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ANTICORROSIVE MARINE DIESEL LUBRICANT

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This invention relates to lubricants for diesel engines. It is more particularly concerned with improved emulsion type lubricants for marine Diesels in which sour fuel oils are used as fuels.

As is well known to those familiar with the art, many types of large marine diesel engines are lubricated by injecting small amounts of a lubricant into the cylinder during each cycle. Such engines do not have conventional crank case type of lubrication wherein the continuous, copious lubrication of the pistons and cylinder walls is effected. As is further known, many of these engines burn fuels usually of the No. 6 bunker fuel type that contain relatively large amounts of sulfur and other corrosive materials. As a result, when these oils are burned in the cylinder, there are formed quantities of corrosive acidic compound, such as sulfuric acid, sulfurous acid, etc. The presence of these materials is detrimental to the operational life of the engine because corrosion is increased and also because the presence of large amounts of strong acid promotes deposit formation and induces greater wear of the piston and of the cylinder walls.

Accordingly, it will be appreciated that it would be highly advantageous to neutralize the acidic sulfur compounds and to eliminate the corrosive effects thereof so that engine life can be prolonged. It is to be noted that the use of conventional high detergency lubricating oils has not proved to be wholly effective. Indeed, in the cases where such oils may be effective, it has been necessary to use such high concentrations of detergents that the overall operation is uneconomical.

In copending application Serial No. 561,344, filed January 25, 1956, which is a continuation-in-part of application Serial No. 541,847, filed October 20, 1955, and now abandoned there was described a water-in-oil type emulsion lubricant for marine diesel engines that is adaped to overcome the corrosive effects of acidic combustion products. It contained an alkali-metal hydroxide in the aqueous phase. In some cases, however, some lubricants prepared in accordance with these applications were lacking in emulsion stability.

As is described in copending application Serial Number 596,400, filed July 9, 1956, a continuation-in-part of the aforementioned 541,847 and 561,344, very stable water-in-oil emulsion lubricants of the type defined in the aforementioned applications can be prepared by the addition thereto of small amounts of certain fatty acids and by careful control of the amounts of the components of the lubricant.

During the operation of certain types of diesel engines and, particularly, when poor quality No. 6 bunker fuels are used, it has been found that hard deposits form on the pistons and valves and that considerable corrosion occurs. These difficulties appear to arise from the presence of large amounts of metals, principally vanadium, in the bunker fuel that combine with the neutralized combustion products. It has now been found that the corrosion and other difficulties attributable to such deposits can be alleviated or eliminated by adding

a small amount of calcium hydroxide or calcium oxide to the aforementioned emulsion lubricants.

Accordingly, it is an object of this invention to reduce corrosion in marine diesel operation. Another object is to provided a stable lubricant that will satisfactorily neutralize acidic corrosive combustion products and remove them from the cylinder, and reduce the formation of corrosive deposits on the valves and pistons. A specific object is to provide a stable emulsion type lubricant that will overcome the harmful effects of corrosive agents while still maintaining effective lubrication of a marine diesel engine. A more specific object is to provide a water-in-oil type emulsion lubricant that has alkali-metal hydroxide in the aqueous phase and a small amount of calcium oxide or calcium hydroxide. Another more specific object is to provide a water-in-oil type emulsion lubricant that has alkali-metal hydroxide in the aqueous phase and contains a small amount of calcium oxide or calcium hydroxide, and which is stabilized by addition of small amounts of certain fatty acids and by careful control of the amounts of the components thereof. Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description.

In general, the present invention provides an emulsion type lubricant for marine diesels which comprises, by weight of the lubricant, between about 10 percent and about 50 percent water (preferably between about 10 and about 35 percent), between about 80 percent and about 45 percent mineral lubricating oil (preferably between about 80 and about 55 percent), between about 1 percent and about 5 percent alkali-metal hydroxide, the amount thereof being sufficient to effect a total Base Number in the lubricant of between about 10 and about 100, between about 0.25 percent and about 0.5 percent calcium oxide, between about 0.5 percent and about 5 percent oil-soluble detergent, between about 3 percent and about 7 percent of an emulsifier that effects water-in-oil type emulsion; and which can also contain between about 0.5 percent and about 1 percent of a saturated fatty acid having 16 to 20 carbon atoms per molecule.

