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3,224,968

LUBRICATING OIL COMPOSITIONS

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This invention relates to lubricating oils particularly adapted to protect ferrous and other metal surfaces from rusting and other types of corrosion. The invention also relates to lubricating compositions having particularly good detergent properties. Specific embodiments relate to hydrocarbon mineral oil containing a non-metallic antirust agent and mineral oil containing both an antirust additive and a detergent of the non-metallic type.

It is well known that lubricating oil affords only limited protection to metal surfaces and cannot be relied on to provide sufficient protection under all conditions, especially in the presence of moisture or high humidity. Accordingly, various additives are utilized to impart to such compositions the required properties. For example, certain additives are employed to impart oxidation stability to the lubricant while other additives may be used to enhance antirust and anticorrosion properties, and still other agents added to improve the detergent characteristics of the oil.

With conventional hydrocarbon motor oils, additives such as barium or calcium sulfonates, used primarily for their detergent properties, also serve to provide the oil compositions with antirust protection. However, certain disadvantages are associated with the use of such metallic additives. One important factor is that when such compositions are burned, a certain amount of ash residue from the metallic constituents is left in the combustion chamber. Under normal automobile operation, varying amounts of lubricating oil bypass the piston rings and are introduced into the combustion chamber. A significant portion of the ash which is formed from combustion of the metallic additives in the oil is left behind as more volatile products are exhausted. This ash contributes to problems such as preignition, detonation, spark plug fouling, valve burning, etc.

Because of these deficiencies, it is highly desirable to reduce or eliminate the use of metallic additives in crankcase lubricating oils. Accordingly, this invention contemplates that metallic detergents are replaced with non-metallic materials. Since detergents of the latter type have essentially no antirust properties, these compositions require an antirust additive which is non-metallic and thus itself ashless.

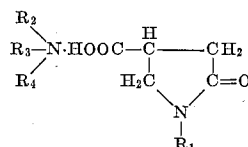
Because the deficiencies of metallic additives have been previously recognized, certain non-metallic or "ashless" rust inhibitors have been developed. However, the performance of the ashless rust inhibitors of the prior art has not been entirely satisfactory. More specifically, these prior art materials have been inadequate in preventing rust under severe operating conditions over a long duration. Another problem is that many prior art materials are not compatible with other additives such as ash-free detergents. Moreover, many of the prior art materials are not economically attractive.

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Accordingly, it is an object of the present invention to provide improved lubricant compositions containing only relatively minor amounts of metallic additives, or more preferably compositions which are completely free of metallic additives. Another object is to provide lubricant compositions capable of protecting metal surfaces against corrosion under severe conditions. Another object is to provide lubricant compositions having improved detergent properties. A still further object is to provide mineral oil compositions containing an antirust additive and a detergent of the non-metallic type.

The objects of the invention are accomplished by providing lubricating oil compositions containing as antirust additives amine salts of certain pyrrolidines. In another embodiment this invention provides lubricating compositions containing a combination of the amine salt and a member or certain classes of detergents. The addition of the amine salt has been found to enhance the anticorrosion properties of the lubricant. The detergents of this invention, in addition to improving the detergent and dispersing characteristics of the oil, are compatible with the antirust additive.

The non-metallic antirust additives of this invention are amine salts of pyrrolidines having the formula



where R_1 and R_2 are aliphatic hydrocarbon groups containing from about 8 to about 25 carbon atoms and having from 0 to 3 double bonds, R_3 and R_4 are selected from the group consisting of hydrogen and aliphatic hydrocarbon groups containing from about 8 to 25 carbon atoms and having from 0 to 3 double bonds. As seen from the above formula the additives of this invention are amine salts of 1-(aliphatic radical)-3-carboxy-5-oxo-pyrrolidines. These amine salts may also be referred to as aliphatic amine 1-(aliphatic radical)-5-oxo-3-pyrrolidinecarboxylates.

Aliphatic hydrocarbon groups R_1 , R_2 , and in appropriate cases R_3 and R_4 may be saturated or olefinic and may be straight chain or branched. They may be, for example, octyl, nonyl, decyl, etc., up to pentacosyl, inclusive, and may be olefinic and branched counterparts of these groups. It is preferred that these aliphatic groups be straight chain olefinic groups containing from 12 to about 20 carbon atoms, and having at least one double bond in the chain.

