Patented Dec. 25, 1951 2,580,274

UNITED STATES PATENT OFFICE

2,580,274

LUBRICANT

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No Drawing. Application March 8, 1947, Serial No. 733,424

13 Claims. (Cl. 252—33.4)

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This invention relates to lubricating compositions, which are especially suitable for use in heavy duty engines. More particularly, this invention pertains to lubricating compositions containing a combination of oil additives which produce improved heavy duty lubricants, particularly suitable for truck, bus, tractor engines, as well as all types of diesel engines, and the like.

Hydrocarbon oils such as mineral lubricating oils and the like, as well as synthetic oils are generally unsuited for heavy duty lubrication due to the extreme pressures, heavy loads and high temperatures developed in above engines under operating conditions. Oils, when subjected to such conditions, rapidly deteriorate and break down, forming sludges, varnish and lacquer coatings, corrosive acidic materials which attack and damage alloyed metals, and other contaminants which cause wear, scratching, scuffing and scoring of engine parts as well as ringsticking and seizure.

Other conditions which accentuate and accelerate deterioration of base lubriants and which account at least in part for their rapid oxidation is the presence of small amounts of moisture formed or present in the lubricant, or blowby vapors from fuels which enter the lubricating system and form harmful deterioration products and the like. Also the close tolerances to which engine parts are machined as well as the restricted clearances between various engine parts aggravate this situation and aid in breaking down the lubricant. This is due to the fact that varnish and/or lacquer coatings on various engine parts such as rings, valves, pistons and cylinder walls, caused by oil deterioration diminish side clearances, act as heat insulators, both conditions causing an increase in oil temperature resulting in further breakdown. Lacquer formations are attributed to oxidation of oils and are hard resinous materials having a tendency to adhere on metal surfaces and form thereon a hard deposit which blisters, chips thereby acting as an abrasive capable of scratching surfaces and blocking oil passages.

Ring and piston sticking, clogging and fouling of an engine is also caused by sludge resulting from oxidation of oils at high loads and elevated temperatures. Sludges are extremely harmful for in addition to causing wear and corrosion they coat and clog up the circulating system of engines thereby decreasing their efficiency.

Oil oxidation and decomposition products are highly corrosive especially to alloys such as copper-lead and cadmium-silver bearings and the like. Other factors can account for corrosion and they are complex in nature and varied in origin. For example, acids found or formed in oil or fuel may attack alloy bearings. Again, the effect at high temperatures on modern bearings of sulfur

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derived from certain of its compounds or even found free in the oil or fuel, may be very serious. Thus the presence of certain sulfur compounds may induce pitting of bearing surfaces, such as exhaust valve stem guides, etc. These conditions which are generally encountered in heavy duty lubrication of engines not only result in heavy damage but frequently in its complete failure.

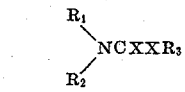
Heavy duty lubricants often must have so-called extreme pressure properties so as to withstand wear and protect bearing surfaces under stringent conditions. It has been found, however, that such additives generally increase engine deposits and are highly corrosive. The problem of compounding a lubricant for heavy duty purposes, having satisfactory anti-oxidant, detergent, anti-wear, anti-corrosion and extreme pressure properties has not been solved up to the present time to the best knowledge of applicants.

It is therefore an object of this invention to provide a heavy duty lubricating composition suitable for use in engines operating at extremely high temperatures and under heavy loads. It is another object of this invention to provide a non-corrosive lubricating composition suitable for heavy duty lubrication. These and other objects of this invention will be apparent from the following description and the appended claims.

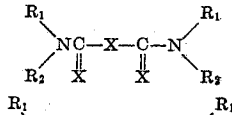
Broadly stated, this invention comprises a lubricant containing minor amounts of substantially oil-soluble derivatives of open-chain organic compounds containing nitrogen, oxygen, and/or sulfur and/or metal derivatives thereof and oil-soluble metal derivatives resulting from the condensation of phenolic and/or thiophenolic compounds with an aldehyde. If desired, lubricants thus compounded can be still further improved by addition thereto of minor amounts of oil-soluble salts of organic sulfonic acids and/or aryl amines.

