

## UNITED STATES PATENT OFFICE

2,427,501

## OIL COMPOUND

Milton P. Kleinholz, East Chicago, Ind., assignor  
to Sinclair Refining Company, New York, N. Y.,  
a corporation of Maine

No Drawing. Application September 6, 1945,  
Serial No. 614,818

2 Claims. (Cl. 252—48.6)

1

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 relatively small proportions of alpha, alpha'-thiodilauryl and alpha-hydroxy lauric acid.

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 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 condi-

2

tions. 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 A. S. T. M. Specification D 665-42T, 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

30 liter of distilled water:

	Grams
NaCl	25.0
MgCl <sub>2</sub> ·6H <sub>2</sub> O	11.0
CaCl <sub>2</sub>	1.2
Na <sub>2</sub> SO <sub>4</sub>	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 Specifi-

fications (Methods for Sampling and Testing), VV-L-791a, 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-di-tertiarybutyl-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 otherwise the same oil composition. My improved mineral oil compositions have been found satisfactory to meet these life tests.

The present invention is predicated on my discovery that while neither alpha, alpha'-thiodilauric acid nor alpha-hydroxy lauric acid, when used alone as a turbine oil addend, will afford sustained, complete protection against corrosion or rusting of metal parts exposed to the oil composition under the severe conditions of the prescribed tests, sustained, complete protection under such conditions may be obtained by the conjoint use of these two compounds, even in the presence of salt water. Further, the conjoint use of these two compounds has been found not to cause the formation of objectionable emulsions.

I have found the alpha-hydroxylauric acid, to be an effective corrosion inhibitor in turbine oils for a substantial period of time after the compounding of the turbine oil. However, upon standing in storage the composition containing alpha-hydroxylauric acid alone has been found to become substantially less effective. When used in conjunction with the alpha, alpha'-thiodilauric acid of my present invention, the resultant composition has been found to afford complete protection against rusting and to retain its effectiveness in this respect over prolonged periods.

The two compounds may be separately prepared by any known method and compounded with the mineral oil constituent in the proportions herein indicated. However, a particularly convenient and effective method of preparing these addends is that described in my co-pending application, Serial No. 614,817 filed concurrently herewith by which there may be prepared a product consisting principally of a mixture of alpha, alpha'-thiodilauric acid and alpha-hydroxy lauric acid in proportions within the range of about 20 to about 50% of the latter and about 80-50% of the former. Such mixtures of the addends have been used most effectively in accordance with my present invention.

The process there described comprises generally the reacting of an alpha-brominated lauric acid in an organic solvent, preferably in benzol solution, with potassium hydroxide, to neutralize the acidity of the lauric acid, thereafter reacting the resultant soap with sodium sulfide in aqueous solution, acidifying the mixture with a mineral acid, for instance hydrochloric, and separating the resultant mixture of alpha, alpha'-thiodilauric acid and alpha-hydroxy lauric acid from the solution. The product thus obtained may with advantage

be used either in the crude or in the recrystallized form.

For the purposes of my present invention, I prefer to prepare an admixture of the addends from alpha-brominated lauric acid, which has with advantage been prepared by reacting bromine with lauric acid in the presence of red phosphorus, for instance, by the following procedure:

200 grams (1.0 mole) of distilled lauric acid, 10 containing about 30% myristic acid, and having an acid number of 268, was placed in a 3-necked flask with 10.3 grams (0.33 gram-atoms) of red phosphorus and this mixture was heated to 170° F. 240 grams (1.5 moles) of bromine was then 15 slowly added over a period of two hours, after which the mixture was heated slowly to 195° F. for an additional 5 hours and the mixture permitted to cool. The cooled mixture then was blown with air to remove unreacted bromine and then diluted with 280 cc. benzene and washed twice with 150 cc. portions of water at 140° F. 20 After the aqueous layer had been separated by settling, the benzene layer, which contained the alpha-bromolauric acid, was filtered. The product 25 separated from a portion of this benzene solution was found to have an acid number of 203 and to contain 24.2% bromine.

The procedure which I have found most desirable, especially in the preparation of mixtures 30 of alpha, alpha'-thiodilauric acid and alpha-hydroxy lauric acid with a low bromine content, is illustrated by the following batch:

*Batch A*

35 1420 grams (5 moles) of alpha-bromolauric acid, prepared as just described from a commercial fatty acid of 8 to 18 carbon atoms per molecule, was charged to a 5-gallon glass-lined Pfaudler kettle equipped with a water jacket, 40 stirrer, thermometer and condenser. A total of 6,000 cc. of benzol was then added, and the stirrer started. 280 grams (5 moles) of potassium hydroxide in 420 grams of water was then added over a period of a minute at an initial reaction temperature of 80° F. Stirring was continued for a 45 total of five minutes to allow the reaction with the potassium hydroxide. A solution of 780 grams of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  in 1170 grams of water was then added and the mixture was heated over a period of one hour to a temperature of 160° F. 50 and held at this temperature for 12 hours with stirring. The stirrer was then stopped and the benzene and aqueous phases allowed to separate by standing for a period of one hour. The aqueous phase was discarded, and the benzene phase 55 topped to a maximum bottom temperature of 212° F. to remove benzene.

