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LUBRICANT COMPOSITION

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The present invention relates to improvements in lubricants and especially to the improvement of lubricating oils principally useful for internal combustion engines operating under severe conditions. The invention will be fully understood from the following description.

Lubricating oils which exhibit improved performances under all types of operating conditions when used for the lubrication of heavy duty gasoline engines and for Diesel engines are coming into greater and greater demand. The requirements for such oils are being steadily made more stringent and it has been proposed to add various ingredients to these oils to improve their behavior in such services. The present invention relates to the production of superior lubricating oil compositions by adding to a base oil an ingredient which will improve the properties of the oil in various ways, particularly in improving the lubricity of the oil, in increasing its resistance to oxidation and consequent formation of corrosive substances, and in reducing its tendency to leave objectionable deposits in the engine. These lubricating oil blends are especially adapted for use under the high temperature conditions prevailing in the cylinders of internal combustion engines, i. e., at temperatures of 200° C. or higher.

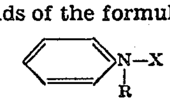
The new addition agents of the present invention include the various quaternary ammonium compounds, particularly the bases and the salts of such bases with organic acids. Various metallic compounds have been proposed for use in lubricating oils to improve their lubricating properties, but such compounds leave an objectionable residue. The quaternary ammonium bases and their salts with weak acids have the ability to impart lubricity to oils and at the same time the great advantage of not leaving residues on engine parts. By reducing oxidation the compounds also aid in preventing the formation of corrosive substances in the oil. The compounds can be made very soluble in lubricating oils by providing one or more sufficiently long hydrocarbon chains which are attached directly to the nitrogen atom or form a part of the acid radical. Compounds quite insoluble may, however, be used by being dispersed in the oil or when dissolved by the aid of a mutual solvent.

The new class of addition agents may be defined in its broadest scope as consisting of compounds having the quaternary ammonium base radical—

R*m*N—

where R is a hydrocarbon radical, for example, an alkyl, cycloalkyl, aryl or aralkyl radical, and *m* is an integer, four or less, the number being chosen according to the valencies of the R groups to satisfy four bonds of the nitrogen atom. The various R groups may be similar or dissimilar. The radicals R may contain substituent atoms, for example, halogen, nitrogen, phosphorus, oxygen, or sulfur, or substituent groups, for example, hydroxyl, aroxy, alkoxy, keto, amino, or mercapto groups. The preferred compounds are those in which the above defined quaternary ammonium base radical is attached to a hydroxyl group or to an organic radical, and in which the R's are alkyl groups. Where an acid radical is joined to the quaternary base radical, such radical may be that of a carboxylic acid, either aliphatic or aromatic, or a radical of widely different type, such as alcoholate, enolate, phenolate, xanthate, carbamate, or the analogous radicals in which sulfur is substituted for part or all of the oxygen.

The most preferred addition agents which are used in accordance with the present invention are those which have a solubility in oil to the extent of at least 0.05% at temperatures above 30° F. Compounds containing alkyl radicals having a total number of carbon atoms in all of such alkyl radicals equal to 12 or more and preferably at least 16, if available, are especially suitable, and branched structures are in general preferred. Typical examples of compounds which are suitable for use in accordance with this invention are those having monovalent alkyl radicals attached to the nitrogen atom, for example, tetramethyl ammonium naphthenate, tetraethyl ammonium naphthenate, tetraethyl ammonium hydroxide, tetraethyl ammonium oleate, tetramethyl ammonium cresylate, tetramethyl ammonium lactate, tetra-n-butyl ammonium oleate, tetrabutyl ammonium tribromophenolate, tetrabutyl ammonium-2,4-dinitrophenolate, tributyl methyl ammonium octylphenolate, the tribenzyl amyl ammonium salt of diisobutyl phenol sulfide, the tetraethyl ammonium salt of wax-alkylated phenol sulfide, tetramethyl ammonium butyl thioxanthate, tetramethyl ammonium ethyl xanthate; those having alkylol or aralkylol groups attached to the nitrogen atom, for example, butyl triethanol ammonium naphthenate, ethyl phenyl diethanol ammonium cresylate and tetrahexanol ammonium oleate; those in which the nitrogen of the quaternary base forms part of a pyridine, quinoline or nicotine group, for example, compounds of the formula



