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COMPOUNDED LUBRICANT COMPOSITIONS AND COMPOSITE ADDITION AGENTS THEREFOR

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This invention relates to composite mineral oil addition agents that are especially adapted to improve the film strength and load carrying characteristics of hydrocarbon lubricating oils. More particularly, the invention relates to compounded hydrocarbon lubricating oils.

Ordinary uncompounded hydrocarbon lubricating oils frequently have been found unsatisfactory for lubricating highly stressed, frictionally engaged metal surfaces, such as reduction gears operated at high speed and under heavy load conditions. Uncompounded hydrocarbon lubricating oil films often tend to rupture at the enormous pressures developed under such conditions, thus permitting metal to metal contact, excessive wear and even seizure.

The present invention relates to improvement of the film strength and load carrying properties of hydrocarbon lubricating oils, whereby such oils are rendered more suitable for use under extreme pressure conditions, such as are encountered by gear lubricants and the like. We have found that the film strength and load carrying capacity of hydrocarbon lubricating oils can be improved substantially by incorporating therein a small amount of a combination of (*a*) a sulfurized monoester addition product of sulfur and an unsaturated ester of an aliphatic monohydric alcohol that contains 14 to 20 carbon atoms and not more than one ethylenic linkage per molecule and an aliphatic monocarboxylic acid that contains 10 to 20 carbon atoms and not more than one ethylenic linkage per molecule, (*b*) a salt of a cycloaliphatic monoamine that contains 5 to 12 carbon atoms per molecule and a dialkyl orthophosphoric acid having one alkyl group containing 8 to 12 carbon atoms and another containing 5 to 8 carbon atoms, and (*c*) a salt of an aliphatic monoamine that contains 8 to 18 carbon atoms per molecule and an N-alkylamidophthalic acid having an N-alkyl substituent that contains 8 to 18 carbon atoms, said small amount comprising at least about 0.003 percent by weight of the composition of said sulfurized monoester, at least about 0.0125 percent by weight of the composition of said salt of said cycloaliphatic monoamine, and at least about 0.005 percent by weight of the composition of said salt of said aliphatic monoamine. Sulfurized monoester addition products of sulfur and mixed, unsaturated esters of C_{14-20} monohydric alcohols and C_{10-20} monocarboxylic acids are especially advantageous, sulfurized sperm oil being an example of a preferred material of this class. The cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl orthophosphate is an example of an advantageous cycloaliphatic amine phosphate. The cocoamine salt of N-cocoalkylamidophthalic acid is an example of an especially effective aliphatic monoamine salt, the use of which is included by this invention. The sulfurized monoester, the cycloaliphatic amine salt and the aliphatic monoamine salt can be employed in varying proportions with respect to one another. It is generally preferred to employ the sulfurized monoester in the lowest proportion and the cycloaliphatic monoamine salt and the aliphatic monoamine salt in proportions of about 2:1 and about 4:1, respectively,

with regard to the sulfurized monoester, but other proportions can be used provided each component is present in at least the respective minimum percentage indicated above. In general, it is preferred to employ the cycloaliphatic monoamine salt and the aliphatic monoamine salt in proportions varying from 8:1 to 1:8 with respect to the sulfurized monoester.

It has not been determined precisely by what mechanism the combination addition agents of this invention function to improve the film strength and load carrying properties of lubricants. Accordingly, the present invention is not limited to any particular theory of operation. However, available evidence points to the fact that the individual components of the combination addition agents of this invention act in conjunction with one another in a highly unexpected manner to enhance the load carrying properties of lubricants in which they are employed.

