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COMPOSITION

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4 Claims. (Cl. 252—56)

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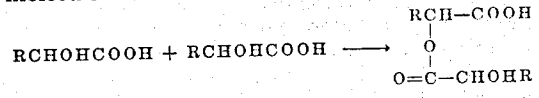
This invention relates to improved mineral oil compositions particularly effective as turbine or hydraulic oils. It relates more particularly to mineral oil compositions consisting principally of a petroleum lubricating oil fraction, the characteristics of the oil being modified by the addition thereto of a small proportion of a semi-lactide of an alpha hydroxy aliphatic acid in which the aliphatic radical contains not less than 10 nor more than 18 carbon atoms.

The semi-lactides of the alpha hydroxy aliphatic acids are formed by condensation of two molecules of the acid with elimination of one molecule of water:



The illustrated reaction is sometimes referred to as "self-esterification" and will be so identified herein.

The mineral oil compositions of my present invention afford particularly effective turbine oils and hydraulic oils and when so used have been found to inhibit the corrosion or rusting of metal parts exposed thereto.

A lubricating oil composition to be used as a turbine oil, and especially in modern marine steam turbines, is subject to very exacting requirements. Not only must it perform the ordinary function of lubricating the turbine over prolonged periods without interruption, but usually it must serve as a coolant, to lubricate the gearing mechanism and to operate oil-actuated governors or control mechanisms having very nice tolerances and lubricate other auxiliary equipment.

Many lubricating oil compositions highly satisfactory for the lubrication of other mechanisms have been found to be wholly unsuitable for use as a turbine oil. This is probably due primarily to the fact that in normal use turbine oils rapidly become contaminated with water. Whatever the cause, it is generally recognized that the performance of a turbine oil is not predictable from conventional tests applicable to other oil lubricants.

Essential characteristics of a satisfactory modern turbine oil include, in addition to ordinary lubricating requirements, extraordinary resistance to emulsification in the presence of water, and the avoidance of the rusting of metal parts within the oil system of the turbine, and auxiliary apparatus, under operating conditions.

The use of many lubricating oil compositions, otherwise satisfactory as turbine oils, has resulted in the rusting of metal parts within the oil system with consequent serious interference with the operation of the turbine, including oil-actuated governors and other parts, depending upon close tolerances. The results of such rusting

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not only interfere with the operation of and tend to clog the delicate clearances of the oil system, but the products of the rusting appear to catalyze oxidation of the oil with resultant sludge formation, which may further aggravate such conditions. The products of the rusting also appear to act as emulsifying agents.

In marine turbine operation, the exacting conditions under which the turbine oil must function satisfactorily are frequently further aggravated by the contamination of the oil with salt water, for instance sea water, which has been found incompatible with many of the corrosion inhibitors previously found suitable as addends for ordinary lubricants. To meet modern turbine oil specifications, particularly Navy specifications, the oil composition must satisfactorily pass tests involving its contamination with salt water.

The unique requirements of a turbine oil have resulted in the formulation of special test methods for determination of the characteristics of the oil with respect to rusting. The results of rusting tests, hereinafter noted, were obtained in accordance with the method prescribed by the American Society of Testing Materials, procedure ASTM specification D665–42T, and designated "Rust-preventing characteristics of steam turbine oil in the presence of water."

In many of the rusting tests, results of which are reported herein, a salt solution was used, as indicated, instead of distilled water prescribed by the test, said salt solution being prepared in accordance with the following Navy formula for synthetic sea water, the proportions being per liter of distilled water:

	Grams
NaCl	25.0
$MgCl_26H_2O$	11.0
$CaCl_2$	1.2
Na_2SO_4	4.0

Test conditions when the salt water is substituted for distilled water are much more severe than when distilled water is used in the test, and oil compositions capable of withstanding such conditions have been found suitable for either land turbine or marine turbine use or as hydraulic oils.

As previously indicated, a further essential characteristic of turbine oils is that they do not form objectionable emulsions under conditions of use. Consequently, in the compounding of such oils, it is necessary to avoid the use of addends which might deleteriously affect the emulsibility of the oil.

