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CORROSION-INHIBITORS FOR
LUBRICATING OILS

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1

This invention relates to additives for lubricants and more particularly to corrosion inhibitors of use in lubricating oils of the crankcase type. Although the additives of the present invention are highly desirable for use in the crankcases of passenger automobiles or similar vehicles, they are especially valuable for heavy duty service in truck, bus, aeroplane, marine and diesel engines which operate for long periods of time at high temperatures.

With the advent of greater horsepower output in internal combustion engines and their operation at higher speeds, it became necessary to generally strengthen or "stiffen" the engines to withstand the increased stresses which are created in the operating parts thereof, for example, in the crankshaft or other rotating or moving parts. New "hard-metal" alloy bearings such as cadmium-silver, copper-lead, nickel-cadmium, and the like have been introduced to replace the softer babbitt metal bearings in an effort to brace these operating parts against distortion due to the greater forces. These hard alloy bearings exhibit superior strength characteristics and are generally more satisfactory than their predecessor babbitt metal bearings but have shown a greater susceptibility toward the corrosive action of the acidic materials developed in the lubricating oils due to oxidation or decomposition during use. As a consequence, efforts have been made to prevent this type of corrosion of the newer type of bearings by the use of corrosion inhibitors in the oil and such has become an important factor in the care and preservation of internal combustion engines.

How these corrosion inhibitors actually function in a composition as complex as the mixture of hydrocarbons found in lubricating oils and under the varying conditions which exist in an operating internal combustion engine is not precisely or positively known. However, it is believed that these inhibitors either prevent the corrosive substances from coming into contact with the metal surfaces of the engine parts by forming a protective coating thereon which is impervious to the corrosive materials and thus act as "passivators," or function by converting the corrosive substances in the oil into harmless, non-corrosive materials by appropriate chemical action.

Various compounds have been utilized in such inhibiting functions and have normally comprised metallic salts of various phosphoric acids. Such have proved quite satisfactory in the industry but, being metallic, are subject to some disadvantages. For example, it has been noted that,

2

upon the combustion of the lubrication oils containing these compounds, there is an objectionable ash or residue resulting from the decomposition of the lubricant. Consequently, there has been a growing demand in some groups in the lubricating oil industry for non-metallic additives which will not leave any ash or residue.

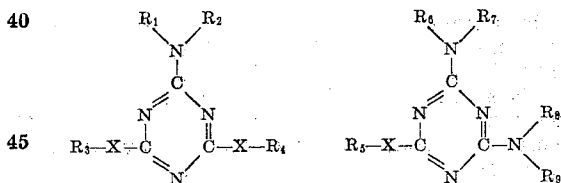
Furthermore, in some cases of these phosphorus-containing compounds, there has been some evidence of valve burning which has been attributed to the presence of the phosphorus.

It is therefore a principal object of the present invention to provide inhibitors for lubricating oil compositions capable of substantially reducing or inhibiting the corrosive effects of such lubricating oils and/or decomposition or oxidation products thereof on metallic elements.

It is another principal object of the present invention to provide an anti-corrosive agent which will leave no ash or residue on decomposition and which will not result in any valve burning.

We have found that the corrosive effects of the acidic materials developed in lubricating oil compositions during use may be substantially reduced or inhibited by the addition to such compositions of a small amount of an oil-soluble compound of the group consisting of N X-substituted ammelides and ammelines wherein each oxygen attached to a carbon of the cyanidine ring is replaced by X which is a member of the group consisting of sulfur, selenium and tellurium and wherein the substituents attached to the N and X atoms are members of the group consisting of alkyl, aryl and cycloalkyl radicals and hydrogen.

These N,X-substituted ammelides and ammelines may be represented respectively by the following structural formulae:



in which X is sulfur, selenium or tellurium; and any R group is an alkyl, aryl and cycloalkyl radical or hydrogen.

It is to be observed that these compounds are non-metallic and, as a consequence, will leave no ash or residue when they are decomposed upon combustion of the lubricating oil compositions containing them. It is further to be noted that

these compounds do not contain any phosphorus, as is commonly found in most anti-corrosive agents, and thus are especially useful where phosphorus compounds have been found to cause valve burning.

The invention will be described in greater detail with particular reference to the sulfur-substituted ammelides and ammelines or thioammelides or thioammelines, but it is to be pointed out that this is not to be construed as limitative of the invention and that similar compounds containing selenium and tellurium can be substituted in order to accomplish the objects of the present invention.

