LUBRICANTS CONTAINING AN AMINO THIOCYANATE AND A CYCLIC AMINE

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5 Claims. (Cl. 252—47.5)

This invention relates to improved synthetic ester lubricating compositions which have excellent extreme-pressure and antiwear properties and which are not corrosive to lead.

Recently, synthetic lubricants have gained prominence in the field of lubrication because of stringent requirements of various new lubricant applications. These lubricants, which are frequently esters, ethers, silicones, or polymeric hydrocarbons are generally designed for special applications where conventional mineral oils are not satisfactory. Synthetic oils have low pour points and desirable viscosity characteristics and, with proper inhibition, can generally be used at temperatures considerably above the decomposition temperatures of most mineral oils. Accordingly, these oils have found use in jet aircraft, missiles, and the like, where wide temperature ranges and extreme operating conditions are likely to be encountered. Proper lubrication of aircraft gas turbines, for example, requires the ability to function at bulk oil temperatures as low as 

\[ -65^\circ \text{F.}\] to as high as 450 to 500\(^\circ\) F. for some applications.

While synthetic esters are good base oils for formulating the gas turbine lubricants, their inherent properties are not sufficient in all respects to meet generally accepted minimum requirements for proper lubrication for long periods of time. Accordingly, to meet commercial specifications, turbine oils generally contain one or more additives to improve various characteristics such as corrosion resistance, oxidation resistance, antiwear properties, etc. A proper choice of additives to optimize desirable lubricant properties involves detailed empirical studies, since additives used to correct one deficiency will often cause another; e.g., amine antioxidants enhance the oxidation stability of esters, but also aggravate corrosivity to certain metals. In addition, it is desirable to have as few additives as possible to achieve desired performance, since a large number of additives is likely to raise problems of incompatibility among the additives.

Antioxidant properties are particularly difficult to impart to synthetic ester oils, since at the very high temperatures of operation of these fluids, continuous films of lubricants are particularly difficult to maintain on parts subject to wear. Furthermore, compounds which do successfully impart antioxidant properties to these esters are likely to be depleted under these extreme conditions or to react with or be rendered ineffective by other additive materials in the oil. In addition, many compounds which impart wear resistance are likely to decrease the oxidation stability or increase the corrosivity of the base oil.

It has now been discovered that synthetic lubricants having excellent antiwear characteristics comprise a major amount of a synthetic ester base lubricating oil and a smaller amount, sufficient to enhance the antiwear properties, of certain hydrocarbyl ammonium thiocyanates.

The thiocyanate additives of the invention may be represented by the formula:

\[
\text{R} + \text{R} + \text{N} \equiv \text{SCN} \ Temporary.
\]

where \( \text{R} \) is a hydrocarbyl group having a valence of \( n \), and having from 1 to 30 carbons each, \( \text{R} \) is independently hydrogen or \( \text{C}_2 \) to \( \text{C}_{30} \) hydrocarbyl, and \( n \) is an integer from 1 to 2. The total number of carbon atoms in \( \text{R} \) and \( \text{R} \) is from 4 to about 30. The hydrocarbyl groups are preferably alkyl groups, because these compounds are superior inhibitors of lead corrosion. The word "hydrocarbyl" is used in its accepted meaning as representing a radical formed from a hydrocarbon by removal of a hydrogen. The hydrocarbyl groups represented by the \( \text{R} \) in the above formula may be any aliphatic saturated or radical composed solely of carbons and hydrogen, whether they be alkyl, cycloalkyl, aryl, aralkyl, aralky, simple, multi-ring, straight chain or branched chain. Representative groups are methyl, tert-butyl, isooctyl, dodecyl, octadecyl, eicosyl, cyclohexyl, phenyl, naphthyl, anthryl, benzy, phenetyl, etc.

The thiocyanate additives of the invention are used in amounts sufficient to increase the load-carrying ability of the synthetic ester oil. Appropriate concentrations are generally in the range of from about 0.01 to about 5% by weight, preferably 0.05 to 5% by weight of the final lubricant composition. Lower amounts may be used, but the resulting increase in EP properties is generally insufficient to justify addition of the thiocyanate; higher amounts are also operable but may cause ancillary problems, such as sludging.

