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LUBRICATING OIL COMPOSITION

William W. Reynolds and Hans Low, East Alton, Ill., assignors to Shell Oil Company, a corporation of Delaware

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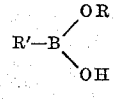
This invention relates to improved lubricating oil compositions, and more particularly, to mineral lubricating oil compositions which are resistant to oxidative deterioration under storage or use in equipment subjected to adverse operating conditions of temperature and pressure.

Lubricating oils such as mineral oils in the lubricating viscosity range tend to deteriorate and break down due to oxidation both in storage and during use, particularly at extremely high temperatures, such as above 400° F. and higher, resulting in the formation of undesirable products such as gums, sludges, resins, acidic products and other deleterious products which decrease the useful life of the oil or render it useless within a short period of time. Mineral oils of this type include aircraft, truck and automobile mineral lubricating oils, industrial oils such as gear oils, transformer oils, hydraulic oils and the like.

It is known that certain aromatic amines are useful as oxidation inhibitors for mineral oils. However, their application is limited because of their tendency to discolor mineral oils and form deposits particularly at elevated temperatures. Other types of anti-oxidants such as alkyl phenols, such as di- and trialkyl-phenols, e.g., 2,4-diamylphenol and 2,6-ditert-butyl-4-methylphenol are effective only in certain types of mineral oil and are oxidatively unstable at elevated temperatures.

It is an object of this invention to inhibit or prevent oxidation of mineral oil. Still another object is to inhibit or prevent deterioration, discoloration and deposit formation in mineral oil during storage and use over a wide temperature range, particularly at elevated temperatures. Other objects of the invention will be apparent from the following description of the invention.

It has now been discovered that various types of mineral lubricating oil including those which contain substantial amounts of aromatic (5–30%) can be effectively stabilized even at temperatures above 400° F. without undesirable side effects by addition thereto of small amounts (0.05–2%, preferably 0.1–1% by weight) each of an oil-soluble aromatic amine having the Formula I RR_1NH, wherein the R's are the same or different mono- or di-aromatic radicals, and an oil-soluble boron compound having at least one OH group and at least one R-B linkage where R is an oil-solubilizing hydrocarbyl radical having at least 6 carbon atoms. Compounds of this type include hydrocarbon boronic acid, $R'B—(OH)_2$ or its monoester



where R' is preferably an alkyl radical of at least 12 carbon atoms and R is an alkyl, aryl or cycloalkyl radical of at least 6 carbon atoms. The C_{12-18} alkyl boronic acids are preferred.

The oil-soluble aromatic amines represented by Formula I include diphenyl, dinaphthyl, phenyl alpha-naphthyl, phenyl beta-naphthyl amines and mixtures thereof.

The above B-hydrocarbyl boronic compounds can be prepared by any suitable means such as described by Krause and Hitsche, Ber., 51, 2784, 1921, and Ber., 55, 1261, 1922, or Khotinsky and Melamed, Ber., 42, 3090, 1909, as well as by the method described by Groszos in U.S. Patents 2,862,952 and 2,884,441.

The hydrocarbyl boronic acids include alkyl boronic acid such as octyl, decyl, dodecyl, tetradecyl, octadecyl boronic acids, cycloalkyl boronic acids such as cyclohexyl boronic acid, 3,5,5-triethylcyclohexyl boronic acid, cyclohexyl-cyclohexyl boronic acid; phenyl boronic acid, cyclohexyl phenyl boronic acid, decylphenyl boronic acid; monoesters of said acids such as monomethyl decyl acid boronate, monoethyl dodecyl acid boronate, monodecyl phenyl acid boronate, and mixtures thereof.

The additive combination of this invention effectively stabilizes a variety of petroleum lubricating stocks such as paraffinic, naphthenic and mixed base mineral oils hava viscosity range of from 50 SUS at 100° F. to 250 SUS at 210° F. A typical useful oil is a refined mineral lubricating oil (X) having the following properties:

Pour point, ° F.	29–31
Flash point, ° F. (COC)	Min. 420
Viscosity SUS, 100° F.	345–355
Unsulfonated residue	Min. 98

Another typical useful oil (Y) is an Oklahoma neutral petroleum fraction having the following properties:

Specific gravity	0.876
Pour point, ° F.	+10
Viscosity at 100° F., cs	56.88
V.I	93.9
Flash point, COC, ° F.	450
Fire point, ° F.	490
Aromatics, percent	23.7

To illustrate the pronounced superiority of the additive combination in stabilizing and preventing oxidation of mineral oil, the following compositions were prepared and evaluated in a micro-oxidation test of the MIL–L–7808 oxidation test under the following test condition: air flow of 1 liter/hour oxidizing agent, 400° F., solid metal catalyst (Ag, Ti, Cu, Mg, Fe), with the results as shown in Table I.

Table I

[Base=refined mineral lubricating oil X, amount of inhibitor=0.0=M=0.002 mole/100 g.]

Inhibitor	Hours to Adsorb 1 millimole O_2/g. oil	Gain due to Inhibitor, Hrs.
(1) None	11	
(2) Phenyl-alpha-naphthylamine	19	8
(3) Beta-beta-dinaphthylamine	17	6
(4) Diphenylamine	15	4
(5) Dodecyl boronic acid	12	1
(6) 2+5	50	39

Other compositions of this invention which would be expected to give comparable results to composition 6, Table I of this invention, include:

(7) Mineral oil X+0.02 M phenyl-alpha-naphthylamine +0.02 M octadecyl boronic acid,

(8) Mineral oil X+0.02 M beta,beta-dinaphthylamine +0.02 M octadecyl boronic acid,

(9) Mineral oil X+0.02 M phenyl-alpha-naphthylamine +0.03 M 3,3,5-triethyl cyclohexyl boronic acid,

(10) Mineral oil+0.02 M phenyl-alpha-naphthylamine +0.02 M monomethyl dodecyl acid boronate.

The additive combination of this invention can be used in neat mineral oils or with mineral oil compositions which contain pour point depressants, viscosity index improvers, corrosion inhibitors, detergents and the like.

We claim as our invention:

1. A mineral lubricating oil composition consisting essentially of a major amount of mineral lubricating oil and from about 0.05 to about 2% each of an oil-soluble aromatic amine selected from the group consisting of

phenyl-alpha-naphthylamine and beta,beta-dinaphthylamine and an oil-soluble B-hydrocarbon substituted boron compound selected from the group consisting of dodecyl boronic acid, octadecyl boronic acid, 3,3,5-triethyl cyclohexyl boronic acid, and monomethyl dodecyl acid boronate.

2. A mineral lubricating oil containing from about 0.05% to about 2% each of phenyl-alpha-naphthylamine and dodecyl boronic acid.

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