The more specific aspects of the present invention are concerned with hydrocarbon substituted thioaminocyanidines which have been rendered oil soluble by the attaching of hydrocarbon substituents to the nitrogen and sulfur compounds so as to be readily blended with hydrocarbon lubricating oils to form lubricating oil compositions having the requisite corrosion inhibiting properties.

As specific examples of particular compounds which have been found satisfactory within the principles of the present inventive concept, the following compounds are cited primarily for purposes of illustration: S,S'-diethyl dithioammelide; S,S'-diallyl dithioammelide; S,S'-dibutyl dithioammelide; S,S'-diallyl-N-dimethyl dithioammelide; S,S'-diallyl-N-dibenzyl dithioammelide; S,S'-dimethyl-N-dicyclohexyl dithioammelide; S,S'-dibenzyl dithioammelide; S,S'-dicyclohexyl dithioammelide; S,S'-dinaphthyl dithioammelide; N-diallyl dithioammelide; N-diethyl dithioammelide; S-octadecyl thioammeline; S-benzyl thioammeline; S-cyclohexyl thioammeline; S-octyl-N,N,N',N'-tetramethyl thioammeline; pentallyl thioammeline; S-benzyl-N,N,N',N'-tetraethyl thioammeline; pentabenzyl thioammeline; S-naphthyl thioammeline; N,N,N',N'-tetraallyl thioammeline, etc.

It is to be noted, however, that the organic radicals selected to be attached to the sulfur and nitrogen atoms must be such that the resulting compound is sufficiently soluble in lubricating oil for the purposes of the present invention and in the concentrations hereinafter set forth.

For example, in the event that there are organic radicals attached to the nitrogen atoms, the necessity for long chain carbon atom radicals on the sulfur atoms is reduced or even obviated. Conversely however, if there are no organic radicals attached to the nitrogen atoms or if they are of very short carbon atom chain length, for example, then the need for longer carbon chain length radicals on the sulfur atoms is correspondingly increased. The criterion in all instances, therefore, is seen to be the requirement of oil solubility and the term "oil soluble," or similar phrase as used herein, is intended to limit the scope of the invention accordingly.

Easy blending of hydrocarbon lubricating oil additives with oils is of considerable importance from a practical and commercial viewpoint and accordingly, while certain of the shorter chain carbon radicals having decreased oil solubility characteristics can be blended with lubricating oils by special techniques, the difficulty and the additional expense of doing so does not warrant their industrial use. It is also customary in the industry to prepare, ship and store these additives in the form of about 50% solutions in lubricating oils, for example, so that the blender of the lubricating oil composition need only pour the

additive compound into the lubricating oil with suitable stirring. Additives of difficult solubility cannot be employed in such facile manner and hence are not as desirable.

The amount of the inhibitor to be mixed with the hydrocarbon lubricating oil or other lubricant will depend to a large extent upon the nature and characteristics of the lubricating oil, itself, upon the particular ester used, upon factors of expense and intended use of the lubricating composition, upon the presence of other additives, etc. Oils having a marked tendency to oxidize or corrode metals will naturally require larger amounts of the additive and, conversely, oils having a lesser tendency to oxidize or corrode metals will not require so much of the additive. In general, we have found that an effective concentration range which is hereinafter sometimes referred to as "stabilizing" amounts may comprise from about 0.1 percent by weight to about 5.0 percent by weight of the lubricating oil. For most oils, we have found that concentrations of from about 0.5 percent by weight to about 2.0 percent by weight of the lubricating oil have proved satisfactory.

If desired or necessary, the inhibitors of the present invention may be used in conjunction with other lubricating oil additives, for example, detergents or dispersants such as metal salts of organic acids, or pour point depressants such as wax naphthalene condensation products, or viscosity index improvers such as high molecular weight resins, or extreme pressure agents such as phosphorous or sulfur containing organic compounds, and the like.

The invention will be further illustrated in greater detail by the following specific examples and test results. It should be understood, however, that although these examples may describe in particular detail some of the more specific features of the inventive concept, they are given primarily for purposes of illustration and the invention in its broader aspects is not to be construed as limited thereto.

Example 1

A 10% aqueous solution of 91 grams of monosodium dithioammelide was stirred at room temperature with 20 grams of sodium hydroxide in 1100 ml. of water, and 80.5 grams of allyl chloride was added slowly with agitation over a thirty minute period. The reaction mixture was then heated for about one hour at about 80-88° C. and then allowed to cool slowly with vigorous agitation. The crystalline solid was filtered off and air-dried. 100 grams of crude material with a strong garlic-like odor was obtained. The material (S,S'-diallyldithioammelide) was recrystallized from isopropyl alcohol. The melting point was found to be 64-67° C. The calculated nitrogen and sulfur content was 23.31% and 26.68%. The actual percentages were found to be: N%=23.26 and 23.27; S%=26.66 and 26.47. The additive was tested in an Underwood corrosion test at 0.5% concentration and the bearing weight loss per whole bearing on cadmium-lead bearings was determined to be 11 mg., as compared to 27 mg. for a control Mid-Continent solvent refined oil without any additive. Increased percentages of additive in the lubricating oil compositions gave correspondingly improved results.

