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INHIBITED OIL.

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The present invention relates to oil compositions, and more particularly to improved lubricating compositions containing as a major constituent a mineral lubricating oil and relatively minor amounts of substances effective to counteract or inhibit certain objectionable reactions. The invention is primarily directed to a motor oil or crankcase lubricant which possesses the unique combined characteristics of providing effective detergent properties, satisfactory motor lubrication and protection of certain motor parts against corrosion during extended use of the motor, and of preserving or protecting metal surfaces of motor parts against rusting during periods prior to use, as during periods of extended idleness.

Internal combustion engines of modern design are capable of carrying considerably greater loads than was formerly the case with the older type engines. This increased load-carrying capacity and the increased severity of engine operating conditions incident thereto necessitates employment of special lubricants. Many of the more modern engines are equipped with hard alloy-type bearings, such as copper-lead alloy, which carry greater loads than Babbitt bearings, but which are subject to rapid corrosion under engine operating conditions. Likewise, the tendency towards deposition of sludge upon rings, ring grooves, pistons and other operating parts, with resulting impairment of engine efficiency, is characteristic in the operation of modern engines.

These difficulties, and others accompanying the advent of modern motors of increased power, have been combatted by incorporation, in crankcase lubricants, of substances acting to inhibit corrosion of alloy-type bearings and sludge deposition. In recent years many such additives have been proposed for use in motor oils.

More recently, and particularly during the present war, a serious difficulty has arisen in connection with rusting of internal engine parts which prior to use are put into storage in humid atmospheres, or which are subjected to salt water atmospheres as during transportation overseas. Under such conditions cylinder walls and other ferrous metal parts become rusted, necessitating dismantling for rust removal and often extensive rebuilding or part replacement before the motor can be put into its intended service. This is especially serious regarding combat vehicles and other motorized equipment needed for immediate use upon arrival at destination.

Although many motor oils containing sub-

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stances intended to inhibit corrosion of alloy-type bearings and to decrease sludge deposition during motor operation were available prior to this invention, they would not satisfactorily inhibit rusting of motor parts under the stated storage and transportation conditions. Use of slushing compounds for this purpose was unsatisfactory since the motor could not be run without danger of bearing corrosion or formation of harmful deposits, and dismantling of the motor to remove the slushing compound usually was required prior to motor operation.

A primary object of the present invention is to provide crankcase lubricant compositions having the dual function of inhibiting rusting of engine parts and forming satisfactory lubricants for use in modern engines.

Another important object is the provision of a motor lubricating oil capable of inhibiting corrosion of alloy-type bearings when used as a crankcase oil in motor operation and capable of inhibiting rusting of ferrous metal motor surfaces during periods of motor idleness.

A further object is to provide an improved rust-inhibiting composition.

A still further object is to provide an improved mineral oil lubricant composition.

Early in the experimental research work leading to this invention it was discovered that, in general, substances which can be dissolved in hydrocarbon lubricating oils and which are effective to inhibit alloy-type bearing metal corrosion, not only are ineffective against rust formation on motor parts, but are mutually incompatible with many known rust-inhibiting agents, and tend to depreciate the effectiveness of the latter-named agents when present therewith in motor oil. Likewise, most substances added to motor oil for the purpose of protecting against rusting result in an increased tendency towards bearing corrosion. In addition to these incompatibilities, it was found that many compounds selected for rust-inhibition caused instability of motor oils in other respects, such as causing foaming, sludge deposition in service, or other undesirable effects.

According to the present invention, in broad aspect, it has been discovered that sulfonic acid derivatives, and more particularly oil-soluble salts of sulfonic acid compounds derived from petroleum, such as oil-soluble alkali metal and alkaline earth metal salts of mahogany acids, are effective rust inhibitors; and in more specific aspect that hydrocarbon lubricating oil compositions containing regulated proportions of such substances together with regulated and related

proportions of certain materials of alloy bearing corrosion inhibitor effectiveness are admirably suited for the dual purpose of effectively lubricating modern internal combustion engines in service and preventing the above-described rusting of metal parts prior to the motor service period and during periods of idleness.

