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3,089,854

OIL-IN-WATER EMULSION LUBRICANTS

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This invention relates to oil-in-water emulsion lubricants employed in the lubricating of large stationary diesel engines.

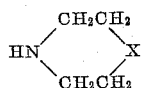
In U.S. 2,744,870, issued May 8, 1956, there are disclosed water-in-oil emulsion lubricants in which the water phase contains a water-soluble salt of a divalent metal and which are reported to be effective lubricants for diesel engines operating on a high sulfur hydrocarbon fuel. These emulsion lubricants containing a water-soluble divalent metal salt are said to reduce ring wear and to neutralize the corrosive action of high sulfur fuels. The present invention involves the discovery that oil-in-water emulsion lubricants containing a water-soluble amine are superior both to the conventional detergent-containing mineral oil lubricants and to the water-in-oil emulsion lubricants of 2,744,870 in reducing ring wear and in combating the corrosive effects of the fuel.

Economy diesel fuels, which term is used to denote high sulfur content fuels which have undergone a lesser degree of refining than conventional diesel fuels, are being used extensively in marine diesel engines and in large stationary diesel engines. The diesel engines which have been operating on these high sulfur diesel fuels, use a separate crankcase lubricant and effect cylinder lubrication by a once-through process wherein measured quantities of lubricant are continually introduced into the cylinders. These economy diesel fuels are very often mixtures of distilled and residual oils and accordingly have a substantial concentration of vanadium complexes which can produce highly corrosive combustion products causing wear. The high degree of corrosion and ring and liner wear obtained with the high sulfur content economy diesel fuels has partially offset the savings resulting from the use of the lower cost fuel. As a consequence, there has been considerable investigation of lubricants which will minimize the corrosive action and ring and liner wear obtained with economy diesel fuels. The subject invention provides a lubricant which is outstanding in reducing the wear and neutralizing the corrosive action of the sulfur and vanadium contents of the economy diesel fuels.

The oil-in-water emulsion lubricants of this invention comprise 50–80 percent mineral lubricating oil, 50–20 percent water, 0.5 to 6 percent hydrophilic emulsifying agent which acts to produce a stable oil-in-water emulsion, and 2 to 10 percent water-soluble amine. The water-soluble amine is an acyclic or cyclic amino compound. The acyclic amine compound has the general formula



where R is a hydrogen atom, an alkyl radical, an aminoalkyl or a hydroxyalkyl radical and R' is an alkyl, aminoalkyl or hydroxyalkyl radical, said alkyl, aminoalkyl and hydroxyalkyl radicals containing 1 to 4 carbon atoms. The cyclic amino compound has the general formula



where X is oxygen, $=\text{CH}_2$ or a $=\text{NH}$ radical.

The mineral lubricating oil component of the oil-in-water emulsion lubricants of this invention is a paraffin

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base, naphthene base, or mixed base distillate or residual fraction. The mineral lubricating oil has an SUS viscosity at 100° F. between about 500 and 1500 with mineral oils having an SUS viscosity at 100° F. between 1000 and 1300 usually being employed. A distillate fraction may be employed as the mineral oil component but it is also possible to combine the distillate fraction with a minor amount of residual oil so that the base oil comprises 5 to 25 percent residual oil and 75 to 95 distillate oil. Naphthene base distillates are usually employed because they frequently form more stable emulsions than paraffin base distillates.

Mineral lubricating oil constitutes 50 to 80 percent of the oil-in-water emulsion lubricant of the invention. The preferred concentration of the mineral lubricating oil component is of the order of 60–75 percent of the total lubricant. An outstanding lubricant has been formulated with about 70 percent mineral oil.

The emulsifying agent employed to form the oil-in-water emulsion lubricants of the invention is selected from the well-known group of hydrophilic emulsifying agents which are capable of forming oil-in-water emulsions. Examples of hydrophilic emulsifying agents that may be employed are the alkali metal petroleum sulfonates, the alkali metal alkaryl sulfonates, alkali metal salts of naphthenic acids and of resin acids, and the alkylene oxide adducts of alkyl-substituted phenols. Mixtures of two or more of the emulsifying agents may also be used. A particularly effective hydrophilic emulsifying agent is the ethylene oxide adduct of an alkyl-substituted phenol; an example of such a compound is ethylene oxide adduct of octyl phenol in which the adduct contains an average of 10 ethylene oxide units. This compound is sold under the commercial trademark of "Triton-X-100" by Rohm and Haas.

The emulsion lubricants of the invention contain 0.5 to 6 weight percent hydrophilic emulsifying agent. The usual concentration of emulsifying agent, however, falls between 1 and 4 weight percent.

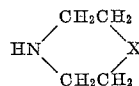
The water content of the emulsion lubricants of the invention is between 20–50 percent of the total lubricant with concentrations between 20 and 35 weight percent being preferred.