The sulfurized monoesters useful in the present invention are well known materials and are characterized by a sulfur content of 6.0 to 16.0 percent. Examples of such materials are the fully sulfurized monoester addition products of sulfur and unsaturated esters of normal decanoic, dodecanoic, dodecenoic, tetradecanoic, tetradecenoic, eicosanoic, and eicosenoic acids and normal tetradecyl, tetradecenyl, hexadecyl, hexadecenyl, eicosyl and eicosenyl alcohols. Individual sulfurized monoesters of the class disclosed herein can be prepared conveniently by the method described in U.S. Patent No. 2,179,065. Mixed sulfurized monoesters useful for the purposes of this invention, such as sulfurized sperm oil, can advantageously be prepared as described in U.S. Patent No. 2,179,064. Commercial sperm oils are defined in U.S. Patent No. 2,179,060 as the product obtained after refining crude sperm oil by refrigeration and pressing to remove spermaceti and like solid waxes of the ester type. Crude sperm oil is obtained from the head cavities and the blubber of the cachelot or sperm whale (*Physeter macrocephalus*). It is composed principally of unsaturated monoesters of fatty acids and monohydric alcohols of relatively high molecular weight. Analysis of sperm whale head oil has indicated the presence of a mixture of saturated fatty acids and monoethenoic fatty acids containing an even number of carbon atoms from 10 to 20, with the unsaturated acids predominating in the proportion of 56.5 percent to 43.5 percent. Sperm whale head oil has also been found to contain a mixture of saturated and monoethylenic fatty alcohols containing an even number of carbon atoms from 14 to 20, with the saturated alcohols predominating in the ratio of 58 percent to 42 percent. Sperm oils sulfurized in accordance with the procedure described in U.S. Patent No. 2,179,064 and that are useful for the purposes of this invention will have a sulfur content in the range of 8 to 14 percent.

The N-alkylamidophthalate amine salts that find use in the combination addition agents of this invention are conveniently prepared by reacting phthalic anhydride with an aliphatic monoamine containing 8 to 18 carbon atoms per molecule in a mol proportion of two mols of amine per mol of phthalic anhydride, at a temperature of not greater than 200° F. and preferably below about 180° F. Examples of N-alkylamidophthalates whose use is included by the present invention are the N-oxo-octyl-, N-n-octyl-, N-lauryl- and N-n-octadecylamidophthalates of the n-octyl, oxo-octyl, lauryl and n-octadecylamines.

The cycloaliphatic monoamine salts, the use of which is included by the present invention, are conveniently prepared in accordance with the procedure disclosed in U.S. Patent No. 2,371,852. Examples of cycloaliphatic monoamine salts within the scope of the present invention are the salts of cycloheptyl, cyclohexyl and cyclopentyl amines

and isoamyl, isooctyl; diisooctyl; di-oxo-octyl; and iso-octyl, lauryl acid orthophosphates.

The combination addition agents of this invention are employed in conjunction with hydrocarbon mineral oil base lubricants in amounts sufficient to improve the film strength and/or load carrying properties of said lubricant. The optimum proportion of the combination addition agent can vary somewhat according to the use to which the finished lubricant will be put. Normally, film strength of a hydrocarbon lubricating oil will be appreciably improved by the use of as little as 0.02 percent by weight of the composition of the combination addition agents of this invention. The use of at least 0.05 percent by weight of the composition will usually result in a major improvement in the load carrying properties of the oil. Normally, little additional benefit insofar as film strength and load carrying capacity are concerned will be obtained by the use of the additive in proportions greater than about 1 percent by weight of the composition. However, oil compositions containing the combination additives of this invention in proportions greater than 1 percent find use as intermediate, addition agent concentrates. The use of such concentrates facilitates blending of the combination addition agents in the finished oil. When such addition agent concentrates are used, we normally prefer to employ the combination addition agents in the form of an approximately 22 percent solution in oil, but other proportions can be used. For example, we have successfully prepared lubricating oil solutions to be used as addition agent concentrates containing about 14 to 26 percent by weight of the combination addition agents of this invention. However, oil solutions containing other proportions of the combination addition agents, for example, 5 percent, 10 percent and 40 percent solutions, are also included by the present invention.

The combination addition agents of this invention can be incorporated in hydrocarbon lubricating oil stocks in any suitable manner. For example, the individual components of the combination agents may be added as such or in the form of mineral oil solutions, either separately in any order, or in previously combined form. After addition of the combination addition agents to the base oil, some circulation of the compounded oil is desirable to facilitate formation of a homogeneous composition, especially when the components of the combination addition agents of this invention are added to the oil in undiluted form. However, this is not absolutely necessary.