An important feature of the invention resides in the discovery of a composite additive for motor oils comprising, as one component, a suitable rust-inhibitor of the class stated and, as another component, an effective agent inhibiting alloy-type bearing corrosion. Of equal or greater importance is the discovery that these two components are mutually compatible and may be used in suitable hydrocarbon lubricating oil without resulting in the objectionable effects stated above. In this regard it has been found that oil compositions of this invention besides functioning to inhibit rusting and bearing corrosion possess excellent detergent properties, in most instances satisfactorily low foaming characteristics and other characteristics desired in a motor lubricant of the type here concerned.

The component incorporated in the lubricants of this invention primarily for the purpose of inhibiting bearing corrosion may be certain organic compounds containing both sulfur and phosphorus, more particularly metal salts of compounds resulting from reacting phosphorus pentasulfide with aliphatic or cyclo-aliphatic alcohols. These compounds are thiophosphoric acid esters, apparently metal (di-aliphatic or dicyclo aliphatic) dithio phosphates. They may contain alkyl substituted groups. One example is zinc di(methyl cyclohexyl) dithiophosphate. Such compounds, while effective as bearing corrosion inhibitors, are ineffective for preventing rusting of ferrous metal motor parts under the conditions stated above, and, in fact, they tend to promote rusting under certain conditions. However, when these compounds are present in suitable hydrocarbon oils along with the stated sulfonates in controlled and balanced amounts, their rust-promoting tendencies are eliminated. Thus, the two components of the inhibitor mutually coact or exhibit interdependence in the lubricant composition.

For motor lubricating oils, minor amounts of the inhibitor components as compared to the amount of hydrocarbon oil present may be employed with satisfactory results. For example, it is seldom necessary to use, in the oil, more than 1 or 2% of the phosphate ester in order to secure adequate protection against bearing corrosion. Usually less than 1% is adequate. Minimum effective amounts of the phosphate ester will vary somewhat with different oils used and with the particular salt or derivative employed. In general, when using the zinc salts mentioned above at least about 0.2% by weight should be incorporated for lubricating oils from Pennsylvania crude and slightly less than this amount as a minimum for those from Mid-Continent crudes.

As indicated, the ratio or balance between the amount of phosphate ester derivative component and the amount of sulfonate component present in the motor oil of this invention is important and must be controlled. The proportional amount of the sulfonate will vary directly with the amount of phosphate ester present, and in any event sufficient of the former must be incorporated to overcome the rust-promoting tendency of the latter, and to inhibit rusting of the ferrous metal surfaces in motors in which the lubricant is to

be employed. In most instances the amount of sulfonate component should be such that the ratio of sulfonate to phosphate ester is at least about 4 to 1. Ratios ranging up to about 10 to 1 have given good results, and higher ratios, as, for example, 12 to 1, may be used if desired. Too little of the sulfonate with respect to the amount of phosphate ester present will result in rusting of ferrous metal motor parts, but a relatively small excess of sulfonate over that required to prevent rusting is not objectionable in most instances.

The following examples will serve to illustrate the invention in setting forth specific embodiments in the form of motor oils compounded for specific usage conditions and possessing properties and qualifications meeting certain rigid tests to be described later herein. Inasmuch as other compositions, not necessarily meeting all of the test requirements are included within the scope of the invention, the following examples should not be considered limitative.

Example I

In a motor lubricating oil, derived from Mid-Continent crude by solvent refining methods, there was dissolved 0.467% of the zinc salt of the reaction product of alkyl cyclohexanol and phosphorus pentasulfide (apparently di(alkyl cyclohexyl) dithio phosphate), 1.1% of a calcium salt of mahogany acids, 2.06% of a sodium salt of mahogany acids, and 0.7% of Parafflow, a wax alkylated naphthalene commonly employed as a pour depressant in lubricating oils. All percentages are by weight. The resulting compounded motor oil lubricant had the following characteristics and analysis:

A. P. I. gravity	degrees	25.1
Flash, C. O. C.	"F	380
Pour	"F	-20/-15
Viscosity (S. U. S.):		
@ 100° F.		197.3
@ 130° F.		102
@ 210° F.		45.3
Viscosity index		82
Color, A. S. T. M.		5%
Per cent ash		0.50
Carbon residue	per cent	0.69
Sulfur, A. S. T. M.	do	0.45
Phosphorus	do	0.045
Chlorine		Nil

The motor oil of Example I was equivalent in viscosity to SAE 10, this being largely determined by suitable selection of the base oil.