The amine salts of this invention may be prepared by any suitable manner known to the art and such methods will not be herein discussed in great detail. One suitable method involves neutralization of 1-(aliphatic radical)-3-carboxy-5-oxo-pyrrolidine with at least one molar proportion of a primary, secondary, or tertiary amine. The 1-(aliphatic radical)-3-carboxy-5-oxo-pyrrolidine in turn may be prepared, for example according to the method disclosed in U.S. Patent 2,757,125, which involves heating equimolar amounts of itaconic acid and a primary amine at $180^\circ\text{--}200^\circ\text{C}$. There is formed the substituted pyrrolidine

compound as a condensation product with the elimination of water. In preparing the salts of this invention, it is convenient to combine the above two steps and directly react at least 2 moles of an appropriate aliphatic amine with one mole of itaconic acid to form the amine salts. For this reaction, a mixture of primary, secondary, and tertiary amines may be used, provided there is present at least one mole of primary amine required to form the heterocyclic pyrrolidine ring. The resulting carboxy-pyrrolidine then further reacts with either primary, secondary, or tertiary amine to form the amine salts of this invention.

While chemically pure amines may be used in the above reaction to form the pyrrolidine, ordinarily it is preferred to use commercial amines which are mixtures of amines of various chain lengths.

One group of such amines are derived from reduction of fatty acid mixtures such as tallow, soya, palm, and coconut oils. From these fatty acid mixtures and ammonia are derived the corresponding fatty amines. Thus soya oil yields a mixture of amines having aliphatic hydrocarbon groups containing from 16 to 20 carbons and having from 0 to 3, predominantly 1 and 2, double bonds in the chain. Coconut oil yields a mixture of amines having aliphatic groups which are predominantly saturated having from 8 to 18 carbon atoms in the chain. In commercial practice, these by-product amines are often derived from a mixture of tallow, soya, and coconut oils and thus yield a wide range of amine products. For the purpose of this invention soya amines are preferred because the predominantly unsaturated nature of this product enhances solubility in lubricants.

Ordinarilly the above described reaction of amine with itaconic acid can be carried out without the use of a solvent. However, in some situations the use of an organic solvent such as benzene or ether improves the yield and purity of the product.

The concentration of ashless antirust additive employed in the finished lubricants is, in general, from about 0.01 up to about 2.0 percent. However, due to the high effectiveness of the substituted pyrrolidines of this invention, in most applications a concentration from about 0.05 to 0.2 percent is optimum.

The rust inhibiting additives of this invention are effective in both hydrocarbon and synthetic lubricant bases. By way of illustration typical substances in which the pyrrolidines are useful as additives include hydrocarbon mineral oil, silicone containing oils including the siloxanes, and silanes; sebacate esters, fluorocarbon oils, diesters such as di-sec-amyl sebacate and di-2-ethylhexyl azelate, and synthetic oils such as the polybutene oils, other polyolefin oils, polyalkylene glycol oils, and tetrahydrofuran polymer oils.

Usable lubricating oils include those derived from animal, vegetable, and mineral stocks. A preferred lubricant base comprises a mineral oil fraction of lubricating grade derived from refining a crude petroleum oil through conventional refining processes. Such refining processes include distillation, solvent extraction, clay filtration, dewaxing, acid treatment, propane deasphalting, etc. A specific and preferred embodiment of this invention comprises a crankcase lubricating oil for automotive use comprising a hydrocarbon mineral oil having a viscosity range corresponding to the Society of Automotive Engineers Classification SAE 5W through 50W containing additives of this invention.

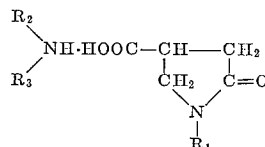
The improved lubricants of this invention are capable of markedly reducing the rust and corrosion which would otherwise occur with untreated lubricants. This is shown by the following examples.

EXAMPLE I

Additive-free lubricants and lubricants containing an antirust additive of this invention were subjected to a modified version of ASTM D-665-54 Test for determin-

ing rust preventative characteristics of lubricating oil. Briefly, the test involves immersing a cylindrical steel specimen in a mixture of 300 ml. of the oil under test and 30 ml. of synthetic sea water. The test is normally carried out for 24 hours at 140° F. and the oil is reported as passing if duplicate specimens are rust-free at the end of the test period. Tests were carried using the above technique but with one modification. In order to make the test more severe and thereby critically evaluate the additives under test, 3 ml. of 0.1 normal hydrochloric acid were added to the oil-water composition.

