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MINERAL OIL COMPOSITION AS LUBRICANT FOR STEAM CYLINDERS AND MARINE ENGINES, AND ADDITIVE THEREFOR

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This invention relates to the provision of an additive for incorporation in mineral lubricating oils in the formulation of steam cylinder and marine diesel lubricants and other lubricating compositions, and is concerned with the additive per se and with a method of producing the same and with lubricating compositions containing the same.

Two desiderata of lubricating oil compositions adapted for use as steam cylinder and marine diesel lubricants are (*a*) satisfactory "wick-feed performance" and (*b*) satisfactory emulsification. Criteria of the former are set out in "Method 200.0.1," November 15, 1948, sect. IV, part 5, of the "Federal Standard Stock Catalog," and criteria of the latter are set out in "Method 320.1.5," November 15, 1948, sect. IV, part 5, of the same authority. The requirement of the wick-feed test covering Navy Symbol Oil 4065 (see National Bureau of Ships Bulletin 431) is that the rate of wick-feeding after 14 days shall be not less than 30% of the rate for the first 48 hours of test. The emulsion test requirements (which differ with the user) may be exemplified by the criterion that not more than 1 ml. of oil separate, from 80 ml. of freshly prepared 50–50 emulsion, after standing for 2 hours at the test temperature.

It heretofore was known that the reaction products produced by the liquid-phase oxidation of petroleum hydrocarbons mixtures (by the "Burwell Process") contained aliphatic carboxylic acids which could—either in isolated form or commingled with the other components of the oxidation reaction mixture—be esterified with aliphatic alcohols to form esters. While the resulting esterified material was satisfactorily soluble in mineral lubricating oils, emulsifying properties were unsatisfactory, making the same unfeasible or inoperative as an additive for mineral lubricating oils intended for use in marine engines or in the lubrication of steam turbines.

It heretofore had been known, further, that inclusion of blown rapeseed oil in lubricating oil compositions tended to adapt the latter for use as steam cylinder and marine diesel lubricants, in that the presence of the blown rapeseed oil improved the emulsification of water in the oil composition.

It has now been found that essentially the same results can be secured by incorporating in the mineral lubricating oil an ester-containing reaction product produced by partially esterifying a polyhydric aliphatic alcohol with an acids-containing reaction mixture produced by a relatively brief oxidation of petroleum (or other suitable petroleum hydrocarbons mixture), as will be more particularly described hereinbelow. The resulting esterified material has a high solubility in oil, e. g., in mineral lubricating oils, and solutions thereof in mineral lubricating oils give good wick feed performance and good to excellent water in oil emulsions. It has been found, further, that the polyhydric alcohol may be associated with a minor proportion of a monohydric alcohol ranging in carbon chain from C_{12} to C_{30}.

While petrolatum is the preferred starting material to be subjected to the brief oxidation, the latter may be any mixture of petroleum hydrocarbons having a mean carbon chain length falling within the range C_{26}–C_{50}.

The polyhydric alcohol itself ranges in carbon chain from C_2 to C_{10}, and is represented chiefly by glycol, glycerol and the polyethylene glycols. It is a characteristic but not a limiting feature of the present invention that the polyhydric alcohol used in esterifying the acids content of the oxidation reaction mixture shall be incompletely esterified, i. e., that the same retain at least one unreacted —OH group.

The invention will now be described, in greater detail, by recourse to the following illustrative specific example.

The oxidation

A body of petrolatum is subjected to liquid-phase oxidation, by the "Burwell process" (Patents Nos. 1,768,523 and 1,828,356), the following conditions preferably being observed:

Temperature	140° C.
Pressure	200 p. s. i. of air.
Air flow	250–300 cu. ft./min., per 2000 gallons.

The oxidation is terminated after four hours, whereby to minimize the formation of oxyacids and lower molecular weight carboxylic acids in the resulting oxidation reaction mixture. This latter is further characterized as follows:

Acid number	8–10
Saponification number	42–46
Ester number (saponification number minus acid number)	32–38
Low mol. wt. acids	Trace
Estimated "unsaponifiables" content—percent	80–85
Estimated unoxidized hydrocarbons content—do	70

It is noted, relative to the last two values given above, that the same are not directly determined but rather are indirectly estimated from other data.

