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LUBRICATING OIL COMPOSITION

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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 trialkylphenols, 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 aromatics (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 diaromatic radicals, and an oil-soluble boron ester having the Formula II $(RO)_3B$, wherein R is an alicyclic group, preferably monocyclic group of non-aromatic character which may contain substituent C_1–C_{18} hydrocarbyl radicals, or polar radicals such as halogen, hydroxyl, amino, nitro, or carboxylate radicals. Boron esters represented by Formula II in which at least one and preferably two R's of cyclohexyl groups 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 tricycloalkyl borates represented by Formula II $(RO)_3B$ are prepared by any suitable means such as by reacting under reflux conditions boric acid with a desired cycloalkanol in a suitable solvent such as a liquid hydrocarbon, e.g., benzene, toluene or the like.

Suitable alicyclic alcohols for use as starting materials in the preparation of compounds of this invention include cycloalkanols, such as cyclopentanols, cyclopentenols, cyclohexanols, cycloheptanols, cycloheptenols, bicycloheptanols, etc. Representative specific compounds are 3,3,5 - trimethylcyclohexanol, 4,6 - ditertiarybutyl - 2 - methyl-cyclohexanol, borneol, isoborneol, abietyl alcohol,

cycloalkanols produced by hydrogenation of isophorone and isophorone bottoms as described in Adelson U.S. Patents 2,481,487 and 2,502,408 as well as cycloalkenols described in U.S. Patents 2,433,008, 2,467,451, 2,493,733, 2,497,349, 2,574,077 and 2,597,843.

Specific representative cycloalkyl borates useful in lubricating compositions of the present invention are tricyclohexyl borate, tri(3,3,5-triethylcyclohexyl)borate, tri(4,6 - ditertbutyl - 3 - methylcyclohexyl)borate, tri(2-cyclohexylcyclohexyl)borate, tri(2 - phenylcyclohexyl)-borate, tri(2 - chlorocyclohexyl)borate, phenyl dicyclohexyl borate, tri(2,3 - dimethylcyclopentyl)borate, tri(2-butylcycloheptyl)borate, dicyclohexylcyclopentyl borate and the like.

The additive combination of this invention effectively stabilizes a variety of petroleum lubricating stocks such as paraffinic, naphthenic and mixed base mineral oils having a 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=0.02 M=0.002 mole/100 g.]

Inhibitor	Hours to Absorb 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) Tri(cyclohexyl)borate	12	4
(6) 2+5	52	41

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+0.02 M phenyl-alpha-naphthylamine +0.02 M tri(3,3,5-triethyl cyclohexyl)borate,

(8) Mineral oil+0.02 M phenyl-alpha-naphthylamine +0.02 M tri(4,6-ditertbutyl-3-methyl cyclohexyl)borate,

(9) Mineral oil+0.02 M beta,beta-dinaphthylamine+0.02 M tricyclohexyl borate,

(10) Mineral oil+0.05 M phenyl-alpha-naphthylamine +0.03 M tri(2-butylcycloheptyl)borate.

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 (1) an oil-soluble aromatic amine selected from the group consisting of phenyl-alpha-naphthylamine and beta-beta-dinaphthylamine and (2) an oil-soluble cycloalkyl borate selected from the group consisting of tri(cyclohexyl)borate, tri(3,3,5-triethyl cyclohexyl)borate, tri(4,6-ditertbutyl-3-methyl cyclohexyl)borate, and tri(2-butylcycloheptyl)borate.

2. A mineral lubricating oil containing from about 0.05% to about 2% each of phenyl-alpha-naphthylamine and tricyclohexyl borate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,084,472	Wiezevich	June 22, 1937
2,160,917	Shoemaker et al.	June 6, 1939
2,312,208	Clayton et al.	Feb. 26, 1943
2,452,319	Patterson et al.	Oct. 26, 1948
2,721,181	Lawrence et al.	Oct. 18, 1955

FOREIGN PATENTS

748,430	Great Britain	May 2, 1956