When an additive-free lubricating oil was subjected to the above described test, heavy rusting of the steel specimens occurred and the oil was considered to have definitely failed the test. Thereafter, the test was repeated using a lubricating composition of this invention comprising the same base oil but containing 0.1 weight percent of the amine salt obtained by reaction of two moles of a mixture of tallow, soya, and coconut amines with one mole of itaconic acid. This amine mixture includes primary and secondary amines whose aliphatic groups contain predominantly from about 12 to 18 carbon atoms and are a mixture of saturates and olefins having 1-3, predominantly 1-2, double bonds. The product mixture may be represented by the general formula



wherein R₁ and R₂ are aliphatic groups as defined above and R₃ is also an aliphatic group as defined or is hydrogen.

When the composition of this invention was subjected to the above test, the steel specimens were found to be completely free of rust and thus the composition passed the test. Even at lower concentrations of the amine salt, the amount of rusting was markedly reduced as compared to the additive-free lubricating oil.

In another embodiment, this invention provides lubricating compositions containing a combination of a non-metallic rust inhibitor as described above, and a detergent additive. Detergents of this invention generally act both as detergents and dispersants. They function to prevent oxidation products and other constituents from becoming insoluble and depositing out on various engine parts. Also, any insoluble materials which may be formed are dispersed and suspended in the oil thereby minimizing agglomeration and settling of deposits. These deposits would otherwise interfere with efficient engine operation in that they are responsible for accelerated piston wear, cylinder wall wear, and also contribute to oil losses by plugging oil ring grooves.

Certain classes of detergents in combination with the antirust additives of this invention provide outstanding benefits. One class of detergents is characterized as polymers containing nitrogen substituents. These materials are copolymers of an essentially non-polar monomer which has the function of contributing to the property of solubility in oil (oleophilic monomer) and a monomer containing nitrogen whose function is to contribute to the surface activity of the polymer. Other monomers may be added which are innocuous with respect to these properties and merely serve to extend the polymer chain.

Examples of oleophilic monomers are polymerizable polycarboxylic acids, vinyl ethers, vinyl substituted aromatic compounds, esters of unsaturated monocarboxylic and polycarboxylic acids, esters such as alkyl acrylates and methacrylates, alkyl fumarates, dialkyl maleates, etc.

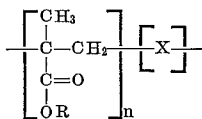
The above type monomers are polymerized with a nitrogen-containing monomer such as vinyl pyridine, vinyl pyrrolidone, dialkylaminoethyl methacrylate, vinyl diethyl-

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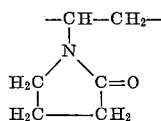
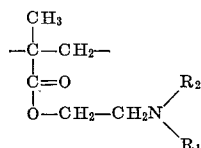
aminoethyl ether, dialkylaminoethyl styrene, vinyl diethylaminoethyl ether, dimethylaminoalkyl, methacrylamide, etc. The ratio of olephilic monomer to nitrogen-containing monomer is usually at least 1:1 and preferably from about 3:2 to 20:1.

A preferred group of polymers involves polymers of alkyl acrylates and methacrylates with various nitrogen-containing monomers susceptible of polymerizing and containing at least one carbon to carbon double bond. These include for example, copolymers of lauryl methacrylate and N-vinyl pyrrolidone; hexadecyl methacrylate with vinyl pyridine; lauryl methacrylate with vinyl diethylaminoethyl ether; decyl acrylate with dimethylaminomethyl styrene; and also terpolymers wherein a hydrocarbon monomer is included such as the terpolymer of lauryl methacrylate, styrene, and dibutylaminoethyl methacrylate.

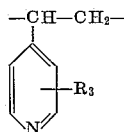
One particularly outstanding group of detergents of this invention comprises the copolymers of alkyl methacrylates and a nitrogen-containing monomer selected from the group consisting of dialkylaminoethyl methacrylates, N-vinyl pyrrolidones, and vinyl pyridines. These polymers have the repeating structure



wherein R is an alkyl group having from about 8 to about 25, preferably 12 to 18 carbon atoms, n is an integer ranging from 1 to about 50, X is selected from the group consisting of



and

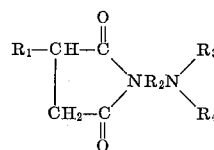


wherein R_1 and R_2 are alkyl groups having from 1 to about 12, preferably 1 to 8 carbon atoms, and R_3 is selected from the group consisting of hydrogen and alkyl groups having from 1 to 12 carbon atoms. These polymers have been found to possess outstanding detergent properties, are compatible with the antirust additives of this invention, and also are viscosity index improvers. The above polymeric detergent-dispersants are added to lubricating oil in an amount ranging from 0.1 to about 10 percent, preferably from about 3 to 8 percent.