Both acyclic and cyclic water-soluble amines are used in formulating the emulsion lubricants of the invention. The acyclic amines have the general formula



wherein R is a hydrogen atom, an alkyl, an aminoalkyl, or a hydroxyalkyl radical and R' is an alkyl, a hydroxyalkyl, or an aminoalkyl radical, said alkyl, hydroxyalkyl and aminoalkyl radicals containing 1 to 4 carbon atoms.

The cyclic amines have the general formula



wherein X is oxygen, a $=\text{CH}_2$ or a $=\text{NH}$ radical. Primary and secondary aliphatic mono- and di-amines and mono- and di-alkanol amines containing 1 to 4 carbon atoms are used in formulating the emulsion lubricants of the invention. Examples of acyclic amines are the following: monoethanolamine, diethanolamine, ethylenediamine, propylamine, isopropylamine, 1,2-diaminobutane, ethylamine, monoisopropanolamine and diisopropanolamine. Examples of the cyclic amines are morpholine, piperazine and piperidine. Mono- and di-alkanol amines in which the alkyl radical contains 2 to 4 carbon atoms and morpholine are the preferred amines for preparing the emulsion lubricants of the invention.

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The water soluble amine constitutes 2 to 10 weight percent of the emulsion lubricant of the invention with concentrations between 3 and 8 weight percent normally being employed.

The emulsion lubricant of the invention advantageously contains a suitable anti-foam agent. A silicone polymer such as dimethylsilicone polymer having a kinematic viscosity at 25° C. of about 1,000 centistokes is preferably employed in the form of a concentrate in a hydrocarbon solvent such as kerosene. For example, a very satisfactory anti-foam agent for this purpose is prepared by diluting 10 grams of a dimethyl silicone polymer (1,000 centistokes at 25° C.) with kerosene to bring the volume to 100 cubic centimeters. A proportion of the order of 0.005 to 0.025 percent by weight of the immediately foregoing concentrate is ordinarily employed, preferably sufficient to provide about 50 to 200 parts per million of the silicone polymer concentrate on the basis of the emulsion lubricant.

In the following examples there are shown the preparation, properties and performance characteristics of the emulsion lubricants of the invention.

Example 1.—13,900 grams of a naphthene base distillate oil having an SUS viscosity at 100° F. of about 1200 and a pour of 10° F. maximum, 5000 grams of water, 700 grams of morpholine, 400 grams of Triton X-100, an ethylene oxide adduct of octylphenol having an average of 10 ethylene oxide molecules, and 2 grams of the previously described anti-foam agent comprising a 10 percent solution of dimethyl silicone polymer in kerosene were introduced into a mixing vessel and stirred until a stable oil-in-water emulsion was formed. The resulting emulsion had the following composition in weight percent.

	Weight, percent
Base oil	69.5
Water	25.0
Morpholine	3.5
Triton X-100	2.0
Anti-foam concentrate	p.p.m. 150

Properties and performance characteristics of this emulsion lubricant are shown in Table I.

Table I

Viscosity, SUS at 100° F.	580-740
Ash, percent	0.01
TBN (total base number)	21.3
Corrosion, copper strip—3 hrs. at 212° F.	Neg. (3)
ASTM Rusting Test ¹	Pass
Navy 4-Ball Wear, microns/min.	12
CFR Low Temp. Wear Test—improvement over an SAE 20 refined paraffin oil, percent	9
Radioactive Ring Wear Test, wear rate, mgm./hr.	27

¹ No water added.

The above data show that the morpholine-containing emulsion lubricant of Example 1 is non-corrosive and passes the ASTM Rusting Test despite its large concentration of water. The good wear properties of the morpholine-containing emulsion lubricant are shown by the results obtained in the Navy 4-Ball Wear Test, the CFR Low Temperature Wear Test and the Radioactive Ring Wear Test which is described in U.S. 2,315,845 issued April 6, 1943. The improvement in wear obtained with the morpholine-containing emulsion lubricant over an SAE 20 grade refined paraffin base distillate oil in the CFR Low Temperature Wear Test is particularly significant.

Example 2.—139 grams of the naphthene base distillate oil employed in Example 1, 50 grams of water, 7 grams of monoethanolamine, and 4 grams of Triton X-100 were introduced into a mixing vessel and stirred until a stable oil-in-water emulsion was formed. Into the resulting emulsion, 0.02 gram of an anti-foam agent comprising a 10 percent solution of dimethyl silicone polymer in kero-

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sene was added. The resulting emulsion had the following composition in weight percent:

	Weight, percent
Base oil	69.5
Water	25.0
Monoethanolamine	3.5
Triton X-100	2.0
Anti-foam concentrate	p.p.m. 150

The properties and performance characteristics of this emulsion lubricant are shown in Table II.