In order to demonstrate the improved film strength and load carrying capacity and the wear reducing properties imparted to lubricating oils by the combination addition agents of this invention, we have caused an oil containing a combination addition agent of the present invention to be subjected to an accelerated test designed to measure the wear reducing, film strength and load carrying capacity of an oil. The test employed is commonly referred to as the Four-Ball Film Breakdown Test. The procedure of this test is essentially as follows: Three steel balls are securely fastened so that rotation is impossible. A fourth steel ball in a rotating spindle is placed so that it is entirely supported by the other three balls, thus forming a pyramid. The three immobile steel balls and the rotating single steel ball are forced into contact with each other in response to a vertically applied load. Sufficient test lubricant is poured into a test cup to cover the three lower balls to a predetermined depth. The spindle is revolved at 1800 r.p.m. while electrical heating units heat the oil to a temperature of 266° F. At the conclusion of the test wear is measured by examination of the scars on the clean surfaces of the three stationary balls, the two maximum right angle diameters of each wear scar being measured to the closest 0.01 mm. and averaged. Film breakdown is usually evidenced by seizure, galling or welding. The load carrying capacity of a lubricant is determined by increasing the lever load until film breakdown or until the maximum test load (51 kilograms) is reached. The anti-wear properties of the test oil are rated by the difference in the scar diameters produced with an inhibited oil and with the test oil. The actual pressure exerted on each point of contact is calculated as a function of the lever load and the scar diameter.

The combination addition agent employed in the test was utilized in the form of a 22 percent solution in a light lubricating oil. This solution consisted of 37.8 weight percent of a 33 percent solution in oil of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl o-phosphate, 5.2 weight percent of a 67 percent solution in oil of a clay-refined, sulfurized sperm oil that as such contained about 11.6 percent sulfur, and that was prepared substantially in accordance with the precedure of Example I of U.S. Patent No. 2,179,064, and 16.2 weight percent of a 33 percent solution in oil of the cocoamine salt of N-cocoalkylamidophthalic acid prepared by reacting cocoamine and phthalic anhydride in a mol proportion of 2:1 at 180° F. for about 30 minutes, the balance of the solution being a light lubricating oil. The combination addition agent of the test is referred to hereinafter as Addition Agent A. The compounded oil of the test was obtained by admixture of the above-described 22 percent oil solution, in an amount sufficient to provide the desired proportion of active material in the finished oil, with a paraffinic turbine oil base stock prepared by solvent refining a Coastal lubricating distillate.

The results of the test are presented in Table A below. In order to demonstrate the conjoint action among the individual components of the combination addition agents of this invention, there have also been included in Table A the results obtained with an uninhibited base oil and with oil compositions containing each of the components of the combination addition agent tested, and a combination of the two components that individually tended somewhat to improve the load carrying and wear reducing properties of the oil. Although the combination addition agent and the respective components employed in the test were utilized in the form of an oil solution, the proportions given in Table A are based on the weight of active material as such.

TABLE A

Experimental turbine oils

Oil Composition	1	2	3	4	5	6
Make-up, Percent by Wt. Turbine Oil Stock	100.0	99.85	99.85	99.85	99.85	99.85
Cyclohexylamine Salt of 3-Methylbutyl,2-ethylhexyl o-Phosphate		0.15				
Sulfurized Sperm Oil			0.15			
Cocoamine Salt of N-cocoalkyamidophthalic Acid				0.15		
Mixture of Cyclohexylamine Salt of 3-Methylbutyl,2-ethylhexyl o-Phosphate and Sulfurized Sperm Oil, Approx. 3.7:1 by Wt.					0.15	
Addition Agent A						0.15
4-Ball Film Breakdown Test, 1,800 r.p.m., 266° F., 1 Hr.:						
Lever Load at Breakdown, kg	31	51	51	28	51	51
Average Scar Diameter, mm	0.64	0.95	0.88	0.65	0.84	0.57
Mean Specific Pressure, psi	56,400	44,300	47,600	49,500	45,200	166,200

From the foregoing results it will be seen that the cycloaliphatic monoamine phosphate as such and the sulfurized monoester as such improved somewhat the film strength and anti-wear properties of the oil while the aliphatic amine salt reduced these properties slightly. The results presented in the table also show that a mixture of the cycloaliphatic monoamine phosphate and the sulfurized monoester produce essentially no greater improvement than corresponding proportions of the individual materials as such. On the other hand, a mixture of the cycloaliphatic monoamine phosphate, the sulfurized monoester and the N-alkylamidophthalate amine salt produced a compounded oil that withstood substantially greater pressures than the other oils without rupture of the oil film and that greatly reduced wear.