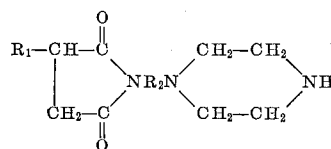
Another preferred group of detergent-dispersants are N-substituted alkenyl heterocyclic imides. These compounds are obtained by reacting a hydrocarbon polymer, preferably the polymer of an olefin having from 2 to 5 carbon atoms, with an acid anhydride, followed by reaction with a compound having an amino function to form the heterocyclic imide. An outstanding example is a detergent formed by reacting a polyisobutene having a

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molecular weight of about 200 to 1500 with an acid anhydride such as maleic anhydride to form monoalkenyl succinic anhydride. This material is then reacted with a nitrogen-containing compound such as for example dialkylaminoalkylamine, to form N-dialkylaminoalkyl monoalkenyl succinimide:



or with N-(aminoalkyl)piperazine to form N-alkylpiperazine monoalkenyl succinimide,

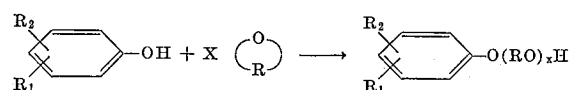


In the above formulae, R_1 is a polyolefin radical having a molecular weight of from about 200 to 1500 derived from olefins having from 2 to 5 carbon atoms, R_2 is a hydrocarbon group having from 1 to about 5 carbon atoms, and R_3 and R_4 are alkyl groups containing from 1 to about 12 carbon atoms.

Another class of detergent-dispersants usable in combination with the ashless antirust additives are reaction products of higher polyhydric alcohols with carboxylic acids. Especially preferred are reaction products of the hexahydric alcohols mannitol, sorbitol, and dulcitol with higher fatty acids having from about 12 to 20 carbon atoms. The reaction of these constituents yields various products depending on the reaction conditions. For example, reaction of sorbitol with fatty acid in the presence of phosphoric acid at a pH of 1-2 yields sorbide esters, whereas reaction in the presence of sodium hydroxide yields predominantly sorbitan esters. One method of producing these products is disclosed in U.S. Patent 2,322,820.

The most preferred dispersants from the above class are the sorbide esters, especially the monesters derived from reaction of sorbitol or sorbide with a fatty acid having from 12 to about 20 carbon atoms and containing up to 3 double bonds. Particularly outstanding are the properties of sorbide monooleate. This product is obtained by reaction of sorbitol with oleic acid in the presence of phosphoric acid at a pH of 1-2 at a temperature of from about 150-300° C.

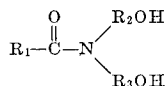
Another class of detergents usable in these compositions are alkylphenol-olefin oxide condensation products. The condensation to yield these products is carried out in the presence of a catalyst such as sodium methoxide at temperatures of about 200° C. The molar ratio of phenol to olefin oxide is from about 1:1 to 1:100, preferably from 1:1 to about 1:20. The overall reaction may be represented as follows:



where R is a polymethylene group, preferably ethylene or propylene, R_1 is an alkyl group having from 6 to 20 carbon atoms, R_2 is selected from the group consisting of hydrogen and alkyl groups having from 6 to 20 carbon atoms, and x is an integer ranging from 1 to 100. A

preferred group of detergents are the condensation products of propylene oxide and p-tertiary-octylphenol reacted in a molar ratio of from 1:1 to 20:1.

Certain fatty acid alkanolamides constitute another group of detergents that can be used in combination with the ashless antirust additive. These are the reaction products of equimolar amounts of an alkanol amine with a fatty acid heated at from about 150 to 250° C. for from 1 to 4 hours in a nitrogen atmosphere. These products have the general formula



wherein R₁ is the organic residue of a straight chain fatty acid containing from 10 to about 20 carbon atoms in the molecule, and R₂ and R₃ are the same or different and are the organic residue of aliphatic alcohols having from 1 to about 8 carbon atoms in the molecule. Preferred products are those wherein R₁ contains from 11 to 17 carbon atoms and R₂ and R₃ are the same and contain from 2 to 4 carbon atoms. Thus, compounds such as lauric diethanoamide, oleic diethanolamide and linoleic diethanolamide are preferred.

EXAMPLE II

Various lubricating oil compositions were subjected to a 16-hour rust test using a single cylinder CLR engine. The procedure followed is essentially the same as reported in the paper "Evaluation of Rusting Characteristics of Motor Oils," D. A. Young and G. J. Ferris, presented at the Society of Automotive Engineers Fuels and Lubricants Meeting, Houston, Texas, November 10, 1961. This short term rust test has shown excellent correlation with the MS sequence used in qualifying motor oils, i.e., oils used in MS service. The American Petroleum Institute Engine Service Classification defines MS service as "service typical of gasoline or other spark-ignition engines used under unfavorable or severe operating conditions, and where there are special lubrication requirements for deposit, wear or bearing-corrosion control, due to operating conditions or to engine design or fuel characteristics."