The hydrocarbyl ammonium thiocyanates useful in compositions of the invention may be considered to be neutral salts of thiocyanate acid or hydrocarbyl thiocyanic acid and mono- or trihydrocarbyl mono- to diamines, where the total number of carbons in the hydrocarbyl substituents is at least 4, preferably from 4 to about 30. The salts may be primary, secondary, tertiary, or quaternary ammonium salts; primary and secondary, especially primary salts are preferred since extreme-pressure activity seems to decrease with the number of hydrocarbyl substituents on the nitrogen atom. A total of at least about four carbon atoms on the amine is necessary to achieve solubility. The upper limit on the number of carbon atoms is less well defined, but it is governed by considerations of solubility and practicality, e.g., the amount of additive required to achieve an effective concentration of the salt. In general, it is unnecessary to have a total number of alkyl carbons in excess of about 30.

Examples of suitable primary amines for use in preparing salts of the invention are butylamine, n-hexylamine, 2-ethylhexylamine, decylamine, dodecylamine, pentadecylamine, octadecylamine, eicosylamine, pentacosylamine, phenethylamine, octylphenylamine, naphthylamine, etc. Particularly appropriate amines are mixtures of tertiary alkyl primary amines having 18 to 22 carbons, such as those marketed by Rohm and Haas as Primene JM-T. Examples of suitable secondary amines are diisobutylamine, di-(2-ethylhexyl)amine, dicaprylylamine, N-methylhexylamine, N-(2-ethylhexyl)decylamine, N-isobutyl-caprylylamine, diphenylamine, phenyl-naphthylamine, diocyclophenyamine, and phenylcyclohexylamine. Examples of suitable tertiary amines are tri-(2-ethylhexyl)amine, tri-caprylylamine, tri-(decyl)amine, N-methyl-di-caprylylamine, N-isobutyl - di-(2-ethylhexyl)amine, N-methyl-N-isobutyl caprylamine, N-ethyl-N-isobutyl decylamine, N-isopropyl - N-(2-ethylhexyl)octadecylamine, N-hexyl diisobutylamine, and N,N-diisobutyl eicosylamine, N-phenyl diisobutylamine, and N-capryyl di-phenylamine. Some examples of diamines for use in the invention are ethylene diamine, propylene diamine, isobutylene diamine, octadecylene diamine, poyisobutylene ethylene diamine, etc.

Some examples of suitable thiocyanates of the invention are octadecyl ammonium thiocyanate, eicosyl ammonium thiocyanate, 2-ethylhexyl ammonium thiocyanate, di(2-ethylhexyl) ammonium thiocyanate, tricapryl ammonium thiocyanate, tricapryl-N-methyl ammonium thiocyanate, etc.
To illustrate the lead corrosion inhibiting properties of the thiocyanate EP agents, SOD Lead Corrosion and MacCoull-Ryder Lead Corrosion tests were run on a typical synthetic base oil with and without varying amounts of these additives. The MacCoull-Ryder test is described in detail in SAE Journal 50, 8, page 338 (August 1942); this test was run for one hour at 325°F. Corrosion was measured in grams of weight loss. In the SOD lead corrosion test, rapidly rotating panels of lead and copper were heated in the oil sample for one hour at 325°F or five hours at 375°F while air was bubbled through the sample. This test is described in Federal Test Method Standard No. 791a, Method 4321.1. The base oil used was a mixture of 67% w. C8-C10 alkyl acid esters of pentaerythritol and 33% w. C8-C10 alkyl acid esters of dipentaerythritol, containing 1.0% wt. phenyl-a-naphthylamine. The results are tabulated in Table II below.

### TABLE I.-RESULTS OF LOAD-CARRYING CAPACITY TESTS

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration, percent wt.</th>
<th>Shell 4-Ball Wear Test</th>
<th>Shell 4-Ball Weld Load, kg.</th>
<th>Souders Gear Load, p.s.i.</th>
</tr>
</thead>
<tbody>
<tr>
<td>None...</td>
<td></td>
<td>18.0</td>
<td>126</td>
<td>1,800</td>
</tr>
<tr>
<td>2-ethylhexyl ammonium thiocyanate</td>
<td>0.5</td>
<td>42.0</td>
<td>234</td>
<td>3,600</td>
</tr>
<tr>
<td>Tricapryl ammonium thiocyanate</td>
<td>0.6</td>
<td>32.8</td>
<td>210</td>
<td>3,300</td>
</tr>
<tr>
<td>Triaocyl-N-nonyl thiocyanate</td>
<td>0.3</td>
<td>25.4</td>
<td>189</td>
<td>2,250</td>
</tr>
<tr>
<td>Palmitoyl ammonium thiocyanate</td>
<td>0.3</td>
<td>16.0</td>
<td>178</td>
<td>1,500</td>
</tr>
</tbody>
</table>

These results show the effectiveness of ammonium thiocyanates as EP agents, and also indicate that at equivalent concentrations, EP effectiveness decreases as more hydrocarbyl groups are attached to the amine nitrogen.

