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MOTOR OIL INHIBITOR

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The present invention relates to lubricant compositions having improved resistance to coking under severe engine operating conditions.

The successful lubrication of internal combustion engines is complicated by the deterioration of the lubricating oil during use. Oxidation of the oil, for example, causes the formation of sludge and lacquers that deposit on parts of the engine and interfere with circulation of the oil. Certain deterioration products are acidic in nature and corrode bearing metals and other metal parts. Considerable progress has been made in developing antioxidant sludge dispersion and corrosion inhibition additives for lubricants to minimize the above-mentioned effects.

Problems of a different nature to those discussed above are frequently encountered in engines operating under extremely severe high temperature conditions. For example, high powered reciprocating aviation engines operate at higher temperatures than are encountered in most lower powered engines. A specific difficulty occurs in the so-called "rocker boxes" in which the rocker-arms are located. Temperatures in excess of 450° to 500° F. develop in these boxes. These temperatures approach the incipient cracking temperature of most conventional petroleum-base lubricants. Consequently, prolonged operation leads to excessive cracking and high-temperature oxidation of the lubricant resulting in deposition of coke or carbon-like materials on the engine parts. Coke deposition frequently becomes so serious that operation of the engine must be discontinued in order to clean and repair it. Problems of this nature are even more serious in the case of turbo-jet engines and the like which operate at somewhat higher temperatures than the reciprocating types.

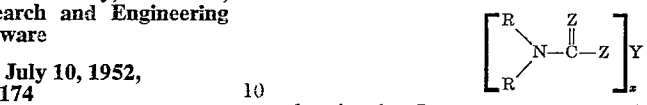
The conventional antioxidant, detergent and corrosion inhibition additives have little or no effect in minimizing coke formation of the afore-mentioned type. It is the primary object of the present invention to prepare a group of lubricant additives that are beneficial in this regard.

In accordance with the present invention, it has been found that the group V metal salts of certain sulfur-containing organic acids, when added to lubricants in minor quantities, minimize coking of the lubricant under high temperature service. Particularly efficacious in this respect are the group V metal salts of thiocarbamic acids, such as dithiocarbamic acids. This result is entirely unexpected. It is known to the art, for example, that the dithiocarbamic salts of metals of groups I, II, III, the so-called Iron Group, and the like of the Periodic Table are effective antioxidants, sludge dispersion and corrosion inhibitor additives for lubricants. However, these compounds are not extremely effective for preventing or retarding high-temperature coking of the lubricants.

Suitable organic sulfur-containing acidic materials from which the group V metal salts may be prepared include mercaptans, xanthic acids, thioxanthic acids,

organic dithiophosphoric acids, alkyl phenol sulfides, thioglycollic acids, thiocarbamic acids and the like. The thiocarbamic acids, particularly the dithiocarbamic acids, are preferred in making the salts.

The dihydrocarbon thiocarbamic salts of the present invention may be represented by the formula:



wherein the R groups represent hydrocarbon radicals similar or dissimilar in nature, Z is selected from the class consisting of sulfur and oxygen and at least one Z is sulfur, Y is a metal of group V of the periodic table which has a molecular weight above 50, and x is the valence of the metal. It is seen that this formula applies to dithiocarbamates, thiolcarbamates and thionocarbamates; however, the dithiocarbamates are preferred from the standpoint of ease of preparation and effectiveness. R may be an alkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkenyl, and the like radicals having in the range of 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms. In order to promote solubility of the compound in lubricants, the R groups should have at least a total of 4 carbon atoms. Alkyl radicals are generally preferred and include methyl, ethyl, isopropyl, butyl, isopentyl, tert.-octyl, dodecyl, and the higher straight and branched chain alkyl groups. Other specific hydrocarbon radicals include phenyl, naphthyl, benzyl, methylphenyl, isopropylphenyl, cyclohexyl, methylcyclohexyl and the like.

The group V metals include vanadium, arsenic, columbium, antimony, tantalum, bismuth, etc. The right-hand metals of group V of the periodic table, namely, arsenic, antimony and bismuth, are preferred. Antimony salts are particularly preferred in the practice of the present invention since these compounds are relatively easy to prepare, are soluble in oils, and are excellent anti-coking agents.

Specific compounds include vanadium diisopropyl, dithiocarbamate, arsenic diethyl thiolcarbamate, antimony diphenyl thionocarbamate, antimony ethyl butyl dithiocarbamate, bismuth dibutyl dithiocarbamate, and the like.