The open-chain organic compounds which contain the elements referred to above can be represented by the general formulas:

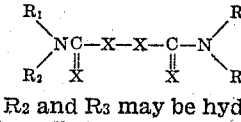
(I)



(II)



(III)



wherein R_1, R_2 and R_3 may be hydrogen, an alkyl, alkaryl, aryl, aralkyl, cycloalkyl and the like, and R_3 may also be a metal, at least one of said radicals being an oil-solubilizing group; X is oxygen or sulfur, at least one of the X's in Formulas II and III being sulfur. The R radicals may contain

various substituent groups particularly oil-solubilizing groups such as branch-chain hydrocarbons, halogen containing organic derivatives and sulfonates. Compounds represented by these formulas are referred to as carbamates, monothiocarbamates, e. g. thiolcarbamates; and thionocarbamates, dithiocarbamates and thiuran sulfides and the like.

The salt derivatives of compounds as represented by Formula I may include the alkali and alkaline earth metals such as Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba as well as other metals such as Al, Cu, Zn, Cd, Va, Cr, Mo, Mn, Fe, Co, Ni and the like, and nitrogen bases such as ammonium, alkyl, aralkyl, aryl, cycloalkyl and heterocyclic amines. Salts of the carbamates which are particularly preferred are Ca, Ba, Al and Zn.

Typical members of additives as represented by Formula I are the Zn, Al, Pb, Fe, Ca, Ba, Na and amine salts of dibutyl mono and dithiocarbamate, diethyl mono and dithiocarbamate, dimethyl mono and dithiocarbamate, dihexyl mono and dithiocarbamate, diamyl mono and dithiocarbamate, dioctyl mono and dithiocarbamate, dipropyl mono and dithiocarbamate, N-butyl-N-ethyl mono and dithiocarbamate, N-ethyl-N-phenyl mono and dithiocarbamate, octyl-butyl mono and dithiocarbamate, dicyclohexyl mono and dithiocarbamate, methyl-octyl mono and dithiocarbamate and the like. Other compounds exemplified by the formulas are ferric dibenzyl amyl dithiocarbamate, ferric piperidine dithiocarbamate, benzyl diethyl dithiocarbamate; dithiocarbamic ethyl ester, ethyl dithiocarbamic ethyl ester, dithiocarbamic phenyl ester, phenyl dithiocarbamic phenyl ester; tetra methyl thiuram sulfide, tetra methyl-thiuram disulfide, tetra ethyl thiuram sulfide, dipentamethylene thiuram tetrasulfide, dibutyl-diethyl thiuram disulfide, tetrabutyl thiuram disulfide, tetraisopropyl thiuram disulfide, tetrapropyl-thiuram disulfide, and the like. The amount of this type of additive which is added to a base oil is generally less than 1% by weight, although greater quantities may be used. The preferred range is between about 0.1% and up to 5% by weight, depending upon the oil base, concentration of the other additive and conditions of use.

The other main additive component of this invention is a metal salt of a condensation product of a phenolic compound with an aldehyde. Suitable phenolic compounds can be represented by the general formula

(IV)
$$\begin{array}{c} XH \\ | \\ R_n—Ar—Y_m \end{array}$$

wherein Ar is a mono or polynuclear aromatic ring compound, X can be oxygen or sulfur, Y is a polar radical such as chlorine, nitro or amine, R is a hydrocarbon having a plurality of carbon atoms and if desired having attached thereon polar groups, n is an integer of at least 1, and m can be zero or an integer of less than 2. Compounds illustrative of Formula IV and which may be used to form the condensation reaction are dibutyl phenol and its thiophenol, amyl phenol and its thiophenol, tertiary butyl phenol and its thiophenol, p-tertiary amyl phenol and its thiophenol, octyl phenol and its thiophenol, p-isooctyl phenol, iso butyl phenol, nonyl phenol and their thiophenyls, cetyl phenol and its thiophenol, alkyl amino phenol, alkyl aminonaphthol and the like.

Aldehydes which can be used to form condensation products with the above phenolic compounds can be aliphatic, aromatic or cyclic aldehydes. Specifically formaldehyde, acetaldehyde, crotonaldehyde, butyraldehyde; benzaldehyde; furaldehyde and the like can be used.