The thiocyanates of the invention are not only excellent extreme-pressure agents, they also function as very good lead corrosion inhibitors in synthetic esters. Lead is corroded much more easily than other metals, such as steel, aluminium, copper, magnesium and silver; also, lead corrosion is not predictable from corrosion results of other metals. Some additives, for example 2,2'-dipropyldiamine, which are corrosion inhibitors for most metals, actually promote lead corrosion. Synthetic ester base stocks exhibit some mild lead corrosion, and this corrosion is often severely aggravated by other additives. It is very difficult to predict particular additives which will be corrosive to lead, since the lead corrosion function seems to be unrelated to the normal corrosion function. Nevertheless, the additives of the invention substantially reduce lead corrosion regardless of the nature of the additives or type of ester base stock which induces it.

Cyclic amine additives, which are useful as antioxidants, are known to cause lead corrosion. Accordingly, the thiocyanates of the invention are particularly useful if used in combination with one or more of these additives. By the term “cyclic amine” is meant herein a primary to tertiary amine, each non-hydrogen substituent of which is a mono- or dinuclear cyclic radical having from 0-2 alkyl substituents of 1-12 carbons. Secondary amines in which the cyclic radicals are aromatic rings are also preferred. Examples of amines which may be used advantageously with the thiocyanates of the invention are phenyl-a-naphthylamine, phenyl-b-naphthylamine, diphenylamine, di-a-naphthylamine, triphenylamine, 2,2'-dipropyldiamine, 2-aminoarylene, p,p'-dicyclohexylamine, 2-aminopyrididine, phenyl-2-pyridylamine, 3-aminquinoline, etc. These amines are usually present in an amount of from 0.2 to about 5% by weight of the final composition.

### TABLE II.-RESULTS OF LEAD CORROSION TESTS

<table>
<thead>
<tr>
<th>Additive, percent wt.</th>
<th>SOD Lead Corrosion 1 Weight Loss, mg./cm.2</th>
<th>MacCoull-Ryder Corrosion 2 Weight Loss, gr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>None...</td>
<td>40.0</td>
<td>-1.500</td>
</tr>
<tr>
<td>0.01 JMT/HSCN</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>0.05 JMT/HSCN</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>0.10 JMT/HSCN</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>0.20 JMT/HSCN</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

1 Pass = 6 mg./cm.2 at 375°F, 5 hours.
2 Pass = 0.1000 gr. maximum.
3 Neutral salt of a mixture of C9-C10 tert-alkyl primary amines and thiocyanic acid.

These results show that the base oil fails both lead corrosion tests, but passes when as little as 0.05% weight of a thiochyanate is added. Addition of 0.2% wt. of the salt almost completely eliminates lead corrosion.

In general, any synthetic ester lubricating oil is a satisfactory base for compositions of the invention. Suitable synthetic lubricant base stocks are esters of alcohols having 1 to 20, especially 4 to 12 carbons and aliphatic carboxylic acids having from 3 to 20, especially 4 to 12 carbons. The ester base may comprise a simple ester (reaction product of a monohydroxyalcohol and a monocarboxylic acid), a polyester (reaction product of an alcohol and an acid, one of which has more than one functional group), or a complex ester (reaction product of a polyfunctional acid with more than one alcohol, or of a polyfunctional alcohol with more than one acid). Also, excellent synthetic lubricants may be formulated from mixtures of esters, such as major proportions of complex esters and minor amounts of diesters.

Monohydric alcohols suitable for making ester base stocks include methyl, butyl, isooctyl, dodecyl and octadecyl alcohols. "Oxo" alcohols prepared by the reaction of olefins with carbon monoxide and hydrogen are suit-
able. Neo alcohols, i.e., alcohols having no hydrogens on the beta carbon atom are preferred. Examples of such alcohols are 2,2,4-trimethylpentanol-1 and 2,2-dimethylpropanol.

Polyalcohols used for the production of base oil esters preferably contain 1 to 12 carbons. Examples of dialcohols are 2-ethyl-1,3-hexanediol, 2-propyl-3,3-hepanediol, 2-buty1-1,3-butanediol, 2,4-dimethyl-1,3-butanediol, and polypropylene glycols having molecular weights of from about 100 to 300. Alcohols having 3, 4, 5 or more hydroxyl groups per molecule are also suitable and are preferred; examples of these polyols are pentaerythritol, dipentaerythritol, and trimethylolpropane. Mixtures of alcohols may also be used.

