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TURBINE OIL

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My invention relates to an improved lubricating composition especially adapted for use in the lubrication of steam turbines, such as marine steam turbines.

In the operation of steam turbines it is not possible to entirely avoid seepage of water into the oiling system from the steam sealing glands which surround the turbine shaft. For this reason it is necessary to add to turbine lubricating oils in order to prevent corrosion of metal parts within the oiling system, a material effective as a rust-inhibitor. Such material, to be satisfactory, must not be capable of promoting the formation of a stable oil-water emulsion.

The improved lubricating composition of my invention is characterized in that it depends for its rust-inhibiting effect on the presence therein of an alkylmercaptoacetic acid and an alkylsulfinylacetic acid.

The alkylmercapto- and alkylsulfinyl- acids adapted for use in my composition are those in which the alkyl group contains at least 12 carbon atoms. Thus, the alkylmercaptoacetic acid may be, for example, hexadecylmercaptoacetic acid or octadecylmercaptoacetic acid, while the alkylsulfinylacetic acid may be, for example, hexadecylsulfinylacetic acid or octadecylsulfinylacetic acid. Other suitable combinations include dodecylmercaptoacetic acid and dodecylsulfinylacetic acid, heptadecylmercaptoacetic acid and heptadecylsulfinylacetic acid, etc. Although preferable, it is not essential that the alkyl group of the mercapto-acid contain the same number of carbon atoms as the alkyl group of the sulfinyl-acid.

The total weight of the acids in my composition can be varied depending upon the degree of protection required but in the composition as I ordinarily prepare it, the weight of the acids is equivalent to from about 0.025 to about 1.0% of the weight of the base oil. The relative proportion of mercapto-acid and sulfinyl-acid may also vary and within a wide range but the mercapto-acid should always predominate. It is generally advantageous to limit the amount of sulfinyl-acid to 5–20% on the total weight of the acids.

It is my usual practice to add the two acids to the base oil in admixture and since the sulfinyl-acids represent oxidation products of the mercapto-acids, it is convenient to prepare the mixture by the partial oxidation of the particular mercapto-acid it is desired to use. The partial oxidation is with advantage carried out using hydrogen peroxide as the oxidizing agent and in the presence of a suitable solvent. The following

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laboratory run is illustrative: 4.1 gms. (0.012 mole) of crude octadecylmercaptoacetic acid were added to 150 cc. of acetone, and the mixture heated to boiling (138–140° F.). Thereafter 0.22 gm. of 30% hydrogen peroxide (equivalent to 0.0018 mole of H_2O_2, or 15% of the theoretical amount for complete oxidation) was added, following which the mixture was refluxed gently for seven hours. The solution was then poured into 125 cc. of water and the thus precipitated mixture of octadecylmercaptoacetic and octadecylsulfinylacetic acids was filtered off, washed with water, and dried in air.

The octadecylmercaptoacetic acid employed in the above run was prepared in accordance with the following equations:

$$RSH + KOH \rightarrow RSK + H_2O$$
$$RSK + ClCH_2COONa \rightarrow RSCH_2COONa + KCl$$
$$RSCH_2COONa + HCl \rightarrow RSCH_2COOH + NaCl$$

The procedure employed was as follows: An aqueous potassium hydroxide solution, previously prepared by adding 12.3 gms. of potassium hydroxide to 75 cc. of water, was added to 500 cc. of methanol. To this mixture was added, with stirring, 57.2 gms. (0.20 mole) of octadecylmercaptan. Partial precipitation of the potassium mercaptide took place and the temperature of the mixture rose from 85° F. to 98° F. A previously prepared aqueous sodium monochloroacetate solution was then added, with stirring. Reaction was rapid, a precipitate forming in 1–2 minutes and increasing in bulk until, in 10–15 minutes, the mixture represented a thin slurry. This consistency was maintained throughout the reaction which was continued for one hour. At the end of the hour during which a maximum temperature of 106° F. was reached, the mixture was acidified with hydrochloric acid, and the methanol distilled. The molten residue was washed with hot water (175–185° F.) until the wash water was neutral to methyl orange. The product was then allowed to stand until suspended water had settled, after which it was allowed to cool and solidify. The recovery of crude octadecylmercaptoacetic acid was 70.5 gms., slightly above theoretical.