An acceptable method for determining the emulsifying characteristics of turbine oil is that designated "Emulsion test for lubricating oils" prescribed by the "Federal Standard Stock catalog, section IV (part 5), Federal specifications for

lubricants and liquid fuels, general specifications (methods for sampling and testing), VV-L-791*a*, October 2, 1934, method 320.12," conventionally known as "Navy emulsion test."

The turbine oil addends of my present invention, though not generally directly effective in inhibiting the oxidation of the oil, have been found to be compatible with many of the known anti-oxidants effectively used in mineral oils, for instance anti-oxidants consisting principally of 2,6-ditertiarybutyl-4-methyl phenol, as the active ingredient, marketed under the trade names "Paranox 441" or "PX 441" and "GX 3."

A further important characteristic of a turbine oil, particularly one containing a rust inhibitor, is the ability of the rust inhibitor to retain its effectiveness over prolonged periods of use. In addition to the rusting tests previously noted, turbine oils are frequently subjected to a life test, designated "R-P life test," which comprises the repetition of the rusting test, using fresh test specimens and fresh salt water but the same oil composition. My improved mineral oil compositions have been found to meet these life tests satisfactorily.

The proportion of semi-lactide used in accordance with my invention may vary over a considerable range, depending primarily upon the severity of conditions under which the oil is to be used and the particular semi-lactide used as the rust inhibitor. Under salt water conditions, advantageous results have been obtained using proportions of the addend within the range of about 0.005% to about 0.10% based on the mineral oil content. Under less severe conditions, even smaller proportions may be used with advantage. Larger proportions may be used, but are not generally required.

The mineral oil constituent of my improved turbine oils may consist of a petroleum lubricating oil fraction or a blend of oils such as ordinarily specified for turbine oils. It may with advantage be highly refined lubricating oil, for instance an acid-treated petroleum lubricating oil fraction, or one which has been subjected to solvent refining, for instance a phenol-treated fraction from East Texas crude. Similarly, in compounding hydraulic oils in accordance with my invention, mineral oil fractions conventionally used for this purpose may be employed. For example, I have used with advantage hydraulic oils obtained from South Texas gas oil by acid treating and compounding with a conventional viscosity index improver. Anti-wear agents and anti-oxidants may also be included. As a turbine oil base oil I have with advantage used, for instance, phenol extracted Mid-Continent neutrals and furfural extracted neutrals produced from San Joaquin Valley crude. The base oil used in the examples subsequently appearing herein was a neutral oil from an East Texas crude, having the following characteristics:

Gravity, °API	30
Flash, °F	400
Fire, °F	445
Viscosity, at 100° F. SSU	160.5
Viscosity, at 130° F. SSU	87.0
Viscosity, at 210° F. SSU	43.4
Pour, °F	+10
Neut. No	0.00
Carbon residue	0.01
Color	1½+
Percent sulfur	0.09

The semi-lactides used in the compounding of

my improved mineral oil compositions, as has been previously indicated herein, may with advantage be prepared by the self-esterification of the corresponding alpha hydroxy acids. It is not necessary to employ highly refined acid, relatively crude material being satisfactory. Thus, I have successfully used alpha hydroxy lauric acid prepared from alpha bromo lauric acid as follows:

482 grams (1.73 moles) of the halogenated fatty acid were introduced into a 3 liter balloon flask and refluxed for 6 hours at 220° F. oil-bath temperature with a solution of 285.6 grams (5.1 moles) of potassium hydroxide in 1850 cc. of water. The reaction solution was acidified with 400 cc. of concentrated hydrochloric acid. An organic phase formed and was separated. It was given two acid washes—the first consisting of 300 cc. of concentrated hydrochloric acid in 200 cc. of water, the second of 200 cc. of concentrated hydrochloric acid in 200 cc. of water—and then a water wash. The crude alpha hydroxy lauric acid was taken up in ether and separated from the aqueous phase. The ether was evaporated at atmospheric pressure and finally under vacuum. A yellowish-white solid was obtained having a neutralization number of 221, a phenol number of 201 and a bromine content of 1.2%.