where R is a hydrocarbon radical and X is an acid radical, e. g., methyl pyridonium oleate. In addition to the examples given above, many other examples of suitable compounds may be derived by combining the quaternary ammonium base radical with various acid radicals, both straight and branched chain, saturated and unsaturated, aromatic and aliphatic, monobasic and polybasic, and containing various substituent atoms and groups. Examples of acids from which suitable quaternary ammonium base salts may be derived include caprylic acid, ricinoleic acid, dihydroxystearic acid, fatty acids derived from waxes, hexahydrobenzoic acid, resinic acids, abietic acids, phthalic acid, and the like. The above examples are illustrative only and are cited to show the great variety of types of compounds which are contemplated in the present invention.

The amounts of the new addition agents which are generally used in lubricating oil compositions range from about 0.05 to about 5% of the base stock present and preferably between 0.1 and 1.0%. The exact amount to be used for optimum results will depend partly upon the particular type of compound being used as well as upon other factors, such as the severity of the operating conditions to which the lubricating oil will be exposed and the nature of the mineral oil base stock itself.

In general, the base stock to be used in the preparation of the lubricants of the present invention may be any refined mineral lubricating oil, preferably having a viscosity from 40 to 150 seconds Saybolt at 210° F., and suitable base stocks include those of high paraffinicity and high viscosity index, such as those which have a viscosity index of 100 or more, as well as low paraffin and low viscosity index oils. Base stocks comprising greases, fatty oils or synthetic oils may also be employed.

The finished oil compositions may contain also other addition agents such as are often found in lubricants, for example, oiliness agents, film strength modifiers, thickeners, viscosity index improvers, pour depressants, solvents, detergents, sludge dispersers, corrosion preventives, antioxidants, dyes, etc.

The effect of the addition of the preferred compounds in improving the characteristics of a finished lubricating oil may be illustrated by the data presented in the following examples. In these examples various standard tests were applied to determine the properties of the oil blend.

The Mougey test was applied as a test of lubricity to determine the number of weights which could be applied to a test bearing carrying the test sample of oil without seizure. This test was carried out according to the method described in National Petroleum News, vol. 23, No. 45, page 47 (Nov. 11, 1931).

The oxygen absorption test was applied to determine the oxidation susceptibility of the lubricating oil under engine operating conditions. A known amount of oxygen is bubbled through 10 cc. of the lubricating oil maintained at 200° C. The oxygen is continuously recycled. At the end of succeeding 15 minute periods the amount of oxygen absorbed by the oil is measured. The results are given as the number of cubic centimeters of oxygen absorbed by 10 cc. of the oil at 15 minute intervals at 200° C.

The Sligh oxidation test was carried out according to the standard A. S. T. M. method. Ten grams of the oil, contained in a stoppered conical flask from which the air has been displaced by oxygen, are maintained at 200° C. in an oil bath for 2½ hours. The number of milligrams of asphaltenes formed, determined by solution of the oil in precipitation naphtha and filtration through a Gooch crucible, is termed the Sligh number of the oil.

Example 1

A sample of a refined mineral lubricating oil of S. A. E. 20 grade containing 2% of tetraethyl ammonium oleate and a blank base oil sample were subjected to the Mougey test to determine the lubricity of the oil. The results obtained were as follows:

Oil or blend	Mougey test wts. carried
Base oil	18
Base oil+2% tetraethyl ammonium oleate	22

These results demonstrate the ability of the addition agent to reduce friction and enable the oil to carry loads without scratching and scuffing of the rubbing surfaces.

