United States Patent Office 3,269,950 Patented August 30, 1966

3,269,950

LUBRICATING COMPOSITION CONTAINING AMIDE, IMIDE AND THIOCYANATE COMPLEXES OF ZINC AND TIN

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No Drawing. Filed May 20, 1964, Ser. No. 369,011
7 Claims. (Cl. 252—46.4)

The present invention relates to a lubricating composition and, in particular, to mineral oil and synthetic ester base lubricating oils containing a complex or adduct of an inorganic compound and an amide or imide to improve the load carrying properties of the lubricating composition.

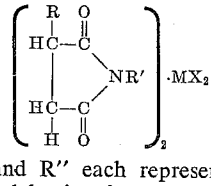
New designs and improvements in machinery are continually raising the operating performance standards of lubricating compositions. In many instances, the pressures and temperatures to which the bearing surfaces of machinery operate under are higher than those which natural or synthetic lubricating oils can withstand. Instances where difficult lubricating conditions are encountered occur in the lubrication of heavily loaded pinion and spur gears, gear trains, bearings, extrusion applications and the like. As a result, there is an increasing need for lubricating compositions having improved properties for these services.

A class of lubricating compositions has been discovered which possesses greatly improved properties for a variety of lubricating applications. These compositions are particularly notable for their improvement in load carrying properties but many of them also possess additional valuable features, such as corrosion resistance, oxidation resistance and stability. These compositions provide the answer to some heretofore difficult lubricating problems.

The present lubricating composition comprises a major proportion of a lubricating oil base, such as a mineral lubricating oil or a synthetic lubricating oil, and a minor amount of an oil-soluble adduct formed between a hydrocarbylamide or hydrocarbylimide and an inorganic halide or inorganic thiocyanate. More particularly, the adduct of this invention is represented by a formula from the group consisting of

(1) $(R-C(=O)-NR'R'')_2 \cdot MX_2$

(2)



wherein, R, R' and R'' each represent hydrogen or a hydrocarbyl radical having from 1 to 30 carbon atoms, the sum of the carbon atoms in R, R' and R'' being at least 12, M is a divalent cation selection from the class consisting of zinc and tin, and X is an anion selected from the group consisting of chloride and thiocyanate anions.

The adducts of the invention are prepared by mixing two moles of an amide or imide defined above with a mole of the inorganic compound from the class set forth. Simple mixing of the reactants will generally produce the reaction. Optionally, the reaction can be effected in the presence of a solvent. Solvents which can dissolve the inorganic compound are suitable. Particularly effective solvents include acetone, methanol and tetrahydrofuran. This reaction is usually exothermic and it is desirable to cool the reaction mixture. Caution should be exercised to keep the reaction temperature below the decomposition temperature of both of the components of

the reaction product which generally means conducting the reaction at a temperature below about 200° C. The reaction generally goes to completion in a short reaction time.

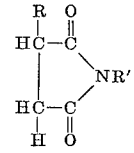
Amides which can be employed for preparing the adduct of the invention are represented by the formula

$$R-C(=O)-NR'R''$$

in which R, R' and R'' each represent hydrogen or a hydrocarbyl radical having from 1 to 30 carbon atoms, the sum of the carbon atoms in R, R' and R'' being at least 12. R, R' and R'' will generally be saturated aliphatic hydrocarbyl radicals. R and R' are preferably radicals having from 8 to 18 carbon atoms. These amides can be prepared by reacting a C_1 to C_{30} carboxy acid with ammonia or an amine, followed by heating with an azeotroping solvent, such as toluene, to remove water of reaction.

Examples of suitable amides for preparing the adducts include oleamide, stearamide, 2-ethylhexyl oleamide, isobutyl oleamide, 2-ethylhexyl stearamide, n-hexyl lauramide, N-2-ethylhexyl C_{18} "Liquid Fatty Acid" amide, dodecenyl oleamide, lauryl stearamide and the like. The N-2-ethylhexyl "Liquid Fatty Acid" amide is the amide of the commercially available C_{18} liquid saturated fatty acid believed to consist essentially of omega-2-n-propyl cyclohexyl) pelargonic acid and sold under the name Emery 3101R.

Imides which can be employed for preparing the adducts are represented by the formula:



in which R and R' each represent hydrogen or a hydrocarbyl radical having from 1 to 30 carbon atoms, the sum of the carbon atoms in R and R' being at least 12. R is preferably an unsaturated aliphatic hydrocarbyl radical. R' is preferably a hydrocarbyl radical having from 8 to 18 carbon atoms. Imides can be prepared by reacting a C_4 dibasic acid or C_4 dibasic anhydride, both having optionally an alkyl substituted side chain, with ammonia or an amine, followed by heating with an azeotroping solvent to remove water of reaction.

