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LUBRICATING OILS

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This invention relates to an improved process for improving the properties of hydrocarbon lubricating oils and improved lubricating oil compositions. More particularly it relates to a process of increasing the spreading pressure of mineral lubricating oils especially refined oils, on solid surfaces to a high level and providing a mineral lubricating oil of high spreading pressure which is maintained during use.

It is known that an important factor affecting the ability of a mineral lubricating oil to lubricate effectively various machine elements such as internal combustion engines, gears, etc. is the spreading pressure of the mineral lubricating oil on the solid surface involved. The higher the spreading pressure of an oil the more efficiently does it function as a lubricant under various adverse engine operating conditions. Various methods of increasing the spreading pressure of mineral lubricating oils on solid surfaces are known, such as by use of certain additives such as oil-soluble acylated aliphatic polyamine salts of aromatic acidic compounds e.g. N-(2-aminoethyl)naphthenamide salt of C_{14-18} alkyl salicylic acid or by blending certain hydrocarbon fractions to obtain an end product having a high spreading pressure value.

It has now been discovered that the spreading pressure of refined mineral lubricating oils on solid surfaces can be substantially increased without removing polar-containing compounds, particularly sulfur and nitrogen-containing compounds present, by treating such refined oils containing small amounts of such nitrogen and sulfur compounds with a small amount of an aqueous solution of hydrogen peroxide and an inorganic acid. Oils treated in this manner can be used as blending agents for improving the spreading pressure of various types of lubricating oils. When these treated oils are used as additives they may be used in amounts varying from 1% to 20% or more.

The refined mineral lubricating oil to be treated in accordance with this invention may have a sulfur content of about 0.45% or higher such as 0.65–1.5% and at least 2%, preferably 5%, polyaromatic and heterocyclic materials (1:10 to 10:1 ratio) and may have been refined by one or more of the conventional refining operations, such as fractional distillation to remove high boiling residual materials; treatment with sulfuric acid or oleum, earth or lime, or solvent extraction with a selective solvent for the aromatic components. It is applicable particularly to paraffinic-type lubricating oil, such as lubricating oils derived from Pennsylvania, Mid-Continent and West Texas crude oils and lubricating oils derived from other sources which may have had their paraffinicity increased by solvent extraction with selective solvents for the aromatic components.

Aromatic extracts from mineral lubricating oils may be treated by the process of the present invention to give particularly valuable blending components for making lubricating oils with a high spreading pressure on solid surfaces. The hydrocarbon lubricating oils treated by the process of the present invention may also be blended with one or more other hydrocarbon oils, fatty oils or synthetic lubricating oils. The amount of treated oil generally used varies from 1% to 20% to as much as 45%.

The aqueous solutions of hydrogen peroxide which may be used in the process of the present invention are those normally available in commercial quantities, for example 100 volume hydrogen peroxide solution which contains about 30% by weight of hydrogen peroxide (H_2O_2). Aqueous solutions of hydrogen peroxide containing concentrations of hydrogen peroxide between 5 and 95% H_2O_2 by weight may be used to carry out the treatment. Hydrogen peroxide solutions containing between 25 to 85% by weight H_2O_2 are usually used and preferably solutions containing between 30 and 50% by weight H_2O_2.

Inorganic acids have been found suitable for use according to the process of the present invention, such as hydrochloric, sulfuric and phosphoric acid and these acids are conveniently used in the strengths in which they are normally available in commercial quantities. The concentrations of the aqueous solutions of inorganic acid suitable for use vary with the particular acid being used. Acids in relatively high concentration are usually preferred but it has been found that dilute aqueous solutions containing up to 50% by weight of the acid are also suitable.

The treatment of the oil is generally carried out at ambient temperature. The oil and the mixture of aqueous hydrogen peroxide solution and inorganic acid are usually agitated to ensure intimate contact for a period of between 5 minutes and 4 hours. The period of agitation necessary to ensure completion of the reaction depends on the size of the batch of oil and to a certain extent on the relative concentrations of the inorganic acid and hydrogen peroxide solution. The proportions by weight of inorganic acid and hydrogen peroxide based on the weight of oil to be treated, which have been found to be suitable are between 0.05% and 10% by weight, respectively, and preferably between 1 and 5% weight. After the treatment the oil is usually separated from the treating solution and washed with water, or an aqueous or alcohol solution of an alkaline material such as caustic soda, or sodium carbonate or ammonia. The oil may be subjected to successive treatments of water, alkaline solution and water to effect the neutralization of the oil. Normally, however, owing to the small proportion of acid used in the treatment, it is only necessary to add a solid alkaline material to the oil and filter it off. Thus, the reaction mixture may be treated with solid sodium carbonate or lime and filtered. A very effective finishing treatment is to add lime and an activated earth, such as is normally used in the finishing of lubricating oils, to the treated oil and the filter.