Alpha bromo lauric acid, suitable for use in the preparation of alpha hydroxy lauric acid is readily produced starting with lauric acid. The following description is illustrative:

2002 grams (10 moles) of lauric acid, analyzing 270 neutralization number, 270 saponification number and 0.2 bromine number, and 103 grams (3⅓ atoms) of red phosphorus were charged to a 5 liter 3 neck flask, provided with a dropping funnel, reflux condenser, and thermometer, and heated by a steam bath. 3200 grams (20 moles) of bromine were added to the molten acid in 3 hours' time, following which a reaction temperature of 190–195° F. was maintained for 5 hours. The reaction mixture was then allowed to stand at room temperature for about 40 hours, following which it was water washed with 3 liters of water and taken up in 6 liters of benzol. 18.08 lbs. of a 33.75% solution of alpha bromo lauric acid in benzene was obtained. A topped sample, benzene free, analyzed 29.6% bromine.

When I desire to use pure alpha hydroxy lauric acid for the self-esterification, I usually prepare the alpha hydroxy lauric acid by the procedure of the following run:

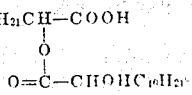
120 grams (2.14 moles) of potassium hydroxide and 2000 cc. of water were added to 200 grams of the bromo-fatty acid (prepared as above) in a 3 liter balloon flask and the resultant solution was boiled about 4 hours. It was then acidified with 200 cc. of concentrated hydrochloric acid. The organic phase was taken up in ether and was given an acid wash and two water washes. The ether was evaporated and the residue crystallized twice from chloroform. 8 grams of pure alpha hydroxy lauric acid, a white, crystalline solid, M. Pt. 73–74° C., was obtained.

The self-esterification of the alpha hydroxy acid with the production of the desired semi-lactide may be easily effected by heating the acid in the presence of a suitable inert solvent, while providing for the removal of the water resulting from the self-esterification. Toluene is a preferred solvent in the instance of alpha hydroxy lauric acid. Care should be exercised to see that the reaction does not proceed to the extent that

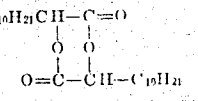
substantial amounts of lactide, i. e. in excess of about 20%, are formed, for the lactide, as will be demonstrated subsequently, is without value as a corrosion inhibitor.

I do not attempt to isolate the semi-lactide from the reaction mixture, but use as the addend all of the material remaining upon evaporation of the inert solvent. The presence of alpha hydroxy aliphatic acids, in which the aliphatic radical contains from 10 to 18 carbon atoms, is not objectionable in corrosion inhibitors added to hydrocarbon oils, in fact these acids of themselves are to some extent effective as corrosion inhibitors in hydrocarbon oils, although when used alone they seem to lose part of their effectiveness upon storage of the inhibited oil. Also, when used alone, that is, in the absence of semi-lactide, they are relatively more prone to cause emulsion difficulties.

the semi-lactide of alpha hydroxy lauric acid



and the lactide of alpha hydroxy lauric acid



Sample A contained the greatest percentage of the semi-lactide (38–77%), while Sample C consisted predominantly of lactide. Sample B was of intermediate composition. Blends of each of the samples in a neutral oil from an East Texas Crude were prepared and subjected to the Navy salt water emulsion and rust tests, along with blends prepared with unesterified alpha hydroxy lauric acid. Results are given in Table I below:

Table I

	Navy salt rust tests			Neut. No.	Navy emulsions	
	Rating [1]	Coating on strip	Etching of strip		H_2O	NaCl
Hydroxy lauric acid				220		
0.015% hydroxy lauric acid	B+	Trace	None	0.03	OK 19	OK 21
0.02% hydroxy lauric acid	A	do	do	0.05	OK 18	OK 20
0.03% hydroxy lauric acid	A	Light	Trace	0.05	OK 24	OK 18
Hydroxy lauric acid, self-esterified 3¾ hours (sample A)				161		
0.010% hydroxy lauric acid, self-esterified 3¾ hours	B++	None	None		OK 8	OK 9
0.015% hydroxy lauric acid, self-esterified 3¾ hours	A	do	do		OK 10	OK 8
0.02% hydroxy lauric acid, self-esterified 3¾ hours	A	do	do		OK 12	OK 7
0.03% hydroxy lauric acid, self-esterified 3¾ hours	A	Trace	do		OK 9	OK 9
0.05% hydroxy lauric acid, self-esterified 3¾ hours	A	Moderate	Trace		OK 11	OK 8
Hydroxy lauric acid, self-esterified 13 hours (sample B)				94		
0.02% hydroxy lauric acid, self-esterified 13 hours	C	None	None			
0.03% hydroxy lauric acid, self-esterified 13 hours	B+	do	do			
0.05% hydroxy lauric acid, self-esterified 13 hours	B++	do	do	0.04	OK 10	OK 8
Hydroxy lauric acid, self-esterified 48 hours (sample C)				30		
0.02% hydroxy lauric acid, self-esterified 48 hours	E	None	None			
0.03% hydroxy lauric acid, self-esterified 48 hours	E	do	do			
0.05% hydroxy lauric acid, self-esterified 48 hours	E	do	do	0.03	OK 17	OK 7

[1] Rust test ratings:
A—Passes test; no rust on strip.
B++—Traces of rust on strip.
B+—Up to 5% of surface rusted.
B—5 to 25% of surface rusted.
C—25 to 50% of surface rusted.
D—50 to 75% of surface rusted.
E—75 to 100% of surface rusted.

My invention is further illustrated by the following example:

Example I

215 grams of crude alpha hydroxy lauric acid, prepared as previously described, and 200 cc. of toluene were placed in a 1 liter, 3 neck flask provided with a thermometer, reflux condenser, and water trap. The mixture was heated by means of an oil bath, and, as the self-esterification began, water of reaction was carried off into the water trap. Samples of the reaction mixture were taken at various intervals and topped free of solvent under vacuum in about one-half hour. They are identified below:

Sample	Wt. in gms. of topped sample	Total reaction time, hours	Reaction temp., °F.	Neutralization number of topped sample
A	36	3¾	210–247	161
B	42	13	247–259	94
C	116	48	259–205	30

The three samples represented mixtures of alpha hydroxy lauric acid

$C_{10}H_{21}CHOHCOOH$

"OK" in the last two columns of the table indicates that the oil satisfactorily passed the emulsion test, and the value following the "OK," where given, represents the minutes required for the emulsion to break completely.

From the table the progress of the esterification may be followed by the drop in neutralization number. It will be noted that after the 3¾ hour esterification the product is more effective than the original material, i. e., the unesterified acid, but that there is a progressive loss in effectiveness upon longer heating. Sample C, containing the greatest proportion of lactide, possibly consisting entirely of lactide, will be seen as completely ineffective against rusting.

The composition containing 0.015% of Sample A, equivalent to from about .0057% to .0115% of the semi-lactide of alpha hydroxy lauric acid, represents a preferred embodiment of the invention.

It is to be clearly understood that my invention is not limited to the semi-lactide of alpha hydroxy lauric acid, since the semi-lactides of other alpha hydroxy aliphatic acids in which the aliphatic radical contains from 10 to 18 carbon atoms are also effective, e. g. the semi-lactides of alpha hydroxy lauric acid, alpha hydroxy capric acid,

alpha hydroxy myristic acid, alpha hydroxy palmitic acid, alpha hydroxy stearic acid, etc.

I claim:

1. An improved mineral oil composition which comprises a petroleum lubricating oil fraction with which there has been compounded a proportion, effective to retard rusting, of a semi-lactide of the alpha hydroxy aliphatic acid in which the aliphatic radical contains from 10 to 18 carbon atoms.

2. The composition of claim 1, in which the proportion of the semi-lactide is within the range of about .005% to about 0.10% by weight.

3. An improved mineral oil composition which comprises a petroleum lubricating oil fraction with which there has been compounded a proportion, effective to retard rusting, of the semi-lactide of alpha hydroxy lauric acid.

4. The composition of claim 3, in which the proportion of the semi-lactide is within the range of about .0057% to .0115% by weight.

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