The lubricants of this invention can be prepared in several ways, with regard to the addition of the lime. In all cases, the alkali-metal hydroxide is dissolved in the water and the oil-soluble detergent and the fatty acid, if it is used, are dissolved in the mineral lubricating oil. Finely-divided lime can be dispersed either in the aqueous solution or in the oil solution. Then, the aqueous phase and the oil phase are emulsified by the addition of a suitable water-in-oil type emulsifying agent by conventional means, such as by agitation. In another method of preparation, the aqueous solution and the oil solution, without the addition of lime, can be emulsified first, followed by the dispersion of lime in the emulsion thus formed. Regardless of the exact manner in which the lime-containing emulsion is formed, it is then homogenized by agitation in any suitable homogenizing equipment, such as a Manton-Gaulin Homogenizer, a Stratco Contactor, or in a mechanically agitated, heated blending kettle.

The lime can be added to the emulsion lubricant in the form of calcium oxide or of calcium hydroxide. Because of the presence of water, the lime will be primarily in the form of calcium hydroxide in the finished lubricant. As was indicated hereinbefore, the lime is dispersed in the lubricant in a finely divided state. The amount to be used will vary between about 0.25 percent and about 0.5 percent, by weight of the lubricant, and expressed as CaO.

The basic materials that are dissolved in the aqueous phase of the lubricant are the alkali-metal hydroxides. In general, lithium hydroxide is preferred because of the lower molecular weight. However, sodium and potassium

hydroxides are effective. The amount of alkali-metal hydroxide used will be between about one percent and about 5 percent, by weight of finished lubricant. Sufficient must be used, however, to produce a total Base Number (ASTM Test D664–54) of 10–100, preferably 10–50.

The mineral oil content of the lubricant of this invention will be the usual hydrocarbon lubricant utilizable for the lubrication of heavy machinery. Generally, this lubricating oil will be a petroleum hydrocarbon fraction or a blend of two or more fractions, of the No. 20 to No. 50 SAE grade. In terms of Saybolt Universal Viscosity, the mineral oil will have a viscosity of 45–100 seconds at 210° F., and preferably of 75–80 seconds at 210° F. The mineral lubricating oil can be obtained from any crude source or sources. It is especially preferred, however, to use a naphthenic oil, such as one obtained from a coastal crude.

The detergents that are dissolved or dispersed in the oil phase are, in general, the additives used in detergent motor oils. Usually they are polyvalent metal salts of organic acids. Nonlimiting examples include petroleum sulfonates, such as barium "mahogany" sulfonate, magnesium petroleum sulfonate, etc.; wax-substituted aryl sulfonates, such as barium di-wax benzene sulfonate, calcium tri-wax benzene sulfonate, barium wax naphthalene sulfonate, etc.; sulfurized or unsulfurized phenates and carboxylates, such as sulfurized calcium phenate, barium wax phenate, magnesium wax benzene carboxylate, etc. The detergents are not exactly equivalent and the selection of a particular detergent will depend upon the emulsifier used. Some detergents will destroy the emulsion characteristics with some emulsifiers, but will be found to be compatible with others.

As has been mentioned hereinbefore, the oil phase and the aqueous phase are maintained in a stable water-in-oil emulsion by means of a suitable emulsifying agent. In general, the emulsifying agent can be a sulfonate, such as sodium mahogany sulfonate, ammonium naphthalene sulfonate, etc.; esters of high molecular weight acids obtained by controlled oxidation of petroleum fractions, such as wax; fatty acid soaps, such as sodium oleate, "red oil" soaps, potassium stearate, ammonium linoleate, etc.; and the like. The preferred type of emulsifiers are a non-metallic material, such as the ammonium soaps and the oxidized petroleum acid esters. It is to be understood, however, that emulsifying agents are not equally effective and that the effectiveness of a given emulsifying agent will be affected by the types and the concentrations of the various other ingredients of the lubricant. The effectiveness of an emulsifying agent in any given formulation can readily be determined by those skilled in the art by subjecting a sample to an oven storage test at 170° F. A stable emulsion lubricant will not separate, even after a month or more on this storage test.

