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AMIDE LUBRICANTS

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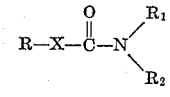
13 Claims. (Cl. 252—47.5)

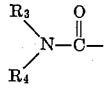
This invention relates to novel synthetic lubricants. In particular, the invention relates to the use of certain N,N-disubstituted amides as lubricant base stocks.

The development of synthetic lubricants has been largely responsive to the very specific and stringent lubrication requirements of modern technology: suitable physical properties over a wide temperature range, high thermal and oxidative stability, and even resistance to nuclear radiation. A particular advantage of synthetic lubricants is the relative ease with which their physical, chemical, or performance properties can be regulated by a proper choice of starting materials. These considerations have given rise to a great number of novel products, some of which have found wide acceptance in industrial and military applications. Synthetic esters for aircraft gas-turbine engines are among the outstanding achievements in this field. As different and more demanding requirements are imposed on lubricants, newer, more stable compositions will be developed. The present invention is an outgrowth of the search for such lubricants.

It has now been discovered that certain N,N-disubstituted amides are effective lubricant base stocks. These compounds are either mono- or diamides having the general formula



where X is a C_3 to C_{12}, preferably C_6 to C_{10}, hydrocarbylene group, preferably alkylene, arylene, alkarylene, or aralkylene; R_1 and R_2 are C_3 to C_{12}, preferably C_3 to C_8, alkyl or aryl groups, preferably alkyl, and R is selected from the group consisting of hydrogen and



where R_3 and R_4 are C_3 to C_{12}, preferably C_3 to C_8, alkyl or aryl groups, preferably alkyl. Representative amides of the invention are N-butyl-N-phenyl-n-octanamide; N,N-di-n-octyl benzamide; N,N-di-n-butyllauramide; bis-(N,N - di - n - hexyl)adipamide; N,N-dicyclohexylbenzamide; N - cyclohexyl - N - propylbenzamide; N,N-di-n-propyl - p - tertbutylbenzamide; bis(N,N - di - n - propyl) phthalamide; bis(N,N-di-n-propyl)isophthalamide; and N-n-hexyl-N-n-propylisophthalamide. The present invention contemplates the use of these compounds and mixtures thereof as base lubricants; i.e., a major proportion (at least half) of the lubricant comprises the above-defined N,N-disubstituted amides. It is preferred that amides of the invention comprise at least 75%, preferably at least 90% by weight of the final lubricant composition. These N,N-disubstituted amides are superior to unsubstituted amides and N-monosubstituted amides in that they are generally lower melting compounds having substantially less tendency to crystallize under conditions of low-temperature operation or shutdown. Furthermore, although the disubstituted amides are lower melting than amides having a lesser degree of substitution, they do not have correspondingly high vapor pressures.

The present invention is based on the discovery that certain N,N-disubstituted amides, when used as lubricants e.g. for gas turbine engines, are particularly effective regarding stability and ability to maintain engine cleanliness even at temperatures over 300° F. In accordance with this discovery, the invention contemplates a method of lubricating an engine, especially a gas turbine engine, which comprises maintaining on a surface to be lubricated such as bearings and other points of wear of the engine a film of lubricant comprising a major portion of N,N-disubstituted amide as defined above.

It has also been found that the amides of the invention are remarkably responsive to common oxidation inhibitors. Addition of small amounts of well-known inhibitors has a considerably greater inhibiting effect on the amides of the invention than on comparable ester lubricants; e.g. pentaerythrityl esters. Oxidation inhibitors which may be employed in the lubricants of the invention are, for example, aryl amines, thiodiarylamines, phenolic compounds, and mixtures thereof. Organic nitrogen-containing antioxidants, especially amines, are preferred. Examples of suitable antioxidants are phenyl-alpha-naphthylamine, dinaphthylamine, phenyl-beta-naphthylamine, diphenylamine, triphenylamine, 2,2'-dipyridylamine, 4,4-dipyridylamine, 2-aminopyridine, 4-aminopyridine, 2,6-diaminopyridine, phenyl-2-pyridylamine, 3-aminoquinoline, phenyl-3-quinolylamine, phenothiazine, 3,7-dioctylphenothiazine, phenylthio-alpha-naphthylamine, phenylthio-beta-naphthylamine, beta,beta-thiodinaphthylamine, alkylated bisphenols, etc. These antioxidants are generally present in an amount of from about 0.1 to 10%, preferably 0.2 to 5%, by weight of the final lubricating composition.