Example 2

Blends were prepared by adding 0.5% of tetramethyl ammonium naphthenate, separately, to a refined mineral lubricating oil of S. A. E. 20 grade and to a refined mineral lubricating oil of S. A. E. 30 grade. To these blends, as well as to corresponding blank samples, was applied the Sligh oxidation test described above. The results are as follows:

Oil or blend	Sligh No.
Base oil, S. A. E. 20 grade	22.4
Base oil, S. A. E. 20 grade+0.5% tetramethyl ammonium naphthenate	15.9
Base oil, S. A. E. 30 grade	20
Base oil, S. A. E. 30 grade+0.5% tetramethyl ammonium naphthenate	10.7

Example 3

Samples of refined mineral lubricating oil of S. A. E. 20 grade were blended, in the first case, with 2% of an oiliness agent consisting of isopropyl esters of oxidized paraffin wax acids, and, in the second case, with 2% of the same oiliness agent and a maximum amount of tetramethyl ammonium cresylate, which was less than 0.2%. The neutralization number and saponification number of these blends were then determined. The results are as follows:

Blend	Neutralization No.	Saponification No.
Base oil+2% oiliness agent	13.8	39.2
Base oil+2% oiliness agent+a maximum amount of tetramethyl ammonium cresylate	2.2	12.4

Example 4

The oxygen absorption test was applied to a blend of a refined mineral lubricating oil of S. A. E. 50 grade with 0.2% of tetra-n-butyl ammonium oleate as well as to a base oil blank sample. The results are as follows:

Oil or blend	Oxygen absorption (cc. of O_2 in each 15 minute interval)
Base oil	103—213—107
Base oil+0.2% tetra-n-butyl ammonium oleate	42—16—21—28

Example 5

Samples of a refined mineral lubricating oil of S. A. E. 20 grade were blended, in the first case, with 2% of isopropyl esters of fatty acids to increase lubricity, and, in the second case, with 2% of the same esters and 0.05% of tetrabutyl ammonium dinitrophenolate. Test bearings of copper-lead alloy and cadmium-silver alloy were immersed in the two oil blends at 280° F. for 22 hours to determine the loss in bearing weight. The acid number of the used blended oils was also determined. The results are as follows:

Blend	Bearing wt. loss		Used oil acid No.
	Cu-Pb	Cd-Ag	
Base oil+2% lubricity agent	0.480	0.587	1.9
Base oil+2% lubricity agent+0.05% tetrabutyl ammonium dinitrophenolate	0.247	0.387	1.3

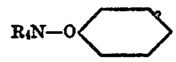
The above described data show the effect of the addition agent in reducing the corrosion of bearings.

It is to be understood that the present invention is not to be considered as limited by any of the examples recited herein, which are given for purposes of illustration only, but is to be limited solely by the terms of the appended claims.

I claim:

1. A lubricant containing dissolved therein 0.05% to 5% of tetramethyl ammonium cresylate.

2. An improved motor oil comprising a hydrocarbon oil subject to deterioration in the presence of oxygen and a compound having the formula



where R is a hydrocarbon radical, said compound being present in an amount sufficient substantially to inhibit such deterioration.

3. A lubricant comprising a hydrocarbon oil subject to deterioration in the presence of oxygen and a compound having the formula

$$R_mN\text{—}OR'$$

where R is a hydrocarbon radical and m is an integer, 4 or less, chosen to satisfy four bonds of the nitrogen atom, and R' is an aromatic radical, said compound being present in an amount sufficient substantially to inhibit such deterioration.

4. A lubricant according to claim 3 in which the group R' is an alkylated benzene nucleus.

5. A lubricant comprising a hydrocarbon oil and a small proportion of a tetraalkylammonium cresylate.

6. A lubricant according to claim 5 in which the tetraalkylammonium cresylate is tetramethylammonium cresylate.

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