Although the combination addition agent employed in the test is exceptionally effective and therefore preferred for use in the lubricating oil compositions of this invention, it will be understood that other combination addition agents of the class disclosed herein can be used to prepare lubricating oil compositions having similarly improved characteristics. Examples of such other suitable combination addition agents and lubricating oils containing such agents are preferred in Table B below.

TABLE B

Oil Composition: Make-up; Active Material, percent by Wt.—					
Sulfurized Monoester:					
Sulfurized Sperm Oil (Approx. 11.6% S)	0.05				
Sulfurized Oleyl Oleate (Approx. 10.7% S)		0.21			
Sulfurized Oleyl Hexadecenoate (Approx. 11.2% S)			3.4		
Sulfurized Hexadecyl Tetradecenoate (Approx. 6.6% S)				0.025	
Sulfurized Eicosenyl Laurate (Approx. 6.25% S)					0.025
Cycloaliphatic Amine Dialkyl o-Phosphate:					
Cycloheptyl Amine Salt of 3-Methylbutyl,2-ethylhexyl o-phosphate		0.6			
Cyclopentyl Amine Salt of Di-(2-ethylhexyl) o-phosphate			12.5		
Cyclohexyl Amine Salt of Di-(Oxo-octyl) o-phosphate	0.0075			0.09	0.09
Aliphatic Amine N-alkylamidophthalate:					
Cocoamine Salt of N-cocoalkylamidophthalate	0.0125				0.04
Lauryl Amine Salt of N-laurylamidophthalate		0.26			
t-Octyl Amine Salt of t-C_{12-15}-alkylamidophthalate			5.4		
n-Octadecyl Amine Salt of N-n-octylamidophthalate				0.04	
Lubricating Oil Stock, Solvent-refined Distillate from Coastal Crude, 450 S.U.S./100° F	99.93	98.93	79.7	99.845	99.845

"Cocoamine" is a mixture of fatty amines consisting chiefly of lauryl amine and containing lesser proportions of octyl, decyl, tetradecyl, hexadecyl, octadecyl and octadecenyl amines. Cocoamine has an average molecular weight of about 200 and a mol combining weight of 206. Cocoamine is derived from coconut oil fatty acids by conversion of the acids to nitriles, followed by catalytic hydrogenation of the nitriles to amines. The expression "cocoalkyl" as used herein refers to the mixed fatty alkyl groups present in cocoamine.

The expression "Oxo-octyl" as used herein is intended to refer to the mixed C_8 highly branched chain alkyl groups, mostly dimethyl hexyl, derived from Oxo-octyl alcohol that has been prepared by hydrogenation of the aldehydic material obtained by hydroformylation of mixed C_7 olefins that are obtained in turn by catalytic condensation of C_3 and C_4 olefins in the usual proportion in which they occur in refinery process gases under the conventional conditions of the so called "Oxo" process.

While we have shown in the examples the preparation of compounded lubricating oils our invention is not limited thereto but includes other hydrocarbon oil lubricant compositions containing the new combination addition agents, such as greases and the like. Also, the compounded lubricants of this invention may include one or more other addition agents designed to improve one or more properties of the lubricants, such as antioxidants, anti-foaming agents, anti-rust agents, bearing corrosion inhibitors, detergents, pour point and viscosity index improvement agents and the like. Many other modifications or variations of the invention as hereinbefore set forth also may be made without departing from the spirit and scope thereof. Accordingly, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricant composition comprising a major amount of a hydrocarbon lubricating oil and containing a small amount, sufficient to improve the load carrying properties of the oil, of a combination of (*a*) a sulfurized monoester addition product of sulfur and an unsaturated ester of an aliphatic monohydric alcohol that contains 14 to 20 carbon atoms and not more than one ethylenic linkage per molecule and an aliphatic monocarboxylic acid that contains 10 to 20 carbon atoms and not more than one ethylenic linkage per molecule, (*b*) a salt of a cycloaliphatic monoamine that contains 5 to 12 carbon atoms per molecule and a dialkyl o-phosphoric acid that has one alkyl substituent containing 8 to 12 carbon atoms and another containing 5 to 8 carbon atoms, and (*c*) a salt of an aliphatic monoamine that contains 8 to 18 carbon atoms per molecule and an N-alkylamidophthalic acid whose alkyl substituent contains 8 to 18 carbon atoms, said small amount comprising at least about 0.003 percent by weight of the composition of said sulfurized monoester, at least about 0.0125 percent by weight of the composition of said salt of said cycloaliphatic monoamine, and at least about 0.005 percent by weight of the composition of said salt of said aliphatic monoamine.

