 lbs. loading. Thus in addition to the other improved characteristics mentioned, the extreme pressure properties are improved. This is, of course, highly desirable particularly in the case of gear oils.

In order further to remove unstable sulfur compounds, the sulfurized oil can be subjected to vacuum distillation either following solvent treatment or preferably between the sulfurization step and the solvent treatment step. This vacuum distillation eliminates considerable hydrogen sulfide and also eliminates heavy sulfur compounds. Distillation over caustic, or caustic treatment of the hot vapors, can be used to advantage.

Instead of using a solvent which has a selective solvent action on the sulfurized compounds as above mentioned, the sulfurized oil can be subjected to treatment with solvents such as the liquefied normally gaseous hydrocarbons. Liquefied propane is preferred but liquefied ethane, butane or pentane can be used and mixtures of various liquefied hydrocarbons can also be used. It will also be understood that combination solvent processes such as those involving the use of both propane and cresylic acid can readily be employed.

The liquefied normally gaseous hydrocarbons precipitate the sulfurized compounds rather than dissolving them as the more selective solvents tend to do.

When using liquefied normally gaseous hydrocarbons, low temperature conditions can be used, for instance, —40° F. or other sub-zero temperature, but it is preferable to use elevated temperatures in the vicinity of the critical temperature of the particular hydrocarbon solvent employed. The temperature used in the case of propane should be at least 100° F. but preferably about 150° F. to about 190° F. When using a normally gaseous hydrocarbon, from about 2 to about 10 volumes of the hydrocarbon solvent per volume of sulfurized oil can be employed but I prefer to use from about 4 to about 8 volumes of hydrocarbon solvent per volume of oil.

While I have described my invention in connection with certain specific embodiments thereof, these are by way of illustration rather than by way of limitation and I do not intend to be restricted thereby but only by the appended claims which should be construed as broadly as the prior art will permit.

I claim:

1. A method of treating a mineral lubricating oil comprising sulfurizing said oil and then solvent treating the sulfurized oil to remove a substantial portion of the sulfurized oil constituents, while permitting sufficient sulfurized oil constituents to remain to effect a substantial improvement in extreme pressure properties.

2. A method of treating a petroleum lubricating oil comprising treating said oil with elemental sulfur to produce substantial sulfurization, solvent extracting the sulfurized oil with a selective solvent, and separating raffinate and extract phases, said raffinate phase having an improved viscosity index and improved extreme pressure properties.

3. A method of producing a mineral lubricating oil of high viscosity index and possessing extreme pressure properties which comprises sulfurizing a mineral lubricating oil stock and treating the sulfurized oil with a selective solvent to remove a substantial part, but substantially less than all, of the sulfurized oil products.

4. A method of producing an improved mineral lubricating oil which comprises heating a mineral lubricating oil stock with elemental sulfur, vacuum distilling the sulfurized oil to eliminate the lowest boiling and highest boiling constituents and solvent treating the remaining sulfurized oil to remove part but less than all of the sulfurized oil constituents, of intermediate boiling points.

5. A method of producing an improved mineral lubricating oil which comprises sulfurizing a mineral lubricating oil stock and then treating the sulfurized oil with a liquefied normally gaseous hydrocarbon to remove a part but less than all of the sulfurized oil constituents.

6. A method according to claim 5 in which said liquefied normally gaseous hydrocarbon is propane.

7. A method according to claim 5 in which the treatment with liquefied normally gaseous hydrocarbon is conducted at elevated temperatures in the vicinity of the critical temperature of the liquefied normally gaseous hydrocarbon used.

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