It is not to be understood from the foregoing that my invention is predicated on any particular method of preparing the mercapto or sulfinyl-acid as any suitable method may be used.

The suitability of a compounded oil for application as a marine turbine oil is now conventionally gauged by testing it according to (*a*) a procedure prescribed by the American Society of Testing

Materials and identified as specfication D665–42T, "Rust-preventing characteristics of steam turbine oil in the presence of water," and (*b*) a procedure commonly known as the "Navy emulsion test" which will be found described in section IV, part 5, of the Federal Standard Stock Catalog, being designated therein as "Emulsion test for lubricating oils." Of late it has been the practice to substitute synthetic sea water for the distilled water called for by the A. S. T. M. test; in fact this is required by United States Navy Turbine oil specification 14–0–15 (INT) of March 1, 1943. The Navy formula for synthetic sea water is as follows, 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

My lubricating composition prepared to contain from 0.04 to 0.05% on the base oil of a mixture of octadecylmercaptoacetic and octadecylsulfinylacetic acids containing from 10–15% of the sulfinyl-acid or from 0.05 to 0.06% on the base oil of a mixture of hexadecylmercaptoacetic and hexadecylsulfinylacetic acids containing from 10–15% of the sulfinyl-acid successfully passed each of the above tests, including the modified A. S. T. M. test. In these tests I used as the base oil a neutral distillate having the following properties:

API gravity	27.2°
Flash	460° F.
Fire	520° F.
Saybolt viscosity:	
@ 100° F	431.0 sec.[1]
@ 130° F	190.3 sec.
@ 210° F	57.16 sec.[1]
Viscosity index	81.9
Pour	+5
Color	2½—
Conradson carbon	0.03%
Ash	0
Acid	0
Sulfur	0.13%
Specific dispersion	111.4
Navy emulsion:	
H_2O	OK 3 min.
NaCl	OK 1 min.

[1] Calculated from kinematic viscosity.

Each of the test samples gave an "A" rating in the modified rust test i. e., there was no detectable corrosion of the test strip. Moreover, there was no coating or etching of the strip. In the emulsion test, the period required for clear settling varied but the result was satisfactory in every instance. The result on a blend prepared by adding to the base oil 0.045% of the mixture of acids produced as described supra by the oxidation of octadecylmercaptoacetic acid was OK–30 minutes for distilled water and OK–11 minutes for salt water. On a blend prepared by adding to the base oil 0.055% of a mixture of hexadecylmercaptoacetic acid and hexadecylsulfinylacetic acid containing slightly less than 15% of the sulfinyl-acid, the result was OK–16 minutes for both distilled and salt water.

I claim:

1. An improved lubricating composition adapted for use as a turbine oil comprising a petroleum oil having compounded therewith an alkylmercaptoacetic acid and an effective but relatively smaller quantity of an alkylsulfinylacetic acid, the alkyl group of each of the acids containing at least 12 carbon atoms, the acids being present in an amount sufficient to impart a corrosion-inhibiting property to the composition but not over 1% on the weight of the oil.

2. An improved lubricating composition adapted for use as a turbine oil comprising a petroleum oil having compounded therewith from 0.025 to 1.0% on the weight of the oil of a mixture of an alkylmercaptoacetic acid and an alkylsulfinylacetic acid the latter acid being present in an effective, though relatively smaller, proportion than the alkylmercaptoacetic acid, the alkyl group of each of the acids containing at least 12 carbon atoms.

3. An improved lubricating composition adapted for use as a turbine oil comprising a petroleum oil having compounded therewith from 0.025 to 1.0% on the weight of the oil of a mixture of an alkylmercaptoacetic acid and the corresponding alkylsulfinylacetic acid containing from 5–20% by weight of the sulfinyl-acid, the alkyl group of the acids containing at least 12 carbon atoms.

4. An improved lubricating composition adapted for use as a turbine oil comprising a petroleum oil having compounded therewith from 0.04 to 0.05% on the weight of the oil of a mixture of octadecylmercaptoacetic acid and octadecylsulfinylacetic acid containing from 10–15% by weight of the sulfinyl-acid.

5. An improved lubricating composition adapted for use as a turbine oil comprising a petroleum oil having compounded therewith from 0.05 to 0.06% on the weight of the oil of a mixture of hexadecylmercaptoacetic acid and hexadecylsulfinylacetic acid containing from 10–15% by weight of the sulfinyl-acid.

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