Examples of effective imides for preparing the adducts includes N-n-butyl dodecenyl succinimide, N-2-ethylhexyl dodecenyl succinimide, N-2-ethylhexyl lauryl succinimide, N-propyl lauryl succinimide and N-propyl decenyl succinimide.

The inorganic compound or component of the adduct of the invention is represented by the formula:

$$MX_2$$

wherein M is a divalent metal selected from the group consisting of zinc and tin, and X is an anion selected from the group consisting of chloride, and thiocyanate anions. Inorganic compounds effective for complexing with the amides and imides include zinc thiocyanate, zinc chloride and tin chloride.

The nature of the inorganic compounds employed for adduct formation is apparently critical since many do not lead to adduct formation. The following inorganic compounds have been found ineffective for adduct formation with the amides or imides of the invention, namely zinc phosphite, zinc acetate, cadmium chloride, copper chloride, zinc silicofluoride and aluminum fluoride.

Examples of particularly effective adducts of this inven-

tion and the mole ratio of the components from which they were formed are given below:

N-2-ethylhexyl C_{18} "Liquid Fatty Acid" amide: zinc chloride (2:1)
N-2-ethylhexyl C_{18} "Liquid Fatty Acid" amide: stannous chloride (2:1)
N-2-ethylhexyl oleamide: zinc chloride (2:1)
Dodecenyl succinimide: stannous chloride (2:1)
N-n-butyl dodecenyl succinimide: zinc chloride (2:1)
N-n-butyl dodecenyl succinimide: stannous chloride (2:1)

The lubricating compositions of the invention are prepared by blending in a conventional way a minor amount of the oil-soluble, load-carrying adduct described hereinabove into a suitable lubricating oil base. Generally, the adduct is employed in an amount in the range of 0.05 to 10 percent by weight based on the weight of the lubricating composition with the preferred proportions being from 0.1 to 3 weight percent.

The base lubricating oil can be a mineral lubricating oil or a synthetic lubricating oil. The mineral lubricating oil can be a predominantly paraffinic or naphthenic or it can be a mixture of both types of mineral oils. Generally, the mineral oil will be a refined oil of predominantly paraffinic nature having a viscosity in the range from 30 to 150 Saybolt Universal seconds at 210° F.

Various types of synthetic lubricating oil bases can be employed in preparing the lubricants of the invention. Aliphatic esters, polyalkylene oxides, silicones, and esters of phosphoric and salicyclic acid can be employed. Examples of the aliphatic esters include di-(2-ethylhexyl) sebacate, the dialkyl azelates, dialkyl suberates, and the dialkyl adipates such as di-hexyl azelate, di-(2-ethylhexyl) azelate, di-2,5,5-trimethylhexyl glutarate, di-(2-ethylhexyl) adipate, tri-amyl tricarballylate, etc. The polyalkylene oxides include polypropylene oxide, polyisopropylene oxide diether, polyisopropylene oxide diesters, etc. The silicones include methyl silicone, methylphenyl silicone, and the silicates includes tetraisooctyl silicate.

Other effective synthetic lubricating oils include the neopentyl glycol esters such as the neopentyl glycol propionates, neopentyl glycol butyrates and neopentyl glycol caprylates and the trimethylol alkanes such as trimethylol ethane, trimethylol propane, trimethylol pentane, trimethylol heptane and trimethylol dodecane and the like. Examples of the phosphate esters include tricresyl phosphate, trioctyl phosphate and tridecyl phosphate as well as mixed aryl and alkyl phosphates.

The anti-scuffing and load carrying ability of a number of the lubricating compositions was determined in the Ryder Gear Test (Federal Test Method 6508). In this test, the lubricant is employed to lubricate two spur gears in a Pratt and Whitney Gear and Lubricating Tester (also called the Ryder Gear Tester). This tester was operated with a gear speed of 10,000 r.p.m. and with an oil inlet temperature of 165° F. A loading pressure of 5.0 p.s.i. was applied during break-in. After ten minutes, the tester was shut down and the gear examined for the percentage of tooth area scuff on each tooth. The procedure was then repeated using high load pressures with increments of 5 p.s.i. until 22.5 percent of the total tooth face area on the driving gear had been scuffed, the load applied in this run being considered the scuff load. The tooth load in pounds per inch of tooth width was then calculated.

The load carrying properties of some of the lubricating compositions was also determined by the Mean Hertz Load Test. This test is run in a machine having four ½ inch diameter bearing balls which are driven under load while the balls are lubricated by the composition under test. This test is described in U.S. 2,600,058.