Amides of the invention were examined and compared to well-known ester lubricants in high-temperature air-oxidation tests.. Air was bubbled at a rate of 70 mls./minute through a 20 gm. sample of oil maintained at 450° F. The induction period of the sample was defined as the test time required before two consecutive readings, one hour apart, showed that 5% v. or more of the oxygen passing through the oil was being absorbed. To provide a standard reference, all oils contained 1% w. phenyl-alpha-naphthylamine and 0.2% w. of a salt of monochloromethylphosphonic acid and mixed C_{18} to C_{22} primary amines. In addition, each sample contained 20 p.p.m. each of Cu and Fe, added as octoates, to simulate operating conditions. The test results are described in Table I below.

TABLE I.—RESULTS OF AIR OXIDATION TESTS

Base stock:	Induction period, hrs.
Pentaerythrityl ester [1]	5
N,N-di-n-butyllauramide	>25
N,N-di-n-propylbenzamide	>45
N,N-di-n-propyl-p-tertbutylbenzamide	>43
Bis(N,N-di-n-propyl)phthalamide	>45
Bis(N,N-di-n-propyl)isophthalamide	>45

[1] A mixture of 67% v. C_5–C_9 acid esters of pentaerythritol and 33% w. C_5–C_{10} acid esters of dipentaerythritol.

As is apparent from the table, the induction periods of amide formulations are far longer than that of an identically-inhibited ester lubricant. Essentially no deposits or sludging were observed in any of the amides that were observed, except for N,N-di-n-butyllauramide which showed a slight amount of sludging. Benzamides and phthalamides, which are preferred lubricants of the invention, formed dark oils but did not contain insolubles even after over 40 hours of testing at 450° F.

To illustrate the lubrication properties of the amides of the invention, four-ball wear tests were conducted at various temperatures and bad conditions using a representative amide, bis(N,N-di-n-propyl)phthalamide. The four-ball wear test is a well-known method of determining lubrication properties; this test is described in detail by Larsen and Perry in Trans. Am. Soc. Mech.

ing., 67, 45–50 (1945). For comparison, similar tests were conducted on a commercially available synthetic ester base oil which is known to have good lubrication haracteristics. This ester (designated "ester base" in he table) is a mixture of 67% pentaerythrity tetraester of C_4–C_9 alkanoic acids, and 33% dipentaerythrityl hexaster of C_5–C_{10} alkanoic acids. The results are shown n Table II below.

TABLE II.—FOUR-BALL WEAR TEST RESULTS

	Speed (r.p.m.)	Temp. (° F.)	Load (kg.)	Time (hr.)	Scar diameter (mm.)
Ester base	1,800	500	15	1	1.08
Bis(N,N-di-n-propyl)phthalamide	1,800	500	15	1	1.10
Ester base	600	500	50	1	1.25
Bis(N,N-di-n-propyl)phthalamide	600	500	50	1	0.81
Ester base	600	175	15	2	0.83
Bis(N,N-di-n-propyl)phthalamide	600	175	15	2	0.44

From these results it appears that the amides have very good lubricating properties, even being superior to well-known synthetic ester oils (under some conditions).

Several well-known methods are available for making he amides of the invention. Two methods which are generally applicable are illustrated below.

Example I.—Preparation of N,N-di-n-propylbenzamide

To two moles of di-n-propylamine in an equal volume of benzene solvent was added, dropwise, with stirring, one mole of benzoyl chloride. An exothermic reaction ensued and continued throughout the addition of the acid chloride. The reaction mixture was refluxed for about one-half hour, cooled, and poured into water. The organic layer was washed with water to remove amine hydrochloride, with dilute sodium hydroxide to remove unreacted acid, and with water until washings were neutral. The solution was dried over sodium sulfate, stripped of solvent, and distilled under reduced pressure. Yield of product was about 75% w.