As was mentioned hereinbefore, if desired, the emulsion lubricants of this invention can be stabilized by the addition of small amounts of certain fatty acids. These acids are the saturated fatty acids that contain between about 16 and about 20 carbon atoms per molecule, e.g., hexadecanoic acid, stearic acid and dodecanoic acid. Stearic acid is especially preferred. The concentration of added acid, based upon the weight of the total lubricant, must be between about 0.5 weight percent and about 1 weight percent.

In order to obtain the stable emulsions of this invention, the concentrations of the ingredients must be controlled within certain limits. It has been found that the ranges within which the concentration of the various components of the emulsion type lubricant of this invention can be varied are within the following ranges, based upon the weight of the finished lubricant:

	Percent
Alkali-metal hydroxide	1–5
Calcium oxide	0.25–0.5
Detergent	0.5–5
Emulsifier	3–7
Mineral lubricating oil	80–45
Water	10–50
C_{16}–C_{20} fatty acids	0.5–1

It is to be understood that the lubricant of this invention can contain other additives for the purpose of imparting other properties to the lubricant. Thus, for example, there can be added anti-rust agents, E.P. (extreme pressure) agents, antioxidants, and the like.

The following examples are for the purpose of illustrating the emulsion lubricants of this invention. It must be strictly understood that the invention is not to be restricted to the specific combinations described in the examples or to the operations and manipulations involved. As those skilled in the art will appreciate, other combinations, as set forth hereinbefore, can be used.

"Emulsifier X," used in these examples, is a mixture of polyhydric alcohol esters of high molecular weight acids that is obtained by controlled oxidation of petroleum wax. The mixture has the following characteristics:

Saponification No. (ASTM D94–52T)	25–40
Acid No. (ASTM D94–52T)	6–15
Melting point (ASTM D127–49) ° F.	115
Flash point (open cup) ° F.	450
Fire point (open cup) ° F.	540

A readily available commercial source of an emulsifier of this type is "Alox 1657," sold by the Alox Corp., Niagara Falls, New York. "Alox 1657" has the following typical properties:

Acid number	Max. of 4.0.
Saponification number	30–40.
Color	Dark brown.
Ash (ASTM–D–482–46)	0.07%.
Melting point (ASTM–D–127–49)	120° F.
Viscosity @ 210° F.	220–240 S.U.S.
Specific gravity @ 146° F.	0.874.
Average weight per gallon	7.3 lbs.
Flash (O.C.)	450° F. (Min.).
Fire (O.C.)	540° F. (Min.).

Further details as to the nature and properties of this material are available in Alox Technical Data Sheet on Alox L–1657, April, 1952.

"Detergent Y," used herein, is calcium mahogany sulfonate. This material, as is well known to those familiar with the art, is prepared from the oil-soluble sulfonic acids obtained by treating lubricating oil fractions with oleum or concentrated sulfuric acid. Typical procedures for preparing mahogany sulfonates are set forth, for example, in U.S. Patents Nos. 2,467,118 and 2,533,303. A typical commercially available additive of this type is "Lubrizol 1220," sold by the Lubrizol Corp., Cleveland, Ohio.

Example 1

Into a blending kettle equipped with a mechanical agitator, were placed 4.5 parts, by weight, of "Emulsifier X," 2 parts, by weight, of "Detergent Y," 0.5 part, by weight, of stearic acid, and 60 parts, by weight, of a mineral lubricating oil (Base Oil A). The mineral lubricating oil is a blend containing 38 volume percent of a solvent refined coastal oil having a Saybolt viscosity of 150 seconds at 210° F. and 62 volume percent of a solvent refined coastal oil having a Saybolt viscosity of 55 seconds at 210° F. This blend has an A.P.I. gravity of 24 degrees and a Saybolt viscosity of about 75 seconds at 210° F. The mixture of oil, detergent, stearic acid, and emulsifier was heated with agitation at 130° F. until the solution was complete. It was then cooled to 100–110° F.

In a separate vessel were dissolved 2.5 parts, by weight, of lithium hydroxide, monohydrate, in 30.15 parts, by weight, of water. Then 0.35 part, by weight, of finely-divided hydrated lime (0.26 part CaO) was dispersed in the aqueous solution, with agitation.