The condensation product is formed at rather elevated temperatures using an acid or basic catalyst. The salts of said condensation products may be alkali, alkaline earth or heavy metal, e. g. Na, K, Li, Ca, Ba, B, Mg, Al, Zn, Cu, Pb, Fe, Ni, Co, Mn, Cr, Sn and the like.

The salts of the condensation product of an alkyl phenolic compound and an aldehyde may be prepared by first condensing at an elevated temperature, for example, an octyl phenol with formaldehyde in the presence of a suitable solvent and catalyst. The condensation product is then removed and dispersed in a hydrocarbon oil to which is added the metal forming constituent such as hydrated lime and the mass is agitated at an elevated temperature until the calcium salt of said condensation reaction forms. The salt formed can be purified by solvent treatment and filtration.

Instead of forming the salt in a two step process it can be formed in one step by simply admixing in a suitable solvent an alkyl phenol, an aldehyde and for example hydrated lime and reacting the mixture at an elevated temperature under agitation until the calcium salt of the alkyl phenol-aldehyde condensation reaction forms. The product is recovered and purified by conventional means.

Typical members of this type of additive are the Ca, Ba, Sr, Na, K, Li, Al, Zn, etc. salts of the condensation reaction between:

Octyl phenol-formaldehyde
Octyl phenol-acetaldehyde
Isooctyl phenol-acetaldehyde
Isooctyl phenol-crotonaldehyde
Octyl phenol-benzaldehyde
Octyl phenol-furaldehyde
Octyl thiophenol-formaldehyde
Octyl thiophenol-furaldehyde
Amyl phenol-furaldehyde
Amyl phenol-formaldehyde

Some of the salts of condensation reaction between a phenolic compound and an adehyde are difficulty soluble in oil. However, these may be solubilized therein for example by the procedure described by Cornell in U. S. Patent 2,042,880. A simpler method which is effective for many of these salts is to dissolve them in a suitable solvent such as benzene, and then, while adding oil, gradually remove the benzene by distillation, for example, by passing an inert gas (nitrogen, natural gas, etc.) through the mixture at an elevated temperature. This generally results in a stable concentrate of the salt in the oil which may be then diluted with more oil to the desired salt concentration. On the other hand, the salt may often be incorporated in an oil, without preparing an intermediate concentrate, by simply adding the desired concentrate of the salt to the oil at an elevated temperature with agitation. The amount of this additive need not be used above about 2% by weight although amounts as high as 5 to 25% can be used. The preferred range is between about 0.05% to 6%. A general practical range is between about 0.2% and about 4% by wt.

Lubricants containing the above discussed additives result in excellent heavy duty compositions, the lubricating properties of which can be enhanced by addition thereto of an oil-soluble salt of an organic sulfonic acid and/or an aryl amine.

The general class of aryl amines are the oil-soluble, relatively stable, aromatic amine, free from corrosive sulfur, preferably having at least two aromatic rings, which may be condensed in one radical attached to the nitrogen atom. Especially valuable are those amines which contain at least one aromatic nucleus having two or more condensed or polycyclic aromatic rings. Thus, preferred compounds are, for example, the naphthylamines: primary, secondary or tertiary alkyl, aryl or aralkyl amines in which the alkyl, aryl or aralkyl radicals are attached to an aromatic nucleus or preferably to the nitrogen atom or both, such as phenyl-alpha or beta-naphthylamine, tetraline naphthylamine, alpha alpha, alpha beta, or beta beta dinaphthylamines, various phenanthryl, anthryl or picyl naphthylamines, xenyl naphthylamines, benzyl phenyl naphthylamines, diphenyl naphthylamines, pheny xenyl naphthylamines, dixenyl naphthylamines; also various phenanthryl, anthryl or picyl phenyl amines, etc. The N-aryl substituted naphthylamines are in general more useful for our purpose.

If desired however, other aryl amines may be used, such as diamino diaryl alkanes, e. g., diamino diphenyl methane, tetramethyl diamino diphenyl methane, tetra methyl diamino triphenyl methane, tetra ethyl diamino triphenyl methane, diamino diphenyl ethane, diamino ditolyl ethane, etc., alkylated diaryl amines, e. g. p-ethyl diphenylamine, m-ethyl diphenylamine, p-isopropyl diphenylamine, mono- and polyamyl, hexyl, heptyl, octyl, nonyl, decyl, hexadecyl, cyclohexyl, methyl cyclohexyl and other alkyl substituted diphenylamines, etc.