It may be mentioned, here, that the oxidate produced by the 4-hour oxidation of the petrolatum differs from that produced by a more protracted (e. g., 8–10 hours) oxidation, under the same conditions, this latter being characterized as follows:

Acid number	23–26
Saponification number	70–75
Ester number	44–52
Low mol. wt. acids	Trace
Estimated "unsaponifiables" content—percent	65–75
Estimated unoxidized hydrocarbons content—do	55–60

The latter oxidate is further distinguished from the former by a higher—but unknown—content of oxyacids, i. e., carboxylic acids containing more oxygen than in the carboxylic group, which higher content of oxyacids appears to depreciate the oil solubility and to cause plugging of the wick in the wick-feed test.

The esterification

For the esterification, the quantity of glycerol is calculated on the basis of two molecules of the carboxylic acids (of the oxidate) for each molecule of glycerol, whereby the esterify two hydroxyl groups of the glycerol and to permit the third hydroxyl group to remain sub-

stantially unchanged. For this purpose, the following mode of calculation can be employed:

$$\frac{\text{Acid No.}}{(2)(56.1)}=\frac{X}{92.1}$$

X=pounds of glycerol per 1000 pounds of acid
56.1=mol. wt. KOH
92.1=mol. wt. glycerol

The above 4-hour oxidate (i. e., total oxidation reaction mixture) and the glycerol are heated together, without or with stirring, at 140–200° C., until no more water (from esterification) is expelled. Usually, the heating is continued for about 4 hours at about 200° C. The acid number of the so-esterified mixture is 2–4 (as against 8–10 for the oxidant per se). The resulting esterified material needs no processing and is ready for use in blending directly with lubricating oil. The esterified product comprises glyceryl-diesters of the carboxylic acids of the oxidate, high mol. wt. esters self-formed during the oxidation, unsaponifiable lower oxidation products (e. g., ketones and alcohols) and unoxidized hydrocarbons.

The blend

The esterified material, above described, is blended with standard marine engine base oils, which may vary in viscosity from 300 to 2000 S. U. S. at 100° F. in varying amounts. Some emulsification will result from the use of as little as 2 to 3% of the above esterified material, although emulsions of such blends do not have the "body" or stability of solutions containing higher concentrations of the esterified material. From 5 to 9% of the esterified material (depending on the oil used) appears to be the optimum blend that will insure satisfactory emulsion test, whereas as much as 25% of the esterified material in oil shows no adverse performance.

A blend consisting of 95% of a base oil of the following properties:

Vis. at 100° F.	1200 S. U. S.
Vis. at 210° F.	70.8 S. U. S.
A. P. I. gravity at 60° F.	23.1
Flash (O. C.)	425° F.
Fire (O. C.)	460° F.

and 5% of the above described esterified material has a steam emulsion value of 1200+ and will pass the Federal Method 200.1.1 emulsion test: less than 1 ml. of oil will separate after 60 minutes at 130° F. The above described blend will pass the wick-feed requirements of Novy Symbol Oil 4065. These data are the same as for 10% blown rapeseed oil in the same 1200 S. U. S. at 100° F. oil. Said oil has the following properties:

A. P. I. gravity at 60° F.	22.2
Flash (O. C.)	430.0° F.
Fire (O. C.)	475.0° F.
Viscosity at 100° F.	1265.0 S. U. S.
Viscosity at 210° F.	76.0 S. U. S.

For the purpose of comparison it may be noted, here, that a blend of 95% of 1200 S. U. S. oil with 5% of the additive produced by esterifying with glycerol the free acids content of the oxidate produced by a 8–10 hour oxidation of petrolatum fails to pass the wick-feed performance test and shows poor solubility, while the emulsifying action is excellent and the emulsion is stable and viscous.