The CLR Test comprises operating the engine for 16 hours under low-temperature, high-humidity, and high blowby test conditions. At the end of the test the hydraulic valve lifters and specially ground push rods (15-20 micron surface finish) are removed from the engine, flushed with solvent, and rated for rust. A rating of 10 is given for an engine part which is completely free from rust, and a rating of 0 indicates maximum rust. The results are reported as the average of the rating of the lifters and push rods.

The engine operating conditions for this test are shown in Table I.

Table I

ENGINE OPERATING CONDITIONS

Test length, hours	16
Speed, r.p.m.	1800
Fuel flow, lb./hr.	4.5
Air-fuel ratio	15.0
Intake mixture temperature, ° F.	175
Cooling water out, ° F.	90
Oil gallery temperature, ° F.	125
Moisture content of air, g./lb. dry air	80
Oil pressure, p.s.i.	30
Blowby, c.f.h.	25

A variety of mineral oil compositions were subjected to the above test. The compositions, in terms of weight percent, and the results obtained are described in Table II.

Table II

CLR ENGINE RUST TEST RESULTS

Blend	Composition, Percent	Rust rating
5 A	Base oil	6.6
B	A + 0.1 antirust additive ¹	9.3
C	A + 0.6 phenolic antioxidant	6.8
	0.4 phosphorus-containing antiwear agent	
D	5.0 detergent ²	9.3
	C + 0.1 antirust additive ¹	

¹ Amine salt of this invention described in Example I.

² Polymer detergent available commercially from the Rohm and Haas Company under the trade name "Acryloid 917" and believed to be a copolymer of lauryl methacrylate and diethylaminoethyl methacrylate.

As shown by the above ratings, the antirust properties of both a base oil (composition A) and the base oil containing various additives (composition C) were improved by the addition thereto of an antirust agent of this invention. Thus, with respect to resistance to rust, compositions of this invention B and D were clearly superior to compositions A and C. The results of the above test also point out that the antirust additives of this invention and a detergent of this invention are compatible and well suited as common additives to lubricating oil.

EXAMPLE III

Lubricant compositions containing an antirust additive and detergent additive of this invention were also subjected to a modified version of the L-38 Polyveriform Test to determine their sludge forming tendency. The original test was described in a paper entitled "Factors Causing Lubricating Oil Deterioration in Engines," Industrial and Engineering Chemistry, Analy. Ed. 17, 302 (1945). The test consists of bubbling air through 100 grams of the lubricant for a period of 48 hours. The test is carried out at a temperature of 300° F. The test was modified in that the steel sleeves and copper test piece described in the original test were not employed. Also oxidation catalysts comprising 0.1 weight percent lead bromide, and copper-lead bearings (1" x 2 1/8") are included in the oil rather than ferric ethylhexoate as described in the original test. This modification not only makes the test more stringent but the results have been found to better correlate with the L-38 Engine Test. After the 48 hour test period, the oil is cooled and graded visually for any sludge that may have been formed. A rating of A+ indicates no visible sludge and a rating of E indicates extremely heavy sludge. The oil is also subjected to an acid number determination and any viscosity increase is measured. Also, the bearings which were included in the oil medium are weighed and any loss in weight is noted. A high bearing weight loss indicated the presence of significant amounts of organic acids produced from oil oxidation and deterioration.

A hydrocarbon mineral oil (Blend A), the same oil containing additives of this invention (Blends C and D), and a commercially available "ashless oil" containing a full complement of ashless additives (Blend B) were submitted to the above described Polyveriform Test. Compositions C and D, contained the combination of a rust inhibitor and a detergent additive of this invention. The rust inhibitor in both cases was 0.1 weight percent of the amine salt of Example I formed from reacting two moles of a mixture of soya, coconut, and tallow amines with one mole of itaconic acid. Blend C contained 5 percent of the polymeric detergent described in Example II, and Blend D contained 5 percent of N-dialkylaminoalkyl polyisobutene succinimide, a detergent of this invention. Both C and D also contained 0.4 weight percent of a phosphorus containing antiwear agent and 0.6 weight percent of a phenolic antioxidant. The results of these tests are shown in Table III.