Table II

Viscosity, SUS at 100° F.	2482
Viscosity index	59
Four, ° F.	+10
Total base No.	59.5
Navy 4-Ball Wear Test, microns/min.	5.6
Corrosion at 140° F., Neg. to Cu, Fe, Pb, Al, and Sn	

As shown above, the ethanolamine-containing emulsion lubricant of Example 2 is non-corrosive and characterized by low wear.

In Table III the wear properties of an oil-in-water emulsion lubricant of the invention are compared with those of a commercial water-in-oil emulsion lubricant containing a water-soluble divalent metal salt as disclosed in the previously identified U.S. 2,744,870. The morpholine-containing emulsion lubricant of Example 1 was compared in the Radioactive Ring Low Temperature Wear Test to a commercial emulsion diesel engine lubricant comprising approximately 69.7 weight percent mineral oil, 22 weight percent water, 6.8 weight percent calcium acetate, 0.8 weight percent calcium sulfonate, and 0.7 weight percent stearic acid.

Table III

	Radioactive ring low temperature wear test
Morpholine-containing emulsion lubricant of Example 1	27
Commercial calcium acetate-containing emulsion lubricant	37

The data in Table III indicated that the amine-containing emulsion lubricant of the invention has a significantly lower wear rate than the commercial calcium acetate-containing emulsion lubricant.

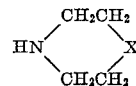
Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. An oil-in-water emulsion lubricant for internal combustion engines consisting essentially of 50-80 weight percent mineral lubricating oil, 50-20 weight percent water, 0.5 to 6.0 weight percent hydrophilic alkylene oxide-alkylphenol adduct emulsifying agent and 2 to 10 weight percent water-soluble amine selected from the group consisting of acyclic and cyclic amines, said acyclic amine having the general formula



wherein R is selected from the group consisting of a hydrogen atom, an alkyl radical, a hydroxyalkyl radical, and an aminoalkyl radical and R' is selected from the group consisting of an alkyl radical, a hydroxyalkyl radical and an aminoalkyl radical, said alkyl, hydroxyalkyl and aminoalkyl radicals containing 1 to 4 carbon atoms and said cyclic amine having the general formula



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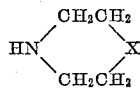
wherein X is selected from the group consisting of oxygen, a $=CH_2$ radical and a $=NH$ radical.

2. An oil-in-water emulsion lubricant according to claim 1 in which said emulsifying agent is an ethylene oxide adduct of an alkyl-substituted phenol.

3. An oil-in-water emulsion lubricant for internal combustion engines consisting essentially of 60-75 weight percent mineral lubricating oil, 20-35 weight percent water, 0.5-6.0 weight percent of a hydrophilic alkylene oxide-alkylphenol adduct emulsifying agent and 3-8 weight percent water-soluble amine selected from the group consisting of acyclic and cyclic amines, said acyclic amine having the general formula



wherein R is selected from the group consisting of a hydrogen atom, an alkyl radical, a hydroxyalkyl radical, and an aminoalkyl radical and R' is selected from the group consisting of an alkyl radical, a hydroxyalkyl radical and an aminoalkyl radical, said alkyl, hydroxyalkyl and aminoalkyl radicals containing 1 to 4 carbon atoms and said cyclic amine having the general formula



wherein X is selected from the group consisting of oxygen, a $=CH_2$ radical and a $=NH$ radical.

4. An oil-in-water emulsion lubricant according to claim 3 in which water-soluble amine is morpholine.

5. An oil-in-water emulsion lubricant according to

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claim 3 in which said water-soluble amine is monoethanolamine.

6. An oil-in-water emulsion lubricant for internal combustion engines consisting essentially of 50 to 80 weight percent mineral lubricating oil, 50 to 20 weight percent water, 0.5 to 6.0 weight percent of an ethylene oxide adduct of octylphenol containing an average of 10 ethylene oxide units as a hydrophilic emulsifying agent and 2.0 to 10 weight percent morpholine.

7. An oil-in-water emulsion lubricant for internal combustion engines consisting essentially of 50 to 80 weight percent mineral lubricating oil, 50 to 20 weight percent water, 0.5 to 6.0 weight percent of an ethylene oxide adduct of octylphenol containing an average of 10 ethylene oxide units as a hydrophilic emulsifying agent and 2.0 to 10 weight percent monoethanolamine.

References Cited in the file of this patent

UNITED STATES PATENTS

1,304,399	Southcombe	May 20, 1919
2,474,325	Rogers	June 28, 1949
2,744,870	Stillebroer et al.	May 8, 1956
2,780,598	Cafcas	Feb. 5, 1957

OTHER REFERENCES

"Triton Surface Active Agents," published by Rohm and Haas Co., Philadelphia, Pa., 1951, pp. 8 and 9 relied on.

"Amines," published by Carbide and Carbon Chemicals Corporation N.Y., N.Y., 1944, pp. 3-9.

Georgi; Motor Oils and Engine Lubrication, pub. by Reinhold Publishing Corporation, N.Y., N.Y., 1950, p. 369.