It has been found that the properties of the additive-oil blends of the present invention may be modified by substituting a glyceryl mono-ester-containing esterified additive for part (5 to 50%) of the glyceryl diester-containing esterified additive. The glyceryl mono-ester-containing additive may be produced by esterifying the free acids content of the oxidation reaction mixture with an

amount of glycerol calculated to leave two unreacted hydroxyl groups to the molecule of glycerol. Or, in the alternative, a mixed glyceryl mono- and di-esters-containing additive may be produced by esterifying the free acids content with more than one but less than two equivalents of glycerol.

It is to be understood that the invention is not limited to the particular 4-hour oxidate specifically described above, or to use of glycerol as the polyhydric aliphatic alcohol for effecting the esterification of the free acids content of the oxidate, or to use of the above specific oil as the base oil into which the ester-containing additive is blended. Thus, the base oil may be one having the properties of one or the other of the following:

	A high V. I. oil	A low V. I. oil
A. P. I. gravity at 60° F	28.3	23.1
Flash (O. C.)° F	330.0	345
Fire (O. C.)° F	350.0	385.0
Viscosity at 100° F S. U. S	550.0	550.0
Viscosity at 210° F S. U. S	55.0	48.5

Likewise, the oxidate may be the product of a relatively brief, e. g., 4-hour, oxidation of a petroleum hydrocarbon mixture (be it petrolatum, or crude scale wax, or a high melting paraffin wax, or a heavy lubricating oil base stock) as produced by any of the known methods of oxidation—either liquid phase or modification thereof.

I claim:

1. As a marine engine lubricating composition, a solution in mineral lubricating oil of the reaction product obtained by partially esterifying a polyhydric aliphatic alcohol having a carbon chain length of from C_2 to C_{10} with the high molecular weight aliphatic carboxylic acids content of an oxidate of a normally non-gaseous petroleum hydrocarbon mixture having a mean carbon chain length falling within the range C_{26}–C_{50} subjected to controlled liquid-phase partial oxidation for a period of the order of 4 hours said oxidate having an acid number of from about 8 to not substantially in excess of 10 and a saponification number of from about 42 to about 46.

2. The lubricating composition defined in claim 1, in which the partial esters of the partially esterified material contain at least one unreacted hydroxyl group per molecule of the polyhydric aliphatic alcohol.

3. The lubricating composition defined in claim 1, in which the polyhydric aliphatic alcohol is glycerol.

4. The lubricating composition defined in claim 1, in which the partial esters are representable by the general formula

$$(R—COO)—CH_2—CHOH—CH_2—(OOCR)$$

where R stands for alkyl chains having mean carbon chain lengths ranging from C_{26} to C_{50}.

5. The lubricating composition defined in claim 1, in which the mineral lubricating oil content amounts to from 95% to 75% of the total composition.

6. The marine engine lubricating composition defined in claim 1, in which the solvent mineral lubricating oil is characterized by the following properties:

Vis. at 100° F	1200 S. U. S.
Vis. at 210° F	70.8 S. U. S.
A. P. I. gravity at 60° F	23.1.
Flash (O. C.)	425° F.
Fire (O. C.)	460° F.

7. A composition of matter consisting essentially of a solution in a petroleum lubricating oil of the reaction product obtained by partially esterifying a polyhydric aliphatic alcohol having a carbon chain length of from C_2 to C_{10} with the high molecular weight aliphatic carboxylic acids content of an oxidate of a normally non-gaseous petroleum hydrocarbon mixture having a mean carbon chain length falling within the range C_{26}–C_{50} subjected to controlled liquid-phase partial oxidation for

a period of the order of 4 hours said oxidate having an acid number of from about 8 to not substantially in excess of 10 and a saponification number of from about 42 to about 46.

References Cited in the file of this patent

UNITED STATES PATENTS

1,668,871 Scanlin ---------- May 8, 1928
2,096,390 Burwell ---------- Oct. 19, 1937
2,221,674 Ellis ---------- Nov. 12, 1940
2,243,420 Frolich ---------- May 27, 1941
2,250,468 Cockeville ---------- July 29, 1941
2,275,494 Bennett ---------- Mar. 10, 1942
2,373,733 Adams et al. ---------- Apr. 17, 1945
2,493,483 Francis et al. ---------- Jan. 3, 1950