Suitable carboxylic acids for making the ester base oils include mono- and dibasic aliphatic carboxylic acids. Examples of appropriate acids are butyric, valeric, sebacic, azelaic, suberic, succinic, caproic, adipic, ethyl suberic, diethyl adipic, oxalic, malonic, glutaric, pentadecanedi-carboxylic, diglycolic, thioglycolic, acetic, propionic, caprylic, lauric, palmitic, pimelic, and mixtures thereof. Preferred acids are sebacic, azelaic, glutaric, adipic, and their mixtures.

Examples of suitable ester base oils are ethyl palmitate, ethyl laurate, butyl stearate, di-(2-ethylhexyl) sebacate, di-(2-ethylhexyl) azelate, ethyl glycol dilaurate, di-(2-ethylhexyl) phthalate, di(1,3-methylbutyl) adipate, di-(2-ethylpropyl) azelate, diisopropyl oxide, dicyclohexyl sebacate, glycerol tri-n-heptanoate, di(undecyl) azelate, and tetraethylene glycol di-(2-ethylene caproate), and mixtures thereof. An especially preferred mixture of esters consists of about 50-80% wt. bis (2,2,4-trimethylpentyl) azelate and 20 to 50% wt. 1,1,1-trimethyl propane triheptanoate.

Especially preferred esters for use as base stocks in the present invention are esters of monocarboxylic acids having 3 to 12 carbons and polyalcohols such as pentaerythritol, dipentaerythritol, and trimethylolpropane. Examples of these esters are pentaerythrityl butyrate, pentaerythrityl tetrahexyl, pentaerythrityl tetrabutyl, pentaerythrityl tetrapropionate, pentaerythrityl dinitrate, mono-, pentaerythrityl butyrate caproate divalente, pentaerythrityl butyrate trivalent, pentaerythrityl butyrate tricaprate, pentaerythrityl tricaprate, mixed C4 to C10 saturated fatty esters of pentaerythritol, dipentaerythritol hexaoleate, dipentaerythritol hexacaprate, dipentaerythritol hexaheptanoate, dipentaerythritol hexacaprylate, dipentaerythrityl tributylcaprate, dipentaerythrityl tricapratecaprate, dipentaerythrityl tricapratecaprate mixed hexesters of C4 to C10 fatty acids and trimethylolpropane heptaoate. Pentaerythrityl esters of mixtures of C4-C12 acids are excellent base oils, and are commercially available from Hercules Chemical Company.

Ester oils may be prepared by simple reaction of the alcoholic and acidic reactants in proportions suitable for producing the desired product; preparation preferably takes place in a solvent such as an aromatic hydrocarbon, and in the presence of a catalyst, such as HCl, HF, HBr, H2SO4, H3PO4, SOCl2, BF3, etc. Preparation of suitable esters is described in Eckemeyer, U.S. 3,038,839, issued June 12, 1962, and Young, U.S. 3,121,109, issued Feb. 11, 1964.

Compositions of the invention may also contain other additives to further improve properties of the oil. Examples of such other additives are extreme-pressure agents, viscosity index improvers, anti-corrosion agents, detergents, antifoams, etc.

I claim as my invention:

1. A lubricant composition comprising a major amount of a synthetic ester lubricating oil and minor amounts, sufficient to increase load-carrying ability of the oil, of an ammonium thiocyanate having the formula

\[
\text{R} \text{R}^2 \text{N} = \text{SCN}^- \text{R}^3
\]

where R is a hydrocarbyl group having a valence of n and having from 1 to 30 carbons, each R' is independently hydrogen or C1 to C10 hydrocarbyl, and n is an integer from 1 to 2 and from 0.2 to 5% by weight of a cyclic amine, each non-hydrogen substituent of which is a phenyl, pyridyl or naphthyl radical having from 0 to 2 alkyl substituents of 1-12 carbons.

2. The composition of claim 1 wherein the thiocyanate is present in the amount of from 0.01 to 5% by weight of the final lubricating composition, and wherein the total number of carbon atoms in R and all R's is from 4 to about 30.

3. The composition of claim 2 wherein hydrocarbyl is alkyl.

4. The composition of claim 2 wherein the ammonium thiocyanate is a neutral salt of a primary amine having from 4 to 30 carbon atoms and thiocyanic acid or a mixture of these salts.

5. The composition of claim 1 wherein the cyclic amine is phenyl-n-naphthylamine.

References Cited

UNITED STATES PATENTS

2,362,890 11/1944 Dietrich 252—47
2,518,256 11/1950 Edwards et al. 252—47.5

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