Example II

In this instance the base oil employed was a blend consisting of 76% by volume of a solvent refined distillate lubricating oil from East Texas crude and 24% by volume of a refined lubricating oil of 230 viscosity at 210° F. and viscosity index of 40, derived from Mid-Continent crude.

A motor lubricant was compounded, using this base oil and having the following composition by weight:

4.37% "Lubrizol 738" (analysis indicates 25% by weight calcium salts of mahogany acids, 10.75% by weight of zinc salts of di(alkyl cyclohexyl) dithiophosphates, dissolved in petroleum oil as the remaining constituent).
2.02% sodium salt of mahogany acids
0.35% "Parafflow"
and, as the remainder, the base oil described in which the listed components were dissolved.

The compounded motor oil of Example II was equivalent in viscosity to SAE 30 and further characterized as follows:

A. P. I. gravity	24.7
Flash, C. O. C.	° F. 415
Pour	° F. -50/-5
Viscosity (S. U. S.):	
@ 100° F.	440
@ 130° F.	197
@ 210° F.	58.2
Viscosity index	85
Color, A. S. T. M.	6½
Ash	per cent. 0.48
Carbon residue	do. 1.02
Sulfur	do. 0.51
Phosphorus	do. 0.06
Chlorine	Nil

Example III

The compounded motor oil of this example consisted of the following constituents by weight:

0.8% of "Lubrizol 728" (analysis indicates 37.1% by weight of zinc salts of thiophosphoric acid esters, presumably zinc salts of di(alkyl cyclohexanyl) dithiophosphates, dissolved in petroleum oil as remaining constituent).

2.79% of sodium salts of mahogany acids.

0.35% of "Paraflow".

Remainder—Blend of solvent refined lubricating oils from Pennsylvania and Mid-Continent crudes.

This composition, equivalent to SAE 10, was characterized as follows:

A. P. I. gravity	28.7
Flash, C. O. C.	° F. 400
Pour	° F. -15
Viscosity (S. U. S.):	
@ 100° F.	196.3
@ 130° F.	102
@ 210° F.	46.3
Viscosity index	99
Color, A. S. T. M.	4¼
Ash	per cent. 0.43
Carbon residue	do. 0.89
Sulfur	do. 0.36
Phosphorus	do. 0.03
Chlorine	Nil

United States Army Ordnance Department Tentative Specification AXS-934 (Rev. 1) of Oct. 13, 1943, entitled "Oil, Engine, Preservative" describes certain tests, each of which preservative engine oils must pass to be accepted by the Army for use in the crankcases of motors for combat use. Lubricant oils passing all of these tests are considered of satisfactory rust-inhibiting and corrosion-inhibiting nature, as well as having other desired motor oil attributes. Such oils are installed in motors shortly after assembly and may not be drained therefrom until the motor has been in operation for some time, thus eliminating necessity for changing oil (and sometimes dismantling the motor to remove rust) between periods of storage or transportation and use. Before storage or transportation the motors may be "run-in," using these oils as lubricants, which results in coating of the parts thereof with the oil.

In brief, the AXS-934 (Rev. 1) requirements are that the preservative oil must possess:

(1) Ability to protect against high humidity and moisture condensation. This is determined by immersing two freshly sandblasted panels of open hearth low carbon steel in the test oil,

draining the surfaces for 16 hours at 130° F. and exposing the drained steel surfaces to an atmosphere of 95 to 100% relative humidity for 200 hours at 100° F. in a special humidity cabinet in such manner that moisture condenses on the said steel surfaces. The oil is considered to have passed this test if after 200 hours exposure at least one of the panels shows no corrosion and the other shows no more than a trace of corrosion. In addition, the freshly sanded steel panels after immersion in the test oil, draining, and exposure to synthetic sea water for 20 hours under specified conditions must not be corroded.

(2) Ability to neutralize acidic products of combustion in an engine. Freshly sanded steel panels, as above described, are dipped in 0.1% aqueous HBr solution and then the panels are alternately dipped in the test oil and exposed to air. After exposure to the air for 4 hours under specified conditions the panels must show no corrosion, staining or other attack if the test oil is to be considered as passed.