Example II.—Preparation of bis(N,N-di-n-propyl)-phthalamide

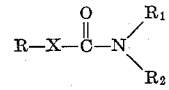
Two moles of di-n-propylamine and one mole of phthalic acid were heated to 175° C. Water produced in the reaction was collected in a trap. The product was purified as in Example I; yield was about 75% w.

The amide lubricants of the invention may be blended with one or more additives to further enhance their properties. Such additives include viscosity-index improvers, pour point depressants, extreme-pressure agents, antifoamants, and the like.

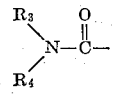
The lubricants of the invention have general applicability for the lubrication of moving metal parts, and are especially preferred for high-temperature lubrication, e.g., over 300° F.

We claim as our invention:

1. A lubricant composition comprising a major amount of an N,N-disubstituted amide having the formula

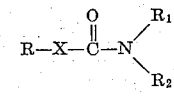


where X is selected from the group consisting of alkylene, arylene, alkarylene, and aralkylene having 3 to 12 carbons, R_1 and R_2 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons, and R is selected from the group consisting of hydrogen and

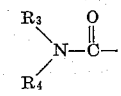


where R_3 and R_4 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons and a minor amount of an oxidation inhibitor.

2. A method of lubrication which comprises maintaining on surfaces to be lubricated a film of lubricant comprising a major amount of an N,N-disubstituted amide having the formula

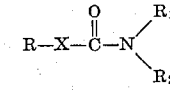


where X is selected from the group consisting of alkylene, arylene alkarylene, and aralkylene having 3 to 12 carbons, R_1 and R_2 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons, and R is selected from the group consisting of hydrogen and

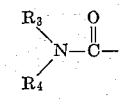


where R_3 and R_4 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons.

3. A method of lubricating a gas turbine engine which comprises maintaining on the bearings and other points of wear of the engine a film of an N,N-disubstituted amide having the formula

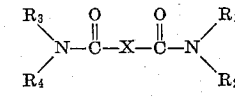


where X is selected from the group consisting of alkylene, arylene, alkarylene, and aralkylene having 3 to 12 carbons, R_1 and R_2 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons, and R is selected from the group consisting of hydrogen and



where R_3 and R_4 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons.

4. A method of lubrication which comprises maintaining on surfaces to be lubricated a film of lubricant comprising a major amount of an N,N-disubstituted amide having the formula

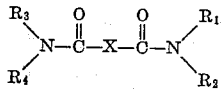


where X is selected from the group consisting of alkylene, arylene, alkarylene, and aralkylene having 3 to 12 carbons, and R_1, R_2, R_3 and R_4 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons.

5. The method of claim 4 wherein X is selected from the group consisting of ortho-, meta-, and para-phenylene.

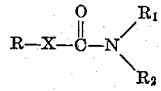
6. A method of lubricating a gas turbine engine which comprises maintaining on the bearings and other points of wear of the engine a film of lubricant comprising a

major amount of an N,N-disubstituted amide having the formula

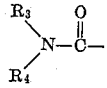


where X is selected from the group consisting of alkylene, arylene, alkarylene, and aralkylene having 3 to 12 carbons, and R_1, R_2, R_3 and R_4 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons.

7. A lubricant composition comprising a major amount of an N,N-disubstituted amide having the formula



where X is selected from the group consisting of alkylene, arylene, alkarylene, and aralkylene having 3 to 12 carbons, R_1 and R_2 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons, and R is selected from the group consisting of hydrogen and



where R_3 and R_4 are selected from the group consisting of alkyl and aryl having 3 to 12 carbons and 0.1% to 10% by weight of an organic nitrogen-containing antioxidant.

8. The lubricant of claim **7** wherein the antioxidant is an organic amine.

9. The lubricant of claim **7** wherein the antioxidant is phenothiazine.

10. The lubricant of claim **8** wherein the amine is an aromatic amine.

11. The lubricant of claim **10** wherein the amine is phenyl-α-naphthylamine.

12. The lubricant of claim **10** wherein the amine is diphenylamine.

13. A lubricant as defined in claim **1** wherein the oxidation inhibitor is a phenolic oxidation inhibitor.

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