The aryl amines may, in some cases, contain one or more substituents, such as hydroxyl, chloro, alkoxy, hydroxyalkyl, amino, n-alkylated amino, n-alkylated amino alkylene, etc radicals. As illustrative of these substituted aryl amines, the following may be mentioned: p-methoxy p'-isopropyl diphenyl amine, and 1,8-diamino naphthalene.

The amount of aryl amine when used as an additive may vary from less than 1% up to 10% by weight, the preferred range being between about 0.05 and 2% by weight.

The other additive which may be added with compositions of this invention are salts of organic sulfonic acids, preferably petroleum sulfonic acids.

Petroleum sulfonic acids which may be used advantageously to produce the metal sulfonates of this invention are preferably of the oil-soluble type which are obtained, for example, in the treatment of relatively heavy mineral oils, with concentrated sulfuric acid. In this kind of treatment, two types of sulfonic acids are produced—the so-called green acids which are substantially oil-insoluble, and mahogany acids which are oil-soluble. It is the mahogany acids which we prefer to use for our purpose, although green acids may also yield certain oil-soluble salts which are applicable for our purpose. These acids constitute complicated mixtures of many different hydrocarbon sulfonic acids, many of which are believed to be of aromatic character, although others are probably of naphthenic and aliphatic origin. Some of them produce better anti-ring-sticking salts than others. In order to isolate the most effective components, the oil-soluble acids or their salts may be subjected to a fractionation by countercurrent extraction with two mutually immiscible solvents, a hydrocarbon liquid such as toluene, benzene, xylene, naphtha, kerosene, etc., and a water-soluble organic solvent such as a lower alcohol, glycol, glycerine, the latter preferably containing some water. The active component of the mahogany acid is concentrated in the hydrocarbon solvent. This method of separation has been described by Retailliau in U. S. Patent 2,158,680.

If desired, lubricating oils containing the sulfonic acid salts may also be produced by heavy acid treatment with concentrated or fuming sulfuric acid of a suitable lubricating oil, separating precipitated and suspended sludge, and neutralizing the dissolved sulfonic acid with lime or other oxide or hydroxide of a suitable polyvalent metal. The preferred salts are the basic salts of petroleum sulfonic acids.

Other oil-soluble organic sulfonic acids suitable for our purpose may be produced by sulfonating alkyl aromatic hydrocarbons, such as alkyl benzenes, alkyl naphthalenes, alkyl anthracene, alkyl phenanthrenes, alkyl picenes, alkyl chrysenes, alkyl diphenyls, etc., provided the number of carbon atoms in the alkyl chain or chains is sufficient to render the resulting sulfonic acids and their salts soluble in the base oil. It is desirable that at least one alkyl radical be relatively long, i. e., contain at least 8 or more carbon atoms, not only because of solubility in oils, but also for the reason that long alkyl chains improve the anti-ringsticking efficiency of the salts formed with the sulfonic acids. Thus, one may produce an aromatic hydrocarbon suitable for the production of highly efficient sulfonic acids by condensing chlorinated paraffin wax, alkyl chlorides such as octyl, decyl, cetyl, etc., chlorides, fatty alcohols, long chain olefins such as may be obtained in the cracking of wax, etc., with the aromatic hydrocarbons by means of suitable condensing agents such as Friedel-Crafts catalysts, sulfuric acid, P_2O_5, phosphoric acid, etc.

The organic sulfonic acids may, if desired, contain substitution radicals such as hydroxyl, primary, secondary or tertiary amine, ether, sulfide, hydrosulfide, disulfide, halogen, etc., radicals which may be attached to the ring or to side chains or both. For example, excellent for the present purpose are paraffin wax substituted naphthalene mono sulfonic acids which contain a sulfonic radical attached to one ring of the naphthalene nucleus and a hydroxyl or amino radical attached to the other ring.