Table III

POLYVERIFORM TEST RESULTS

Blend	Composition	Bearing wt. loss, mg.	Acid number	Percent viscosity increase, SUS at 100° F.	Visual sludge rating
A-----	Base oil-----	205	13.4	339	B
B-----	Commercial "Ashless Oil."-----	107	10.4	142	A
C-----	Composition of this invention-----	47	1.5	60	A+
D-----	do-----	23	2.8	35	A

The above tests show that the base oil was susceptible to sludge formation and to a high degree of viscosity increase. As evidenced by the relatively high acid number and large bearing weight loss, the base oil underwent oxidation during the test with the production of organic acids. The commercial oil, which contained a full complement of ashless additives to impart the desired characteristics to the oil, showed some improvement over the base oil. However, the blend showed a high acid number and a significant viscosity increase and bearing weight loss. The compositions of this invention (C and D) showed an improvement over both the base oil and the commercial ashless oil. Sludge was essentially absent and only a relatively minor increase in viscosity was noted. Also, the acid number and bearing weight loss were very low. Thus the compositions of this invention are clearly superior to the base oil and to the commercially available ashless oil.

The results of the tests described in the foregoing examples clearly show that the amine salts of this invention are effective in protecting metals against rust and also that compositions of this invention containing the antirust additive and a detergent have a minimum tendency to form sludge, show only a minor increase in viscosity, and are resistant to oxidation.

Some typical compositions of this invention are shown in the following examples.

EXAMPLE IV

To 980 parts of a phenol-treated, mixed base mineral oil having a viscosity of 300 Saybolt Universal seconds (SUS) at 100° F. and 52 SUS at 210° F. and having a viscosity index (VI) of 102, is added 20 parts of sec-nonylamine 1 - nonyl - 5 - oxo-3-pyrrolidinecarboxylate. The resulting mixture is stirred to assure homogeneity. The finished lubricant contains approximately 2 percent of the amine salt.

EXAMPLE V

The procedure of Example IV is repeated using 5 parts of tert-laurylamine 1-lauryl-5-oxo-3-pyrrolidinecarboxylate and also 15 parts of copolymer of lauryl methacrylate and vinyl pyridine. The finished lubricant contains approximately 0.5 percent of the amine salt and 1.5 percent of the polymeric detergent.

EXAMPLE VI

To 999 parts of a solvent-extracted Pennsylvania bright stock having a Saybolt viscosity at 100° F. of 660 and at 210° F. of 76, a viscosity index of 107 was added 1 part of di-(9-octadecenyl) - amine 1-(9-octadecenyl)-5-oxo-3-pyrrolidinecarboxylate. After physical agitation the finished lubricant contains about 0.1 percent of the additive.

EXAMPLE VII

Ten parts of pentacosylamine 1-pentacosyl-5-oxo-3-pyrrolidinecarboxylate, 50 parts of a copolymer of hexadecylmethacrylate and N-vinyl pyrrolidone, and 940 parts of a conventionally refined Pennsylvania bright stock having a Saybolt viscosity at 100° F. of 550 SUS and at 210° of 65 SUS, a viscosity index of 100, are intimately

ly mixed. The homogeneous finished oil contains approximately 1 percent of the amine salt and 5 percent of the polymeric detergent.

EXAMPLE VIII

The procedure of Example VI is repeated using 1 part of a mixture of various amine pyrrolidinecarboxylates. The product is obtained from reaction of 2 moles of a mixture of soya, coconut, and tallow amines with 1 mole of itaconic acid. The resulting product is a mixture of aliphatic amine 1-(aliphatic radical)-5-oxo-3-pyrrolidinecarboxylates. The aliphatic amine portion of the salt is derived from a mixture of primary and secondary amines whose aliphatic hydrocarbon groups contain from 12 to 20 carbon atoms and up to three double bonds. The aliphatic radical bonded to the heterocyclic nitrogen atom is derived from a mixture of primary aliphatic amines having from 12 to about 20 carbon atoms and up to three double bonds. The finished lubricant contains 0.1 percent of the amine salt mixture.

EXAMPLE IX

To the composition of Example VIII is added 100 parts of the copolymer of lauryl methacrylate and diethylaminoethyl methacrylate. The finished lubricant contains approximately 0.1 percent of the antirust additive and 10 percent of a detergent of this invention.

EXAMPLE X

To the composition of Example VI is added 30 parts of N-dimethylaminopropyl polyisobutene succinimide. The finished composition contains approximately 0.1 percent of the antirust additive and 3 percent of the imide detergent.

