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MARINE DIESEL LUBRICANT

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This invention relates to lubricants for diesel engines. It is more particularly concerned with 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.

It has now been found that corrosion and wear in the operation of marine diesels can be reduced effectively and economically. It has now been discovered that the effects of harmful deposits in marine diesels can be overcome by lubricating the engines with a novel emulsion type lubricant that tends to neutralize acidic corrosive materials and to remove them from the combustion section of the engine.

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 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.

It has now been found that extremely stable emulsion lubricants can be produced by a method that is simple and economically feasible. It has been discovered that very stable water-in-oil emulsion lubricants 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.

Accordingly, it is an object of this invention to reduce corrosion in marine diesel operation. Another object is to provide a stable lubricant that will satisfactorily neutralize acidic corrosive combustion products and remove them from the cylinder. A specific object is to provide

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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 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 0.5 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 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 are prepared by dissolving an alkali-metal hydroxide in the water and the oil soluble detergent in the mineral lubricating oil. The aqueous and the oil solution are then emulsified by the addition of a suitable water-in-oil type emulsifying agent by any conventional means. Thus, for example, the emulsion can be produced 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 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 compound 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, the emulsion lubricants of this invention are 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
Detergent	0.5-5
Emulsifier	3-7
Mineral lubricating oil	80-45
Water	10-50

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 and of demonstrating the effectiveness thereof. 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 a calcium mahogany sulfonate. 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 5 parts, by weight, of "Emulsifier X," 2 parts, by weight, of "Detergent Y," 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, 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 was dissolved three parts by weight of lithium hydroxide, monohydrate, in thirty parts, by weight of water.

This solution was slowly added to the oil blend 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 3000 to 3500 pounds p.s.i.g. Continuous agitation was maintained in the blending kettle while the emulsion was being transferred to the homogenizer.

The water-in-oil emulsion lubricant thus produced had the following physical characteristics:

A.P.I. gravity	17.6
SUS viscosity at 100° F.	2,247
SUS viscosity at 130° F.	868
SUS viscosity at 210° F.	168.5
Viscosity index	112
Total base No.	40

This lubricant was placed aboard a commercial motor vessel that was powered with an 8 cylinder, 2 cycle, double acting Gotaverkin diesel engine. This ship was operated continuously for seven days coastal voyage. During this time, two cylinders were lubricated with the emulsion lubricant of this example and six cylinders were lubricated with a standard marine lubricant of the mineral oil type. This oil was a blend of 57 volume percent solvent refined coastal oil of 150 seconds Saybolt at 210° F. and 43 volume percent solvent refined coastal oil of 55 seconds Saybolt at 210° F. It had an A.P.I. gravity of 24° and a Saybolt viscosity at 210° F. of 97 seconds. At the completion of the run, it was found that the cylinders lubricated with the emulsion type lubricant operated freely and had received adequate lubrication.

In order to test the emulsion stability of the formulations described, a sample (about 2 oz.) of the blend under test is stored in a tall 4-oz. bottle at 170° F. The sample is observed daily for signs of separation of the emulsion. An emulsion is rated satisfactory (S), as to stability, if there is no water separation and no more than a trace of oil separation visible after 30 days. An unsatisfactory (U) emulsion will display visible signs of

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separation, usually within several days. The blend described in Example 1, when subjected to this test had a "U" rating, separation being visible after one day.

EXAMPLE 2

Using the procedure set forth in Example 1, an emulsion lubricant was prepared that had the following composition, expressed in parts by weight:

	Parts
Base oil A	60
Water	30
Emulsifier X	4.5
Lithium hydroxide monohydrate	3.0
Detergent Y	2.0
Stearic acid	0.5

When subjected to the aforescribed stability test, this lubricant had a stability rating of S, no separation of emulsion occurring even after 66 days. In testing this lubricant in marine diesel installations aboard motor ships, it was found that excellent lubrication and protection of the engines against the effects of corrosive gases was achieved.

EXAMPLES 3 AND 4

Two emulsion lubricant formulations were prepared in accordance with the formulation described in Example 2, with the exception that the amount of stearic acid used was varied, together with the concentration of Emulsifier X. Pertinent variations from the formulation of Example 2 and emulsion stability test results are set forth in Table I.

Table I

Example	Stearic Acid, Parts by Wt.	Emulsifier X, Parts by Wt.	Emulsion Stability Rating
3	0.25	4.75	U.
4	1.0	4.0	S.

From the data of Table I, it will be appreciated that 0.25 part stearic acid, by weight, is insufficient to impart stability to the emulsion. As noted from Example 2, 0.5 part is sufficient, as is 1 part (Table I). Greater amounts of stearic acid failed to impart stability to the emulsion formulation. An emulsion stability rating of S was obtained with a formulation, as in Example 2, wherein palmitic (hexadecanoic) acid was substituted for the stearic acid. When, however, oleic acid was used, the emulsion was not stable. Therefore, the range of concentration of saturated fatty acid having between 16 carbon atoms and 20 carbon atoms falls within the relatively narrow range varying between about 0.5 part and about 1 part by weight of the finished lubricant.

In preferred practice, the stabilization of the emulsion lubricant is effected by replacing part of the emulsifier with a saturated fatty acid of 16-20 carbon atoms. For example, if 5 parts of emulsifier is used in an emulsion formulation that proves to be unstable, the addition of 0.5-1 part fatty acid to stabilize it is accompanied by a corresponding reduction of emulsifier concentration, in this case from 5 parts to 4.5-4.0 parts.

The amount of emulsifier must also be controlled within limits. This will be apparent from the following examples.

EXAMPLES 5 THROUGH 10

A series of emulsion lubricants was prepared using the formulation described in Example 2, with the exception that the concentration of Emulsifier X was varied, there being, however, no variation in the concentration of stearic acid or of the other components. The pertinent variations and corresponding emulsion stability test results of these lubricants are set forth in Table II.

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Table II

Example	Emulsifier X, Parts by Wt.	Emulsion Stability Rating
5	2	U.
6	3	S.
7	4	S.
8	5	S.
9	7	S.
10	10	U.

From the data in Table II, it will be noted that poor emulsion stability results when the lubricant contains only 2 parts emulsifier and also when it contains as much as 10 parts, even with stearic acid present. On the other hand, stable emulsions are formed when the concentration of emulsifier is between about 3 parts and about 7 parts, by weight. Thus, it is another feature of this invention that the formulation must contain, together with 0.5-1 part fatty acid as aforescribed, between about 3 parts and about 7 parts emulsifier, by weight; the emulsifier preferably being of the non-ionic type.

This application is a continuation-in-part of 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.

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 consists of, 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 petroleum 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, and between about 0.5 percent and about one percent saturated fatty acid having between 16 and 20 carbon atoms per molecule.

2. An emulsion lubricant for marine diesels which consists of, 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 petroleum 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, and between about 0.5 percent and about 1 percent stearic acid.

3. An emulsion lubricant for marine diesels which consists of, 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., 3 percent lithium hydroxide, 2 percent calcium petroleum sulfonate, about 4.5 percent of a mixture of polyhydric alcohol esters of high molecular weight acids obtained by controlled oxidation

of petroleum wax, and about 0.5 percent stearic acid; said oil lubricant having a total base number of about 40.

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