The oil fraction may also be treated by successive portions of the inorganic acid and hydrogen peroxide and it has been found that this viariant is particularly advantageous for the treatment of oil fractions which are liable to form sludges in the presence of inorganic acids. The tendency to sludge formation is a particular problem when concentrated sulfuric acid is used as the inorganic acid and consequently the method, which has been found preferable with sulfuric acid, comprises treating the oil with sulfuric acid which has been diluted with water to a concentration of about 70–80% by weight, decanting the oil layer from the mixture of acid and sludge and subsequently treating the separated oil layer with an aqueuos solution of hydrogen peroxide. This treatment increases the spreading pressure of the oil without the addition of further acid due to the residual acidity in the oil after the sludge separation. The treated oil may be subsequently finished to remove residual acidity, hydrogen peroxide and water by one of the methods described above.

The process of the present invention is illustrated by the following examples.

Example I

A sample of 100 parts by weight of a solvent refined mineral lubricating oil having a viscosity of 330 seconds Redwood I at 140° F., a sulfur content of 0.66% and a spreading pressure on steel of 7.8 dynes per centimeter was mixed with 1 part by weight of a 100 volume hydrogen peroxide solution, containing 30% H_2O_2 by weight, and 1 part by weight of a 12 N solution of hydrochloric acid containing 44% HCl by weight, and the whole mixture was stirred for 2 hours at room temperature. The treated oil was washed with water, aqueous caustic soda solution and finally with water. The finished oil had a sulfur content of 0.65% and a spreading pressure on steel of 15.6 dynes/cm.

Example II

100 parts by weight of oil sample used in Example I was treated under identical conditions using the proportions of 100 volume aqueous solution of hydrogen peroxide and 12 N solution of hydrochloric acid shown in the following tabulation. The spreading pressure of the oil on steel before treatment was 7.8 dynes/cm. and the spreading pressure of the oil after the respective treatments is included in the tabulation.

Treatment	Hydrochloric acid, parts by weight	100 volume hydrogen peroxide solution	Spreading pressure after treatment
A	3	1	19.9
B	3	3	17.8
C	0.25	1	15.0

Example III

The treatment of the oil sample used in Example I was treated under identical conditions using 6 N hydrochloric acid containing 20% by weight HCl as the inorganic acid. 100 parts by weight of the oil were mixed with 1 part by weight 6 N hydrochloric acid and 1 part by weight of 100 volume hydrogen peroxide solution. The spreading pressure of the oil on steel was increased from 7.8 dynes/cm. to 15.0/cm. by the above treatment.

Example IV

A sample of 100 parts by weight of the solvent refined mineral lubricating oil described in Example I was treated with a mixture of 1 part by weight of 100 volume hydrogen peroxide solution (30% H_2O_2 by weight) and 1.8 parts by weight of 18 N sulfuric acid containing 88% H_2SO_4 by weight. The mixture was stirred for 2 hours at room temperature and the treated oil was washed with water, aqueous caustic soda solution and finally with water. The spreading pressure on steel of the treated oil was 15.8 dynes/cm. compared with the spreading pressure before treatment of 7.8 dynes/cm.

Example V

100 parts by weight of the mineral lubricating oil described in Example I were treated in the same manner as outlined in Example IV with a mixture of 1.7 parts by weight of perchloric acid solution containing 72% $HClO_4$ by weight. The spreading pressure of the treated oil was 18.2 dynes/cm. compared with the spreading pressure of the oil before treatment 7.8/dynes/cm.