EXAMPLE XI

To the composition of Example VIII is added 40 parts of sorbide monooleate. After mixing the finished lubricant contains approximately 0.1 percent of the antirust additive and 4 percent of the detergent.

EXAMPLE XII

To 980 parts of di-2-ethyl-hexyl-sebacate are added 5 parts of 9-octadecenylamine 1-(9-octadecenyl)-5-oxo-3-pyrrolidinecarboxylate and 20 parts of lauric diethanolamide. The finished lubricant contains 0.5 percent of the antirust additive and approximately 2 percent of the detergent.

EXAMPLE XIII

To 950 parts of polyalkylene glycol is added 1 part of 9 - octadecenylamine 1 - (9 - octadecenyl) - 5 - oxo - 3-pyrrolidinecarboxylate and 50 parts of the condensation product of p-tert-octylphenol with propylene oxide reacted in a molar ratio of 1:6. The finished lubricant contains 0.1 of the antirust additive and 5 percent of the detergent.

EXAMPLE XIV

To 700 parts of a conventionally refined Pennsylvania bright stock having a Saybolt viscosity at 100° F. of 570 SUS and at 210° F. of 60 SUS a viscosity index of 100 are added 20 parts of a mixture of various amine pyrrolidine carboxylates and 280 parts of a polymeric detergent. The amine salt is the product obtained from reaction of soya, tallow, and coconut amines with itaconic acid as defined in Example I. The detergent is a copolymer of lauryl methacrylate and diethylaminoethyl methacrylate. The finished composition comprises lubricating oil containing approximately 2 percent of the amine salt and 28 percent of the detergent.

EXAMPLE XV

To 650 parts of the base oil of Example XIV is added 15 parts of 9-octadecenyl amine 1-(9-octadecenyl)-5-oxo-3-pyrrolidinecarboxylate and 330 parts of N-dimethylaminopropyl polyisobutene succinimide. The resulting

composition comprises mineral oil containing approximately 1.5 percent of the amine salt and 33 percent of the detergent.

The antirust agents and the detergent-dispersants of this invention while being highly suitable for addition directly to the finished lubricating oil, may also be incorporated into "ashless packages." Such packages are concentrates of various ashless additives dispersed in oil to be added as a whole to the finished lubricating oil. Thus an embodiment of this invention is an ashless concentrate comprising a carrier oil, preferably mineral oil containing a high concentration of an antirust additive and a detergent-dispersant of this invention. The oil may contain as high as 50 percent additives, depending on the solubility of the particular additives employed. We usually prefer to use concentrates wherein the additives are present in a concentration of from about 20 to 35 percent. Examples of such concentrates are Examples XIV, and XV above.

The compositions of this invention can also contain other additives commonly used in the lubricant art to improve various characteristics of lubricants. While greatest benefits are obtained from oil compositions completely free of metallic additives, the additives of this invention are still effective in oils containing significant amounts of metal-containing additives and can be so used. With crankcase lubricants, some of the metallic additives that may be used include antioxidants such as zinc dialkyldithiophosphate, metal carbamates such as zinc dibutyl-dithiocarbamate; metal salts such as calcium cetylphenate; dispersant-detergents such as sulfonate or phenate salts of barium or calcium; antiwear agents such as dialkyltin sulfides, lead naphthanate, etc.

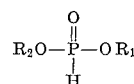
While in some cases amounts of metal-containing additives may be employed, the preferred crankcase lubricants are completely free of metallic additives. Other ashless additives that can be incorporated into the concentrate or added directly to the oil include among others, oxidation inhibitors. These additives are widely used to decrease the amount of oxygen taken up by the oil thereby reducing the formation of acidic materials. The inhibitor may also terminate oil oxidation by formation of inactive soluble compounds, or the inhibitor itself may be oxidized in preference to the oil. Usable inhibitors include organic amines such as diphenyl amine, phenyl-naphthylamine, tetramethyl diaminodiphenylmethane, lecithin, alizarin; sulfur compounds such as sulfides, hydroxysulfides, thioethers, sulfurized terpenes such as sulfurized pine oil, sulfurized wax olefins, sulfurized sperm oil; halogen compounds and phosphorus compounds such as the addition products of phosphorus pentasulfide with a polyolefin such as terpene; phosphorus compounds such as tributyl phosphite, triphenyl phosphite, etc. Antioxidants are usually added to lubricating oil at a concentration ranging from 0.05 to 2 percent, usually from 0.3 to 1.0 percent.