The lubricating compositions employed were prepared from two different base oils. Base Oil A was a mineral lubricating oil having an SUS viscosity at 210° F. of about 100. Base Oil B was a synthetic lubricating oil consisting essentially of di-2-ethylhexyl sebacate sold under the

name Plexol 201J and having an SUS viscosity at 210° F. of about 37. All the lubricating compositions contained 1 percent by weight of the indicated adduct. In every case, the adduct consisted of two moles of the amide or imide per mole of the metal compound. The results of these tests are given in Table I below.

TABLE I.—ANTI-SCUFF, ANTI-WEAR PROPERTIES IN RYDER GEAR AND MEAN HERTZ LOAD TESTS

Nature of Adduct	Base Oil	Ryder Gear Test, p.p.i.
	Oil B	2,300
2-ethylhexyl oleamide/$Zn(SCN)_2$	do	4,270
	Oil A	2,600
N-2-ethylhexyl C_{18} "Liquid Fatty Acid" Amide/$SnCl_2$.	do	3,620
		Mean Hertz Load, kg.
	Oil B	16
2-ethylhexyl oleamide/$Zn(SCN)_2$	do	32
	Oil A	27
N-2-ethylhexyl C_{18} "Liquid Fatty Acid" Amide/$SnCl_2$.	do	42

The Navy Four Ball Test is another test for determining the anti-wear properties of a lubricant. The test machine comprises a system of 4 steel balls, 3 of which are in contact with each other in one plane in a fixed, triangular position in a reservoir containing the oil sample and a fourth ball above and in contact with the other three. In carrying out the test, the upper ball is rotated while it is pressed against the lower three at any desired pressure by means of a suitable weight applied to a lever arm, and the diameters of the scars on the three lower balls are measured by the means of a low power microscope. The average diameter, measured in two directions on each of the three lower balls, is taken as a measure of the anti-wear characteristics of the lubricant. Base oil B defined above was also employed in these tests. The results of these tests are given in Table II below.

TABLE II

Oil Composition (weight)	Base Oil	Navy Four Ball Wear, micron/min.
	Oil B	10.2
2-ethylhexyl oleamide/$Zn(SCN)_2$	do	1.9
N-n-butyl dodecenyl succinimide/$ZnCl_2$	do	5.5

The lubricating compositions containing the above-described adducts have substantially improved anti-wear properties. They also have good corrosion resistance, oxidation resistance and storage stability making the lubricants of the invention suitable for a broad range of lubricating applications.

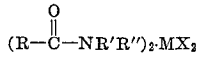
It is understood that the lubricating compositions of the invention can contain numerous additives conventionally used to improve the properties of lubricating oils. Commonly employed additives are the methacrylates as V. I. improvers and pour point depressors, the the alkylphenols as oxidation inhibitors, alkaline earth metal salts of petroleum sulfonates or alkaryl sulfonates as detergents, metal dialkyl dithiophosphate corrosion inhibitors and silicone anti-foam fluids.

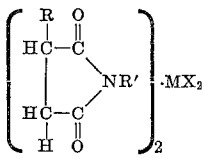
Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating composition comprising a major proportion of a lubricating oil and 0.05 to 10 percent by

weight of an oil-soluble adduct represented by a formula selected from the group consisting of

(1) 

(2) 

in which R, R′ and R″ each represent a member selected from the class consisting of hydrogen and a hydrocarbyl radical having from 1 to 30 carbon atoms, the sum of the carbon atoms in R, R′ and R″ being at least 12, M is a divalent cation selection from the class consisting of zinc and tin and X is an anion selected from the group consisting of chloride and thiocyanate ions.

2. A lubricating composition according to claim **1** in which said adduct consists of 2-ethylhexyl oleamide and zinc chloride in the mole ratio of 2:1 respectively.

3. A lubricating composition according to claim **1** in which said adduct consists of dodecenyl succinimide and stannous chloride in the mole ratio of 2:1 respectively.

4. A lubricating composition according to claim **1** in which said adduct consists of N-n-butyl dodecenyl succinimide and zinc chloride in the mole ratio of 2:1 respectively.

5. A lubricating composition according to claim **1** in which said adduct consists of 2-ethylhexyl oleamide and zinc thiocyanate in the mole ratio of 2:1 respectively.

6. A lubricating composition according to claim **1**, in which said adduct consists of N-2-ethylhexyl-omega-2-n-propylcyclohexylpelargonic acid amide and zinc chloride in the mol ratio of 2:1 respectively.

7. A lubricating composition according to claim **1**, in which said adduct consists of N-2-ethylhexyl-omega-2-n-propylcyclohexylpelargonic acid amide and stannous chloride in the ratio of 2:1 respectively.

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