2. The composition of claim 1 where said combination is present in a proportion of about 0.02 to 1.0 percent by weight of the composition.

3. The composition of claim 1 where said salt of said cycloaliphatic amine and said salt of said aliphatic amine are present respectively in a ratio in the range of 8:1 to 1:8 with respect to said sulfurized monoester.

4. A lubricant composition comprising a major amount of a hydrocarbon lubricating oil and containing a small amount, sufficient to improve the load carrying properties of the oil, of a combination of (*a*) sulfurized sperm oil, (*b*) the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl o-phosphate, and (*c*) the cocoamine salt of the N-cocoalkylamidophthalic acid, said small amount comprising at least about 0.003 percent by weight of the composition of said sulfurized sperm oil, at least about 0.0125 percent by weight of the composition of said salt of cyclohexylamine, and at least about 0.005 percent by weight of said salt of said cocoamine.

5. A combination addition agent for hydrocarbon oil lubricant compositions comprising (*a*) a sulfurized monoester addition product of sulfur and an unsaturated ester of an aliphatic monohydric alcohol that contains 14 to 20 carbon atoms and not more than one ethylenic linkage per molecule and an aliphatic monocarboxylic acid that contains 10 to 20 carbon atoms and not more than one ethylenic linkage per molecule, (*b*) a salt of a cycloaliphatic monoamine that contains 5 to 12 carbon atoms per molecule and a dialkyl o-phosphate having one alkyl group that contains 8 to 12 carbon atoms and another that

contains 5 to 8 carbon atoms, and (*c*) a salt of an aliphatic monoamine that contains 8 to 18 carbon atoms per molecule and an N-alkylamidophthalic acid whose N-alkyl substituent contains 8 to 18 carbon atoms, said salt of said cycloaliphatic monoamine and said salt of said aliphatic monoamine being present respectively in the ratio in the range 8:1 to 1:8 with respect to said sulfurized monoester.

6. A combination addition agent for hydrocarbon oil lubricant compositions comprising a major amount of a hydrocarbon lubricating oil and containing about 10 to 40 percent by weight of the composition of a combination of (*a*) a sulfurized monoester addition product of sulfur and an unsaturated ester of an aliphatic monohydric alcohol that contains 14 to 20 carbon atoms and not more than one ethylenic linkage per molecule and an aliphatic monocarboxylic acid that contains 10 to 20 carbon atoms and not more than one ethylenic linkage per molecule, (*b*) a salt of a cycloaliphatic monoamine that contains 5 to 12 carbon atoms per molecule and a dialkyl o-phosphate having one alkyl group that contains 8 to 12 carbon atoms and another that contains 5 to 8 carbon atoms, and (*c*) a salt of an aliphatic monoamine that contains 8 to 18 carbon atoms per molecule and an N-alkylamidophthalic acid whose N-alkyl substituent contains 8 to 18 carbon atoms, said salt of said cycloaliphatic monoamine and said salt of said aliphatic monoamine being present respectively in the ratio in the range 8:1 to 1:8 with respect to said sulfurized monoester.

7. A combination addition agent for hydrocarbon oil lubricant compositions comprising a major amount of a hydrocarbon lubricating oil and containing 10 to 40 weight percent of a combination of (*a*) sulfurized sperm oil, (*b*) the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl o-phosphate, and (*c*) the cocoamine salt of N-cocoalkylamidophthalic acid, said cyclohexylamine salt and said cocoamine salt being present respectively in a weight ratio in the range 8:1 to 1:8 with respect to said sulfurized sperm oil.

8. A combination addition agent for hydrocarbon oil lubricant compositions comprising (*a*) sulfurized sperm oil, (*b*) the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl o-phosphate, and (*c*) the cocoamine salt of N-cocoalkylamidophthalic acid, said cyclohexylamine salt and said cocoamine salt being present respectively in a weight ratio in the range 8:1 to 1:8 with respect to said sulfurized sperm oil.

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