It is preferred to use as antioxidants phenolic derivatives. These include substituted phenols such as the cresols, di- and tri-alkylated phenols substituted with alkyl groups such as ethyl, propyl, and butyl. Highly preferred compounds are the sterically hindered phenols wherein at least one tertiary alkyl substituent is positioned ortho to the hydroxy group. Examples are 2,6-di-tertiary alkyl phenols, especially 2,6-di-tertiary butylphenol. I can also use biphenyl derivatives containing hydroxy and alkyl substituents. Other usable phenols are methylene bisphenol derivatives, such as 4,4'-methylene bisphenol, and similar compounds substituted with lower alkyl groups. Outstanding among the latter type are the symmetrical sterically hindered phenols such as 4,4'-methylenebis(2,6-di-tertiary butylphenol).

I can also use methylene bisphenols wherein the methylene group has substituents thereon such as alkyl groups or another aromatic nucleus, also bisphenols wherein the aromatic nuclei are joined by a polymethylene

group may be used. Other compounds that may be used as antioxidants are phenol ethers and sulfur bisphenols, i.e., wherein the aromatic nuclei are joined by sulfur.

Other additives that may be included are extreme pressure and antiwear additives. These compounds are useful in reducing friction, scoring, and wear of contacting metal parts. Such additives often contain chlorine, phosphorus, and sulfur. Illustrative of these compounds are chlorinated waxes, organic phosphites and phosphates such as tricresyl phosphate, etc. A preferred group of these additives comprises phosphonates having the formula



wherein R_1 and R_2 are alkyl groups having from 1 to about 8 carbon atoms. In a particularly outstanding embodiment, both R_1 and R_2 are secondary alkyl groups having from about 3 to 6 carbon atoms. These compounds are usually included in a concentration of from 0.1 to 1 percent.

Metal deactivators may also be included in my compositions. This class of compounds may act by either precipitating dissolved metal ions out of the oil, or by forming inactive complexes with the metal compounds. Also, the deactivator may function passively by forming an inactive film on the metal surface. Commonly used metal deactivators include complex amines and sulfides, mercapto-benzothiazole and zinc dibutyl-dithiocarbamate. Concentrations of these additives usually range from about 0.05 to 0.2 weight percent.

Pour point depressants are used to prevent growth and crystallization of waxy constituents at reduced temperatures thereby lowering the pour point of the oil. Commonly used materials for this purpose include complex condensation products of paraffin wax and naphthalene, prepared by chlorinating the wax and condensing it with naphthalene by Friedel-Crafts reaction; condensation products of chlorinated wax with phenols; high molecular weight polymerization products of esters of methacrylic acid and higher fatty alcohols such as cetyl, lauryl, etc.

My compositions may also contain viscosity index improvers which lower the rate of change of viscosity with temperature. These materials include polymerized olefins and isoolefins, especially butylene polymers. Also, usable for this purpose are methacrylic acid ester polymers and alkylated styrene polymers. Foam inhibitors to prevent formation of stable foams may be included. An outstanding example are the silicone polymers. In addition other additives such as dyes and color stabilizers may be included in the compositions. The latter materials include certain hydroquinones, dithiocarbamates, aliphatic amines, dicyclohexyl amines, etc.

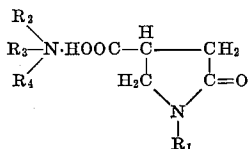
It is to be understood that although specific classes of ashless detergent-dispersants have herein been described, other classes of such additives can be included in the compositions of this invention. Any ashless detergent which is compatible with the antiwear and antirust agents of this invention and which has the requisite solubility can be included either in combination with the detergents herein described or in place thereof. The detergents may be of the polymeric type such as alkyl methacrylate-methacrylic acid polymers and these polymers esterified with polyols such as pentaerythritol and polyethylene glycol; of the polyester type such as polyesters of dibasic acids or anhydrides with diethanolamines, i.e., polyesters of alkenylsuccinic anhydride with alkyldiethanolamines; or they may be monomeric compounds such as aromatic dialkanolamines, i.e., mixed xylyl dipropanolamines; etc.

I claim:

1. A lubricant composition comprising a major portion of a lubricating oil and from 0.01 to about 2

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percent by weight of aliphatic amine 1-(aliphatic radical)-5-oxo-3-pyrrolidinecarboxylate having the formula



wherein R₁ and R₂ are aliphatic hydrocarbon groups containing from 8 to about 25 carbon atoms, and R₃ and R₄ are selected from the group consisting of hydrogen and aliphatic hydrocarbon groups containing from 8 to about 25 carbon atoms.

2. The composition of claim 1 wherein said aliphatic groups contain from 12 to about 20 carbon atoms and up to three double bonds.

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