The salts are usually added to lubricants in amounts in the range of about 0.01 to 5.0% by weight, based on the total composition, although amounts in the range of about 0.05 to 2% are generally satisfactory. The proportions giving the best results in any given case will vary somewhat according to the nature of the lubricant base oil, the specific purpose for which the oil is used, and the specific additive employed. Conveniently, the additive is prepared as a concentrated oil solution containing in the range of 20 to 50% by weight of the additive. The concentrate may be stored and transported in this form and blended with a base oil in the required amount in making a finished lubricant. If necessary, a solubilizer may be used to increase the solubility of the metal salt in the concentrate or finished lubricant.

The lubricating oil base stock used in preparing the composition may be straight mineral lubricating oils or distillates, bright stock residua and the like. Synthetic lubricants, such as hydrogenated oils, dibasic acid esters, glycol ethers, and other polyester and poly-ether synthetic lubricants may be used. Mixtures of synthetic oils and petroleum base mineral oils will also be useful. The lubricant base stock may vary considerably in viscosity such as in the range of 40 to 150 seconds Saybolt viscosity at 210° F. The lubricant compositions are particularly useful in severe high-temperature service and thus qualify for lubricating certain types of aviation re-

ciprocating engines, Diesel engines, turbines, turbo-jet engines, etc.

The finished lubricant will generally contain other types of additives. It is sometimes particularly desirable to include a corrosion inhibitor since the metal salts are often corrosive to metals and alloys such as copper, bronze, etc. Other additives include pour depressors, sludge dispersers, antioxidants, viscosity index improvers, oiliness agents, and the like.

The benefits to be derived by the practice of this invention will be demonstrated by the following examples. These examples are given for the purpose of illustration only and are not to be construed as limiting the scope of the invention in any way.

Example I

Various metal salts of dibutyldithiocarbamic acid were evaluated as inhibitors of coking in an aviation engine lubricant having 120 seconds Saybolt viscosity at 210° F. The coking test was carried out in the following manner: The test lubricant containing the desired amount of additive was placed in an aluminum measuring cup and stirred while heat was applied. The sidewalls of the cup were maintained at a temperature of about 500° F. while the oil was heated from the bottom until it reached a temperature of 550° F. The stirrer was then stopped for ten minutes, followed by stirring for ten minutes, and alternate non-stirring and stirring periods were repeated until the end of the fourth non-stirring period. The oil was then discarded and the coke deposit weighed. A sample of the lubricant containing no additive was also evaluated for comparative purposes. The results of the tests follow:

Additive Employed	Amount in Oil, Wt. Percent	Coke Formed, mg. Coke/75 g. Oil
1. None		56
2. Antimony Dibutyldithiocarbamate	0.1	7
3. Antimony Dibutyldithiocarbamate	0.5	0
4. Antimony Dibutyldithiocarbamate	1.0	3
5. Zinc Dibutyldithiocarbamate	0.5	16
6. Nickel Dibutyldithiocarbamate	0.1	10
7. Nickel Dibutyldithiocarbamate	0.5	14
8. Lead Dibutyldithiocarbamate	0.5	53
9. Sodium Dibutyldithiocarbamate	0.4	39
10. Sodium Dibutyldithiocarbamate	[1] 0.5	
11. Ba Dibutyldithiocarbamate	[1] 0.1	

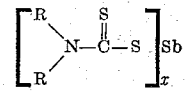
[1] Insoluble in the oil at this concentration.

The antimony salt, when used in an amount of 0.1% by weight, was superior to the other metal salts. At a concentration level of 0.5 and 1.0% by weight, the antimony salt was markedly superior to the other metal salts in suppressing coking of the mineral lubricant.

What is claimed is:

1. A composition comprising a mineral lubricating oil and a minor amount, sufficient to suppress coking of said oil, of an antimony salt of a dihydrocarbon dithiocarbamic acid, each of the hydrocarbon portions of said acid having in the range of 1 to 20 carbon atoms.

2. A mineral lubricant composition for use under high temperature conditions containing a minor amount, sufficient to suppress coking of the lubricant, of an antimony salt having the formula:



wherein the R groups represent hydrocarbon radicals, each having in the range of 1 to 20 carbon atoms, and x is the valence of the antimony.

3. A composition as in claim 2 wherein said R groups are alkyl radicals having in the range of 1 to 10 carbon atoms.

4. A composition as in claim 3 wherein said R groups are butyl radicals.

5. A composition as in claim 2 wherein said minor amount is in the range of 0.01 to 5.0% by weight, based on the total composition.

6. A mineral lubricant composition containing in the range of 0.05 to 2% by weight, based on the total composition, of antimony dibutyldithiocarbamate.

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