The sulfonates can be made soluble in any type of mineral lubricating oil ranging from the lowest to the highest V. I. This is in marked contrast to many of the commercial anti-ringsticking salts of carboxylic acids which are soluble only in low V. I. oils. The importance of being able to produce both high V. I. and low V. I. oils having good anti-ringsticking properties cannot be overestimated, because in certain types of diesel engines, low V. I. oils simply will not stand up, while in other types of diesel engines, low V. I. oils give as good or better results than the oils of higher V. I.

Salts suitable for our use in composition of this invention must be free of free acid, and may be normal and preferably basic. If necessary, the sulfonic acids may be subjected to a hydrolyzing treatment before use in the compounded oil, to eliminate sulfate or other contaminants which may be present. If desired, salts of two or more of metals may be employed.

The amount of sulfonate when used as an ad-

ditive may vary from less than 1% up to about 25% by weight, the preferred range being between about 0.05% and 10% by weight.

Basic oils may be selected from a wide variety of natural oils such as paraffinic, naphthenic and mixed base oils having a wide viscosity range. In addition synthetic oils may be used such as polymerized olefins, copolymers of alkylene glycols and alkylene oxides, organic esters, e. g. 2-ethyl hexyl sebacate, dioctyl phthalate, trioctyl phosphate; polymeric tetra hydrofuran; polyalkyl silicon polymers and the like. Mixture of natural and synthetic oils can be used also.

To more fully illustrate the present invention the following are a few txamples of compositions of this invention which have been compounded, tested and found extremely effective for heavy duty lubrication. The base oil was an SAE 30 oil having a viscosity of 55. Composition of this invention passed the CRC Tests L1, L2, L3, L4 and L5. For purpose of illustration the following test results of oil compositions of invention are listed when subjected to a CRC Test L-4-545 which is a 36 hour test in a Chevrolet engine using the following conditions:

	Minimum	Maximum	Average
Engine speed, R. P. M.	3,130	3,165	3,150
Engine load, B. H. P.	29.8	30.5	30
Oil temp. in sump, °F.	277	284	280
Oil pressure, P. S. I.	13.5	14.1	13.8
Jacket outlet coolant temp., °F.	197	203	199
Exhaust pressure, in Hg.	0.7	0.9	0.8
Intake depression, in Hg.	12.2	12.8	12.5
Fuel consumption, seconds per 300 cc.	70.0	72.9	71.3

The following table shows the composition of the lubricants run for comparative purposes, together with the average bearing weight loss occasioned by the use of the respective lubricants:

Table

[Base oil 600 SUS at 100° F. motor stock.]

Ca Salt of Petroleum Sulfonate Per Cent by wt.	Ca salt of the Condensation Product of Octyl Phenol and formaldehyde per cent wt.	Zn salt of dibutyl dithiocarbamate per cent wt.	Phenyl α naphthyl-amine per cent wt.	Bearing wt. loss mg. per bearing	Piston Lacquer Rating
0	0	0	0	805	2½
1.8	0	0	0	[1] 1,489	------
0	0	0	0.4	242	1
0	1.0	0	0.4	174	1
1.2	1.0	0	0	169	10
0.6	1.0	0	0.2	186	10
2.7	0	1.0	0	67	10
1.2	1.0	0.4	0	39	10
1.2	1.0	0.4	0.2	30	10

[1] 9 hours.

Compositions of this invention were also subjected to Oxygen Absorption Test and a modified Thrust Bearing Corrosion Test, the results of which are self-explanatory and are listed below. The modified Thrust Bearing Corrosion Test gives critical corrosion temperature of 5 to 10° C. lower than regular Thrust Bearing Corrosion Test which is described in the National Petroleum News, September 17, 1941, pp. 294–296.

Oxygen absorption test and thrust bearing corrosion test

[Base oil 600 SUS at 100° F. motor stock.]

Ca salt of Petroleum Sulfonate, per cent wt.	Ca salt of the Condensation Product of Octyl phenol and Formaldehyde, per cent wt.	Zn salt of dibutyl dithiocarbamate, per cent wt.	Phenyl α naphthyl-amine, per cent wt.	½% crankcase Catalyst 1500 ml. oxygen, time (hours)	Tests in Thrust Bearing Corrosion Machine, Estimated Critical Corrosion, Temp. ° C.
0	0	0	0	1.3	[1]
0.9	0	0	0	1.3	100–120
0.9	0	0	0.2	20.6	155+
0	1.0		0	23.4	150+
1.2	1.0		0	23.4	150+
1.2	1.0	0.4	0.2	28.7	155+

[1] Impossible to complete test because of excessive lacquering.