At the end of the reaction period above described, the potassium salt of the thiodilauric acid was found to contain about 2% bromine. In order to reduce this bromine content, there was added to the reaction mixture from which the benzene had been removed, 7500 grams of a 1% potassium hydroxide solution. The mixture was heated slowly to 200° F. and the retreatment with potassium hydroxide continued for 8 hours. The reaction mixture was then cooled and benzene and excess hydrochloric acid added to acidify the salt. After a one-hour reaction period the mixture was settled to permit the separation of the aqueous phase and the benzene phase. The aqueous phase was discarded and the benzene phase was again washed with acid and then with water. 60 After again separating the aqueous phase, the benzene was topped off from the benzene phase,

70

and the residue stripped by blowing with steam at 200° F. maximum bottom temperature. The residue was then blown with air for 15 minutes to remove any condensed moisture, and the hot stripped product was finally filtered and found to contain 4.90% sulfur and 1.02% bromine.

By the retreatment of the intermediate reaction product with potassium hydroxide prior to acidification, the bromine content of the product may be reduced to a minimum. Such retreatment removes substantially all of the bromine, where the acid from which the alpha-bromoacid was prepared was substantially free from unsaturates. Even where unsaturates were present in the raw material, all but an unobjectionably small amount of bromine may be removed. Such retreatment of the intermediate reaction product for the removal of bromine is preferably carried out in aqueous solution in the substantial absence of benzene or other organic solvent.

By the foregoing procedure, suitable mixtures of alpha, alpha'-thiodilauric acid and alpha-hydroxy lauric acid have been prepared from alpha-bromolauric acid containing as little as 24.1 to as high as 30.7% bromine. Suitable mixtures of the hydroxy lauric and thiodilauric acids have been prepared from crude fatty acids containing from 8 to 18 carbon atoms per molecule and also from substantially pure lauric acid. The alpha, alpha'-thiodilauric acid mixture, prepared as described, has been found to contain from 20 to 50% of alpha-hydroxylauric acid.

The tendency toward the formation of alpha-hydroxylauric acid is increased where the original neutralization of the fatty acid is not promptly followed by the addition of the sodium sulfide. Thus, where it is desirable to increase the proportion of alpha-hydroxylauric acid present in the mineral oil composition, this may be effected by an appropriate modification of the process by which the alpha, alpha'-thiodilauric acid mixture is produced, or the alpha-hydroxylauric acid may be separately produced and added as such to the mineral oil composition in conjunction with alpha, alpha'-thiodilauric acid.

#### Batch B

A further satisfactory batch of the admixed addends was prepared from alpha-brominated lauric acid produced from distilled lauric acid containing about 30% myristic acid and having an acid number of 268 by the general procedure previously described, but omitting the further digestion with hydroxide for the elimination of residual bromine. The product was an admixture of alpha, alpha'-thiodilauric acid and alpha-hydroxy lauric acid in proportions within the previously described range and was found by analysis to have an acid number of 236 and to contain 2.77% bromine, 4.58% sulfur and no ash.

#### Batch C

A further batch of the admixed addends was prepared from an alpha-brominated lauric acid resulting from the bromination of the lauric acid used in batch B using two moles of bromine per mole of lauric acid and having an acid number of 191 and containing 28.1% bromine. The product was prepared by the general procedure used in the preparation of batch B and was an admixture of alpha, alpha'-thiodilauric acid and alpha-hydroxy lauric acid, in proportions within the previously indicated range, and had an acid number of 233 and contained 0.035% bromine, 5.06% sulfur and no ash.

It has been found particularly desirable, in the preparation of these mixtures of alpha, alpha'-thiodilauric acids and alpha-hydroxy lauric acid by the described process, to maintain the reaction temperature following the addition of the sodium sulfide at about 155-160° F. At this temperature, the major portion of the reaction has been found to have been effected in about four hours. Higher temperatures may be employed, for instance up to about 200° F., but at the higher temperatures objectionable foaming is likely to be encountered. Also, to effect a clean separation of the aqueous phase from the organic phase, it is desirable to settle the mixture at a temperature of about 130-140° F.

No particular precautions are necessary in the compounding of my oil compositions. The ingredients may be added to the base oil or blends of various base oils by conventional methods, and thoroughly dispersed therein by agitation.

The proportions of the addends used in accordance with my present invention may vary over a considerable range, depending primarily upon the severity of conditions under which the oil is to be used. Under salt water conditions, advantageous results have been obtained using proportions of the addend admixture, of the composition previously described, within the range of about 0.01% to about 0.2%, 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 Examples VI, VII, VIII and IX, subsequently appearing herein, was a solvent-treated 420 neutral from an East Texas crude. The base oil used in Examples I to V, inclusive, was a phenol extracted Mid-Continent neutral having the following characteristics:

Gravity, °API	28
Flash, °F.	465
Fire, °F.	525
Viscosity, at 100° F. SSU	427
Viscosity, at 210° F. SSU	57
Viscosity index	84
Pour, °F	0
Acid No.	.03
Navy Emulsion tests at 130° F.:	
Salt water	OK-10
Distilled water	OK-18

The Navy Emulsion test referred to in the foregoing, and in the following tabulations, is that 75 previously identified herein. The "O. K." indi-

cates that the oil satisfactorily passed the test and the value following the "O. K." where given, indicates the minutes required for the emulsion to break completely.