Example 2

144 grams of butyl bromide was added with vigorous stirring to a mixture of 91 grams of monosodium dithioammelide and 20 grams of sodium

5

hydroxide in 1200 ml. of water at a temperature of approximately 25°-30° C. over a thirty-minute period. The reaction mixture was then heated further for forty minutes at a temperature of approximately 85°-90° C. and S,S'-dibutyldithioammelide was obtained as a crude material. This was tested in an Underwood corrosion machine and found to possess similar corrosion inhibiting properties to that exhibited by the additive prepared in Example 1.

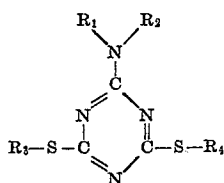
Example 3

The procedure set forth in Example 1 was followed except that 134 grams of benzyl chloride was used to react with the monosodium dithioammelide and sodium hydroxide to form S,S'-dibenzyl dithioammelide. Underwood corrosion tests on this material gave similar improved results over ordinary control oils without the additive as stated in Example 1.

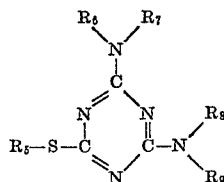
Although we have described but a few specific examples of our inventive concept, we consider the same not to be limited thereby or to the specific substances mentioned therein but to include various other compounds of equivalent constitution as set forth in the claims appended hereto. It is understood that any suitable changes, variations and modifications may be made without departing from the spirit and scope of the invention.

We claim:

1. A hydrocarbon oil composition comprising a relatively large proportion of a hydrocarbon lubricating oil having dissolved therein a relatively small amount, sufficient to reduce the corrosive effect of said composition on metallic elements, of an oil-soluble compound of the group consisting of N,S-substituted dithioammelides and thioammelines, respectively having the following structural formulae



and

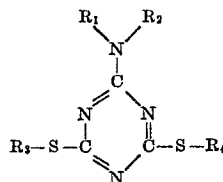


wherein the substituents attached to the N and S atoms are members of the group consisting of alkyl radicals having from 1 to 18 carbon atoms, allyl, aryl and cycloalkyl radicals and hydrogen.

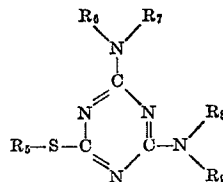
2. A hydrocarbon oil composition comprising a relatively large proportion of a hydrocarbon lubricating oil having dissolved therein from

6

about 0.1% by weight to about 5.0% by weight of an oil soluble compound of the group consisting of N, S-substituted dithioammelides and thioammelines, respectively having the following structural formulae



and



wherein the substituents attached to the N and S atoms are members of the group consisting of alkyl radicals having from 1 to 18 carbon atoms, allyl, aryl and cycloalkyl radicals and hydrogen.

3. A hydrocarbon oil composition comprising a relatively large proportion of a hydrocarbon lubricating oil having dissolved therein a relatively small amount of S,S'-diallyldithioammelide as an anti-corrosive agent.

4. A hydrocarbon oil composition comprising a relatively large proportion of a hydrocarbon lubricating oil having dissolved therein a relatively small amount of S,S'-dibutyldithioammelide as an anti-corrosive agent.

5. A hydrocarbon oil composition comprising a relatively large proportion of a hydrocarbon lubricating oil having dissolved therein a relatively small amount of S,S'-dibenzyl dithioammelide as an anti-corrosive agent.

6. A hydrocarbon oil composition comprising a relatively large proportion of a hydrocarbon lubricating oil having dissolved therein from about 0.1% by weight to about 5.0% by weight of S,S'-diallyldithioammelide as an anti-corrosive agent.

7. A hydrocarbon oil composition comprising a relatively large proportion of a hydrocarbon lubricating oil having dissolved therein from about 0.1% by weight to about 5% by weight of S,S'-dibutyldithioammelide.

8. A hydrocarbon oil composition comprising a relatively large proportion of a hydrocarbon lubricating oil having dissolved therein from about 0.1% by weight to about 5.0% by weight of S,S'-dibenzyl dithioammelide.

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