Example VI

The effect of treating a solvent-refined mineral lubricating oil having a viscosity of 330 seconds Redwood I at 140° F. for varying periods of time using a mixture of hydrogen peroxide and hydrochloric acid will be described in this example. Five separate samples of 100 parts by weight of the mineral oil were treated separately with a mixture of 1.2 parts by weight of 12 N hydrochloric acid containing 40% HCl by weight and 1 part by weight of 100 volume hydrogen peroxide solution. The five mixtures of oil, hydrogen peroxide, and acid were stirred for 15, 30, 60, 90 and 120 minutes respectively and the spreading pressure on steel of the treated oil was measured after separating, and washing the oil with water, caustic soda solution and finally water.

The spreading pressure of the oil before treatment was 7.8 dynes/cm. and the spreading pressure of the oil after each treatment is given below corresponding to the different times of treatment.

Sample	Time of treatment in minutes	Spreading pressure, dynes/cm.
1	15	15.4
2	30	18.5
3	60	18.8
4	90	19.8
5	120	20.0

Example VII

A sample of 50 parts by weight of a mineral lubricating oil which had been solvent-refined and had a viscosity of 330 seconds Redwood I at 140° F. and a sulfur content of 0.5% was diluted with 50 parts by weight of a light petroleum spirit having a boiling range of from 60 to 80° C. and then mixed with 9 parts by weight of sulfuric acid containing 90% H_2SO_4 and stirred for 15 minutes. The oil layer was decanted and then stirred with 0.6 part by weight of 100 volume hydrogen peroxide solution containing 30% H_2O_2 by weight for a further period of 12 minutes. The mixture was stirred for a further 15 minutes with 1% activated earth by weight and 2% solid sodium carbonate by weight based on the weight of the mixture. The mixture was allowed to settle, then filtered through a No. 3 sintered glass filter, and finally the solvent was stripped off under vacuum. The spreading pressure of the oil before this treatment was 7 dynes/cm. and after the treatment the sulfur content was essentially unchanged and the spreading pressure was 16.0 dynes/cm.

Example VIII

The procedure outlined in Example VII was repeated with the same mineral oil and sulfuric acid in identical proportions. The decanted oil layer was then further treated with 0.65 part by weight of an aqueous hydrogen peroxide solution containing 80% H_2O_2 by weight for a period of 120 minutes. The oil layer was given the same treatment as in Example VII and the spreading pressure of the treated oil was 20.6 dynes/cm. compared with the spreading pressure of 7 dynes/cm. for the untreated oil.

We claim as our invention:

1. A process for improving the spreading pressure of a mineral lubricating oil containing at least 2% aromatic and heterocyclic materials and at least 0.45% sulfur, which comprises treating the oil at ambient temperature for from 5 minutes to 4 hours with from 0.05% to 10% each of an inorganic acid selected from the group consisting of sulfuric acid and hydrochloric acid and an aqueous solution of 5% to 95% hydrogen peroxide without essentially affecting the sulfur content of the oil.

2. A process as claimed in claim 1, wherein the inorganic acid is sulfuric acid.

3. A process as claimed in claim 1, wherein the inorganic acid is hydrochloric acid.

4. A process for improving the spreading pressure of a solvent refined mineral lubricating oil having a sulfur content of at least 0.45% and at least 2% aromatic and heterocyclic material which comprises treating the oil at ambient temperature for from 5 minutes to 4 hours with from 0.05% to 5% of an aqueous solution of 20% to 50% hydrochloric acid and an aqueous solution of 5% to 95% hydrogen peroxide and thereafter treating the oil with a mixture of lime and an activated earth.

5. A process for improving the spreading pressure of a solvent refined mineral lubricating oil having a sulfur

content of at least 0.45% and at least 2% aromatic and heterocyclic material which comprises treating the oil at ambient temperature for from 0.05% to 5% of an aqueous solution of 5% to 95% hydrogen peroxide and thereafter treating the oil with a mixture of lime and an activated earth.

6. A process for improving the spreading pressure of a solvent refined mineral lubricating oil having a sulfur content of at least 0.45% and at least 2% aromatic and heterocyclic material which comprises treating the oil at ambient temperature for from 5 minutes to 4 hours with from 0.05% to 5% of an aqueous solution of 20% to 50% perchloric acid and an aqueous solution of 5% to

95% hydrogen peroxide and thereafter treating the oil with a mixture of lime and an activated earth.

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