LUBRICATING COMPOSITIONS HAVING IMPROVED OXIDATION STABILITY AND ANTIRUST PROPERTIES

6 Claims, No Drawings

ABSTRACT: Lubricating oil compositions comprising essentially a major amount of lubricating oil and a minor amount of a mixture of basic group II metal salts of aromatic carboxylic acids and napthenic acids have improved oxidation stability and antirust properties. The composition optionally contains zinc dialkyldithiophosphate.
LUBRICATING COMPOSITIONS HAVING IMPROVED OXIDATION STABILITY AND ANTI-TRUST PROPERTIES

This invention relates to improved lubricating oil compositions which are particularly suitable for use in large marine diesel propelling engines and in shipboard auxiliary equipment. It is common practice to burn heavy fuels in the operation of large marine diesel engines. These fuels are generally residual products derived from topping, vacuum distillation or cracking operations, and often contain relatively large amounts of sulfur. Upon combustion of the fuel, sulfur dioxide and sulfur trioxide are formed which, either alone or in combination with the other combustion products cause serious corrosion problems in the engine. In order to minimize the severity of this corrosion problem, basic additives have been incorporated into lubricating oils to neutralize the acidic fuel combustion products and thus converting them to an innocuous form. The basic compounds most commonly used for this purpose are alkaline earth metal naphthenates which are effective in neutralizing acidic combustion products, but are not adequate in promoting oxidation stability or anti-trust properties. A number of other highly basic compounds such as calcium naphthasulfonates, barium versatesates, calcium phthalates, etc., might improve the oxidation stability and anti-trust properties but are not suitable for use in main engines because they tend to either emulsify, leach out, or form gels with salt water often found in the crankcases of marine diesel engines. A lubricating composition which would be capable of neutralizing acidic combustion products, and also possessing good oxidation stability and anti-trust characteristics therefore would be extremely desirable. The compositions of the present invention fulfill these requirements.

It has now been found that the addition of a minor amount of group II metal salts of carboxylic acids, such as alkyl salicylates, to lubricating oils impart greatly improved oxidation stability and anti-trust properties in addition to neutralizing acidic combustion products. These improvements make it possible to use the lubricating compositions of this invention not only in marine diesel engines but also in auxiliary equipment aboard ship, e.g., diesel generators. Heretofore it has been necessary to use separate lubricants for the main engine and the auxiliary equipment.

The excess basicity of the group II metal salicylates, however, is less than that of the naphthenates used in the prior art; therefore, in order to maintain the basicity of the final composition at a desired level it is necessary to combine the metal salicylates with other basic salts such as metal naphthenates which have a greater inherent basicity. According, by using a mixture of metal salts as herein defined, a final composition is obtained in which the basicity is held at an acceptable level, while the anti-trust and oxidation stability properties of the final blends are greatly improved.

Such a lubricant composition according to the present invention consists essentially of a hydrocarbon lubricating oil and a mixture of highly basic oil-soluble group II metal salts of aromatic carboxylic acids and highly basic oil-soluble group II metal salts of naphthenic acids wherein the group II metal salts have an atomic number of from 12 to 56.

The hydrocarbon lubricating oil, employed in the present invention, can be a mineral oil or a synthetic oil. The preferred mineral oils are generally paraffinic and/or naphthenic or character and may contain substantial proportions of hydrocarbons having an aromatic structure. The viscosity can vary within wide limits so that the oils belonging to S.A.E. classes 5W, 10W, 20, 30, 40, 50, 60, or 70 are acceptable. Suitable oils can also be derived from highly paraffinic crude in which case distillation and/or dewaxing may be necessary to provide a suitable base stock. Chemical or selective solvent treatment can be used if desired. Mixed base crudes and highly aromatic crudes which contain paraffinic hydrocarbons also provide suitable oil base stocks after refining.

The mineral oil base may be blended of distillate lubricating oils and bright stocks. The mineral oils may be mixed with, or even entirely replaced by, synthetic lubricants or polymerized olefins, for example polyisobutylene.

Preferably the highly basic oil-soluble group II metal salts of aromatic carboxylic acids include such compounds as basic calcium, barium, magnesium, strontium and zinc salts for hydrocarbon-substituted benzoic, salicylic, resorcylic, anthranilic and naphthoic acids. Examples of such salts are basic calcium, barium, magnesium and/or zinc salts of \( C_6H_4-Carboxylic \), \( C_6H_5-Carboxylic \), \( C_6H_4-Carboxylic \), \( C_6H_4-Carboxylic \) and mixtures thereof.

The preferred salts are the basic barium, calcium, magnesium, and zinc salts of lauryl-salicylic acid, or of stearyl-salicylic acids or a mixture of alkyl-salicylic acids in which the alkyl groups contain from 8 to 22, preferably 14 to 22, carbon atoms. The basic calcium salts of these alkyl salicylic acids have been found to be particularly satisfactory. The salts are present in an amount of 1 to 6 percent by weight based on the lubricant composition.

The excess basicity of the salts is defined by the formula

\[
\left( \frac{M}{E} \right) = 100\%
\]

wherein \( M \) represents the number of equivalents of metal, and \( E \) the number of equivalents of organic acid per 100 grams of basic salt, to give a neutralization number by potentiometric titration determined according to ASTM method No. D 664-58 or IP 177/64, hereinafter referred to as the TNBE (Total Base Number Electrometric) per 1 percent in the lubricating oil between 1 and 1.5 m KOH/g.

The oil-soluble group II metal salts of naphthenic acids comprise the salts of strontium, magnesium, zinc, barium, and calcium, those particularly preferred being barium and calcium. The naphthenic acids may be derived from mixtures of naphthenic acids obtained from various petroleum fractions. The naphthenic acids preferably have average molecular weights in the range from 150 to 750, although lower or higher molecular weight materials may also be used.