(3) Ability to withstand "C. L. R. Procedure for 36 Hour Engine Test for Oxidation Characteristics of Heavy Duty Crankcase Oil" at a crankcase oil temperature of 250° and 265° F., respectively, for two specified grades of oil. In this test the oil is employed as lubricant in an internal combustion engine containing alloy bearings under loaded conditions. Loss in weight of the alloy bearing as a measure of corrosion occurring during the run and the amount of sludge deposited on the piston and ring grooves are indicative of the stability and inhibitor effectiveness of the test oil under intended use conditions.

(4) Volatile matter of less than 2.0% maximum.

(5) Excessive foaming of the oil must not occur under specified test conditions.

(6) Other requirements include viscosity and pour point limits and compatibility with certain other oils.

Motor oil lubricants of this invention, illustrated in the above examples, have successfully passed all of the AXS-934 tests. These oils have proven satisfactory in protecting moderate engines against rusting under relatively severe conditions during storage and transportation periods, and in lubricating said engines in service following such periods.

In addition to the bearing corrosion and rust inhibitor substances set forth above, it is desirable in certain instances to have present in the composition a material of alkaline nature for the purpose of providing an alkaline reserve. Preferably such materials are amine compounds. Satisfactory results are obtained using, as this material, relatively low molecular weight alkyl amines, such, for example, as amino methyl propanol. Relatively low proportional amounts, usually less than 1% by weight of the oil composition, are effective, the actual amounts which can be incorporated, as regards particular amines, being governed by their solubility in the oil employed. Motor oils having the composition of those of the above examples to which have been added about 0.2% of 2-amino 2-methyl 1-propanol are quite satisfactory in this respect. Such oils are contemplated within the scope of the invention.

We claim:

1. A composition suitable for lubricating modern engines comprising a hydrocarbon lubricating oil in major proportion, a minor proportion of a thiophosphoric acid bearing corrosion inhibiting

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material and a sufficient amount of a sulfonic acid substance effective in the composition to inhibit the rusting of ferrous metal motor parts, said sulfonic acid substance and said bearing corrosion inhibiting material being present in a weight ratio of not less than about 4 to 1.

2. A lubricant composition as defined in claim 1 in which the substance effective to inhibit rusting is a metal sulfonate selected from the group consisting of oil-soluble alkali metal sulfonates and alkaline earth metal sulfonates.

3. A lubricant composition adapted for the lubrication of internal combustion engines equipped with alloy-type bearings comprising a refined petroleum lubricating oil, a bearing corrosion-inhibiting proportion of a suitable metal salt of the phosphorus and sulfur-containing reaction product obtainable by reacting an alcohol of the class consisting of aliphatic and cyclo-aliphatic alcohols with phosphorus pentasulfide, and a sufficient amount of an oil-soluble sulfonate to inhibit rusting of ferrous metal engine parts contacted by said composition, said oil-soluble sulfonate and said metal salt being present in a weight ratio of not less than about 4 to 1.

4. A motor lubricant composition comprising a hydrocarbon lubricating oil of motor oil character and a material effective to inhibit corrosion of alloy-type motor bearings and having rust-promoting tendency and an oil-soluble sulfonate rust-inhibiting agent in amounts effective to inhibit rusting under humid atmospheric conditions of ferrous metal motor surfaces to which the composition is applied, said oil-soluble sulfonate and said material effective to inhibit corrosion of alloy-type motor bearings being present in a weight ratio of not less than about 4 to 1.

5. A motor lubricating composition comprising a refined petroleum lubricating oil, an amount of a metal salt of an organic thiophosphoric acid ester effective to inhibit alloy-type bearing corrosion and an oil-soluble metal sulfonate having rust-inhibiting properties, said sulfonate and ester being present in the composition in a weight ratio of not less than about 4 to 1.

6. A motor lubricating composition comprising a refined petroleum lubricating oil, a bearing corrosion inhibitor comprising a zinc salt of a thio-

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phosphoric ester obtainable by reacting an alcohol of the group consisting of aliphatic and cyclo-aliphatic alcohols with phosphorus pentasulfide, and an oil-soluble metal sulfonate having rust-inhibiting properties, said sulfonate and said bearing corrosion inhibitor being present in the composition in a weight ratio of not less than about 4 to 1.