The resultant dispersion, or slurry, was slowly added to the oil blend in the blending kettle. Continuous vigorous agitation was maintained throughout the blending period. After all the aqueous phase had been added, vigorous agitation was continued for an additional 15 minutes in order to obtain the emulsion. This emulsion was then passed through a Manton-Gaulin Homogenizer operated at 1000 p.s.i.g. Continuous agitation was maintained in the blending kettle while the emulsion was being transferred to the homogenizer.

As was mentioned hereinbefore, the lime can be added to the oil phase, instead of to the aqueous phase. A typical method of operation is set forth in the following example.

Example 2

Into a blending kettle equipped with a mechanical agitator, were placed 4.5 parts, by weight, of "Emulsifier X," 2 parts, by weight, of "Detergent Y," 0.5 part, by weight, of stearic acid, and 60 parts, by weight, of Base Oil A (Example 1). This mixture was heated with agitation at 130° F. until solution was complete. Then, 0.35 part, by weight, of finely-divided hydrated lime (0.26 part CaO) was dispersed in the oil solution with agitation. The resultant dispersion, or slurry, was cooled to 100–110° F. In a separate vessel were dissolved 2.5 parts, by weight, of lithium hydroxide, monohydrate, in 30.15 parts, by weight, of water.

The aqueous solution was slowly added to the oil dispersion in the blending kettle. Continuous vigorous agitation was maintained throughout the blending period. After all the lithium hydroxide solution had been added, vigorous agitation was continued for an additional 15 minutes, in order to obtain the emulsion. This emulsion was then passed through a Manton-Gaulin Homogenizer operated at 1000 p.s.i.g. Continuous agitation was maintained in the blending kettle while the emulsion was being transferred to the homogenizer.

The emulsion lubricants that were prepared by the procedures set forth in Examles 1 and 2 were substantially alike in appearance and properties. They are particularly useful, in the lubrication of marine diesel engines that burn heavy fuels of high metal (vanadium, etc.) and sulfur content, to reduce or eliminate the formation of corrosive deposits on the pistons and valves, as well as to reduce the wear on cylinder liners that is attributable to the corrosive products of combustion.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. An emulsion lubricant for marine diesels which comprises, by weight of the lubricant, between about 10 percent and about 50 percent water, between about 80 percent and about 45 percent mineral lubricating oil, having a Saybolt Universal viscosity of between about 45 seconds and about 100 seconds measured at 210° F., between about 1 percent and about 5 percent alkali-metal hydroxide, the amount thereof being sufficient to effect a total base number in the lubricant of between about 10 and about 100, between about 1 percent and about 10 percent calcium mahogany sulfonate, between about 3 percent and about 7 percent of a mixture of polyhydric alcohol esters of high molecular weight acids obtained by controlled oxidation of petroleum wax, between about 0.5 percent and about one percent saturated fatty acid having between 16 and 20 carbon atoms per molecule, and between about 0.25 percent and about 0.5 percent lime, expressed as CaO.

2. An emulsion lubricant for marine diesels which comprises, by weight of the lubricant, between about 10 percent and about 35 percent water, between about 80 percent and about 55 percent mineral lubricating oil having a Saybolt Universal viscosity of between about 75 seconds and about 80 seconds measured at 210° F., between about 1 percent and about 5 percent lithium hydroxide, the amount thereof being sufficient to effect a total base number in the lubricant of between about 10 and about 50, between about 1 percent and about 10 percent calcium mahogany sulfonate, between about 3 percent and about 7 percent of a mixture of polyhydric alcohol esters of high molecular weight acids obtained by controlled oxidation of petroleum wax, between about 0.5 percent and about 1 percent stearic acid, and between about 0.25 percent and about 0.5 percent lime, expressed as CaO.

3. An emulsion lubricant for marine diesels which comprises, by weight of the lubricant, about 30 percent water, about 60 percent naphthenic mineral lubricating oil having a Saybolt Universal viscosity of about 75 seconds measured at 210° F., 2.5 percent lithium hydroxide, 2 percent calcium petroleum sulfonate, about 4.5 percent of a mixture of polyhydric alcohol esters of high melocular weight acids obtained by controlled oxidation of petroleum wax, about 0.5 percent stearic acid, and about 0.26 part lime, expressed as CaO.

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