The basisity of the group II metal naphthenates may be calculated using the same formula as that employed for the alkyl salicylic acid salts disclosed above, wherein \( M \) represents the equivalents of metal and \( E \) the equivalents of combined naphthenic acid in 100 grams of the basic salt, and will be probably in excess of 400, preferably in excess of 600 and maybe 800 or more up to the limit which is practically attainable. The salts will be chosen for use in the present invention so that they will give a TNBE per 1 percent in the lubricating oil of between 1.5 and 3.0 m KOH/g. Preferably the salts are present in an amount of 0.5 to 3 percent by weight based on the lubricant composition.

The two additives as defined above are present in such amounts as to give an overall TNBE in the range 5 to 12, preferably 6 to 10, the preferred value being 8.

It is desirable to use in the compositions of the present invention relatively small amounts (e.g., from 0.01 to 2.0 percent, preferably from 0.05 to 1.0 percent by weight) of other additives. One class of suitable additives is constituted by the metal triphosphates such as calcium or zinc dialkyldithiophosphates, especially those wherein the alkyl groups are aryl and/or butyl. Alkyl phenols, e.g., di- and tri-alkyl phenols, or alkyl bisphenols, e.g., bis (3,5-di-tertiary-butyl)-4-hydroxyphenylmethane, constitute a second class. A third class is formed by aryl-amine such as phenyl-alpha-naphthylamine or phenyl-beta-naphthylamine. These various classes may be used in admixture if required.

Other well-known additives which may also be incorporated into the lubricating composition for the purposes of the present invention are for example antiscuffing agents, e.g., phosphorus esters; anti-foaming agents, e.g., silicone polymers; viscosity index improvers, e.g., polymeric acrylic esters; extreme pressure additives, e.g., dibenzyl disulfide; rust inhibitors, e.g., the condensation product of maleic anhydride and long chain olefins; oiliness agents, e.g., acidless tallow; and surface-active agents, e.g., peroxided aromatic extracts.

The following examples illustrate the present invention but should not be considered as limiting the scope of the invention in any way.
Composition A, wt. percent:
Highly basic calcium naphthenates (800% excess basicity) 5.0
Santolube 394 C* (cycloalkylthiophosphonate) 0.2
Phenyl-type anti-oxidant (6,6-di-tertarybutyl-4-methyl phenol) 0.2
A medium viscosity index mineral oil with Redwood viscosity of 170 seconds at 140°F Balance

* Santolube 394 C is a commercially available additive.

Composition B, wt. percent:
Highly basic calcium alkyl salicylates (200% excess basicity) 2.0
Zinc dialkyldithiophosphate 2.0
A medium viscosity index mineral oil with Redwood viscosity of 170 seconds at 140°F Balance 10

Composition C, wt. percent:
Highly basic calcium alkyl salicylates (200% excess basicity) 2.0
Zinc dialkyldithiophosphate 2.0
A medium viscosity index mineral oil with Redwood viscosity of 170 seconds at 140°F Balance 15

The above results indicate that although composition A has a high TBN-E number it gives poor piston cleanliness ratings. Compositions B and D have satisfactory cleanliness ratings but have unsatisfactory TBNE numbers. Compositions C, E, and F of the invention give satisfactory TBNE numbers combined with acceptable cleanliness ratings.

The combined results of tables 1 and 2 clearly establish that compositions of the present invention represented by compositions C, E, and F have greatly improved antitrust and oxidation stability properties and also improve engine cleanliness while still maintaining the required basicity.

We claim as our invention:

1. A lubricating composition consisting essentially of a major amount of a mineral lubricating oil and a mixture of from 1 percent to 6 percent basic group II metal salts of aromatic carboxylic acids and from 0.5 percent to 3 percent basic group II metal salts of naphthenic acids wherein:
   a. The aromatic carboxylic acids are selected from a group consisting of C_{14}-C_{18} alkyl benzoic, C_{14}-C_{18} alkyl salicylic, C_{14}-C_{18} alkyl naphthenic and mixtures thereof;
   b. The naphthenic acids have an average molecular weight of from 150 to 750;
   c. The basic group II metals have an atomic number of from 12 to 56;
   d. The salts are present in an amount necessary to give a TBNE value of from 5 to 12.

2. The composition of claim 1 in which the aromatic carboxylic acids are C_{14}-C_{18} alkyl salicylic acids.

3. The composition of claim 2 in which the basic metal salts of the aromatic carboxylic acids are selected from the group consisting of barium, calcium, magnesium, and zinc.

4. The composition of claim 3 in which the group II metal salts of the naphthenic acids are selected from the group consisting of barium and calcium.

5. The composition of claim 4 in which the aromatic carboxylic acids are C_{14}-C_{18} salicylic acids and the basic salts of these acids are calcium salts.

6. The composition of claim 1 which contains from 0.01 percent to 2 percent of zinc dialkyldithiophosphate.

7. The composition of claim 2 containing from 0.01 percent to 2 percent of zinc dialkyldithiophosphate.

8. The composition of claim 3 containing from 0.01 percent to 2 percent of zinc dialkyldithiophosphate.

9. The composition of claim 4 containing from 0.01 percent to 2 percent of zinc dialkyldithiophosphate.

10. The composition of claim 5 containing from 0.01 percent to 2 percent of zinc dialkyldithiophosphate.

11. The composition of claim 6 containing from 0.01 percent to 2 percent of zinc dialkyldithiophosphate.

12. The composition of claim 7 containing from 0.01 percent to 2 percent of zinc dialkyldithiophosphate.

13. The composition of claim 8 containing from 0.01 percent to 2 percent of zinc dialkyldithiophosphate.