7. A composition comprising a hydrocarbon oil, at least about 0.2 per cent by weight of zinc di(methyl cyclohexyl) thio phosphate and an oil-soluble sodium salt of mahogany acids in an amount by weight at least four times the amount of said zinc salt present.

8. A composition as defined in claim 5, in which the sulfonate is selected from the group consisting of sodium and calcium salts of mahogany acids and a mixture of said sodium and calcium salts.

9. A motor lubricating composition comprising a refined petroleum lubricating oil, an amount of a zinc salt of the reaction product obtained by reacting an aliphatic or cyclo-aliphatic alcohol with phosphorus pentasulfide effective to inhibit alloy-type bearing corrosion and a material effective to inhibit ferrous metal corrosion comprising sodium mahogany sulfonate and calcium mahogany sulfonate in amounts equivalent to from about 6 to about 10 times the amount of said zinc salt present.

10. A composition as defined in claim 6 including an oil-soluble proportion of an organic amine.

11. A composition as defined in claim 7 including amino methyl propanol dissolved therein.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,261,047	Asseff	Oct. 28, 1941
2,182,992	Lebo	Dec. 12, 1939
2,113,150	Wiezevich	Apr. 5, 1938
2,369,632	Cook et al.	Feb. 13, 1945

Certificate of Correction

Patent No. 2,417,876.

March 25, 1947.

ARTHUR W. LEWIS ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 2, line 6, for "stortge" read *storage*; column 5, line 6, for the numeral "50" read *10*; column 6, line 47, for "moderate" read *modern*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of May, A. D. 1947.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.

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2. A lubricant composition as defined in claim 1 in which the substance effective to inhibit rusting is a metal sulfonate selected from the group consisting of oil-soluble alkali metal sulfonates and alkaline earth metal sulfonates.

3. A lubricant composition adapted for the lubrication of internal combustion engines equipped with alloy-type bearings comprising a refined petroleum lubricating oil, a bearing corrosion-inhibiting proportion of a suitable metal salt of the phosphorus and sulfur-containing reaction product obtainable by reacting an alcohol of the class consisting of aliphatic and cyclo-aliphatic alcohols with phosphorus pentasulfide, and a sufficient amount of an oil-soluble sulfonate to inhibit rusting of ferrous metal engine parts contacted by said composition, said oil-soluble sulfonate and said metal salt being present in a weight ratio of not less than about 4 to 1.

4. A motor lubricant composition comprising a hydrocarbon lubricating oil of motor oil character and a material effective to inhibit corrosion of alloy-type motor bearings and having rust-promoting tendency and an oil-soluble sulfonate rust-inhibiting agent in amounts effective to inhibit rusting under humid atmospheric conditions of ferrous metal motor surfaces to which the composition is applied, said oil-soluble sulfonate and said material effective to inhibit corrosion of alloy-type motor bearings being present in a weight ratio of not less than about 4 to 1.

5. A motor lubricating composition comprising a refined petroleum lubricating oil, an amount of a metal salt of an organic thiophosphoric acid ester effective to inhibit alloy-type bearing corrosion and an oil-soluble metal sulfonate having rust-inhibiting properties, said sulfonate and ester being present in the composition in a weight ratio of not less than about 4 to 1.

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7. A composition comprising a hydrocarbon oil, at least about 0.2 per cent by weight of zinc di(methyl cyclohexyl) thio phosphate and an oil-soluble sodium salt of mahogany acids in an amount by weight at least four times the amount of said zinc salt present.

8. A composition as defined in claim 5, in which the sulfonate is selected from the group consisting of sodium and calcium salts of mahogany acids and a mixture of said sodium and calcium salts.

9. A motor lubricating composition comprising a refined petroleum lubricating oil, an amount of a zinc salt of the reaction product obtained by reacting an aliphatic or cyclo-aliphatic alcohol with phosphorus pentasulfide effective to inhibit alloy-type bearing corrosion and a material effective to inhibit ferrous metal corrosion comprising sodium mahogany sulfonate and calcium mahogany sulfonate in amounts equivalent to from about 6 to about 10 times the amount of said zinc salt present.

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