Specific examples of my improved mineral oil compositions and the characteristics thereof, as shown by results obtained by subjecting these oil compositions to the previously identified rusting tests and Navy Emulsion test, are set forth in the following tabulation. The base oils used were as previously indicated. The proportions are by weight, based on the mineral oil content.

5

mineral oil compositions for use as hydraulic oils, I have, for instance, used as the base oil, a fuming acid-treated, 300° F. flash, 70/100° F. viscosity fraction from a South Texac crude.

6 In the compounding of hydraulic gear oils, it is frequently desirable to incorporate in the compound, in addition to my improved rust-inhibiting addends, one of the known viscosity index improvers, for instance one in which the active ingredient consists primarily of an isobutylene polymer. Anti-oxidants such as the "Paranox 441" or "GX3" previously identified

Example	Inhibitor		Navy Emulsion Test		Rusting Tests	
	Per cent	Batch	Distilled Water	1% salt Solution	Distilled Water	Synthetic Sea Water
I	None					E
II	0.05	B	OK-17	OK-13	A	A
III	0.05	B	OK-15	OK-15	A	A
IV	0.05	C	OK-12	OK-13	A	A
V	0.05	C	OK-18	OK-12	A	A
VI	0.06		OK	OK		B ++ to B
VII	0.06		OK	OK		A
VIII	0.06		OK	OK		A
IX	0.06	A	OK-16	OK-23		A

In addition to the addends shown in the foregoing tabulation, the compositions of Examples III and V also contained 0.5% of "Paranox 441" as an anti-oxidant. The inhibitor used in Example VI was substantially pure alpha-alpha'-thiodilauric acid, obtained by the crystallization and recrystallization, as the potassium salt, from the composite of several batches of alpha-alpha'-thiodilauric acid made substantially as herein described, and contained no substantial amount of alpha-hydroxy lauric acid. This example is included to illustrate that such turbine oil compositions do not afford complete protection against rusting.

In Examples VII and VIII the inhibitors used consisted, respectively, of 0.045% and 0.04% of the crystallized alpha-alpha'-thiodilauric acid of Example VI and 0.015% and 0.02% of substantially pure, crystallized alpha-hydroxylauric acid.

The alpha, alpha'-thiodilauric acid inhibitor used in Example IX contained 28% of alpha-hydroxylauric acid.

The results of the rusting tests are reported, as is customary, in terms of the amount of rusting on the test specimen. Letter A indicates that at the end of the test, the specimen was clean and bright, with no indication of rust. B++ indicates that there was a trace of light rust on the specimen. B indicates that rust covered 5 to 25% of the surface of the test specimen. E indicates that rust covered 75 to 100% of the surface of the test specimen.

The designation of the inhibitor used refers to the batches previously described herein.

In the foregoing disclosure of my improved mineral oil compositions, emphasis has been placed upon their use as turbine oils. It will be understood, however, that the invention also contemplates mineral oil compositions suitable for use as hydraulic oils, for instance, hydraulic gear oils. For this purpose, base oils such as conventionally used in the compounding of hydraulic oils, may be used. In the compounding of my

may also be used with advantage in the composition.

In addition to inhibiting rusting, the addends of my present invention are effective in increasing the oiliness and the film strength of the composition. In higher concentrations they are effective EP agents.

I claim:

1. An improved mineral oil composition which comprises a petroleum lubricating oil fraction with which there has been compounded minor proportions, effective to retard rusting, of alpha, alpha'-thiodilauric acid and alpha-hydroxylauric acid, the relative proportions of the alpha, alpha'-thiodilauric acid and the alpha-hydroxylauric acid being within the range of about 80 to 50 parts of the former to about 20 to 50 parts of the latter.

2. An improved mineral oil composition which comprises a petroleum lubricating oil fraction with which there has been compounded minor proportions, effective to retard rusting, of alpha, alpha'-thiodilauric acid and alpha-hydroxylauric acid, the relative proportions of the alpha, alpha'-thiodilauric acid and the alpha-hydroxylauric acid being within the range of about 80 to 50

parts of the former to about 20 to 50 parts of the latter, and the summation of the proportions of the two being within the range of about 0.01% to about 0.2%.

MILTON P. KLEINHOLZ.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
2,087,603	Mikeska	July 20, 1937
2,237,096	Dearborn	Apr. 1, 1941
2,368,605	White	Jan. 30, 1945
2,371,207	Zublin	Mar. 13, 1945
2,363,513	Farrington	Nov. 28, 1944