Other additives can be added to the compositions of this invention in order to improve their performance. Thus E. P. additives such as sulfurized, sulfur-halogenated, and phosphor-sulfurized organic compounds can be used; also oiliness agents, e. g. oleic or stearic acid, pour point depressors, anti-foaming agents, e. g. organic silicons, fluoro organic compounds, nitro paraffins and the like.

Many modifications and variations of this invention as hereinbefore set forth can be made without departing from the spirit and scope thereof and only such limitation should be imposed as indicated in the appended claims.

We claim as our invention:

1. A lubricant comprising a major amount of a lubricating oil and the combination of minor amounts, sufficient to prevent deterioration of said oil, of from 0.05% to 6% of an oil soluble calcium salt of a condensation product of an alkyl phenol with formaldehyde and from 0.1% to 5% of zinc dibutyl dithiocarbamate, and minor amounts of from 0.05% to 10% of a hydrocarbon aromatic amine and of from 0.05% to 10% of an oil-soluble metal salt of a petroleum sulfonic acid.

2. A heavy duty lubricant comprising a major amount of a lubricating oil and the combination of minor amounts, sufficient to prevent deterioration of said oil, of from 0.05% to 6% of an oil soluble calcium salt of a condensation product of an alkyl phenol with formaldehyde and from 0.1% to 5% of zinc dihexyldithiocarbamate and of from 0.05% to 10% of a hydrocarbon aromatic amine and of from 0.05% to

10% of an oil-soluble metal salt of a petroleum sulfonic acid.

3. A heavy duty lubricant comprising a major amount of a lubricating oil and the combination of minor amounts, sufficient to prevent deterioration of said oil, of from 0.05% to 6% of an oil soluble calcium salt of a condensation product of an alkyl phenol with formaldehyde and from 0.1% to 5% of calcium dibutyl dithiocarbamate and a minor amount of from 0.05% to 10% of a hydrocarbon aromatic amine and of from 0.05% to 10% of an oil-soluble metal salt of a petroleum sulfonic acid.

4. A heavy duty lubricant comprising a major amount of a lubricating oil and the combination of minor amounts, sufficient to prevent deterioration of said oil, of from 0.05% to 6% of an oil soluble calcium salt of a condensation product of an alkyl phenol with formaldehyde and from 0.1% to 5% of zinc dibutyl dithiocarbamate and a minor amount of from 0.05% to 10% of an oil-soluble metal salt of a petroleum sulfonic acid.

5. A heavy duty lubricant comprising a major amount of a lubricating oil and the combination of minor amounts, sufficient to prevent deterioration of said oil, of from 0.05% to 6% of an oil soluble calcium salt of a condensation product of an alkyl phenol with formaldehyde and from 0.1% to 5% of zinc dihexyldithiocarbamate and a minor amount of from 0.05% to 10% of an oil-soluble metal salt of a petroleum sulfonic acid.

6. A heavy duty lubricant comprising a major amount of a lubricating oil and the combination of minor amounts, sufficient to prevent deterioration of said oil, of from 0.05% to 6% of an oil soluble calcium salt of condensation product of an alkyl phenol with formaldehyde and from 0.1% to 5% of calcium dibutyl dithiocarbamate and a minor amount of from 0.05% to 10% of a hydrocarbon aromatic amine.

7. A heavy duty lubricant comprising a major amount of a lubricating oil and the combination of minor amounts, sufficient to prevent deterioration of said oil, of from 0.05% to 6% of an oil soluble metal salt of condensation product of an alkyl phenol with an aldehyde and from 0.1% to 5% of an oil soluble metal salt of dithiocarbamic acid.

8. A heavy-duty lubricant having the following formula:

	Percent weight
Ca salt of octyl phenol-formaldehyde condensation product	1
Zn dibutyldithiocarbamate	0.4
Ca petroleum sulfonate (oil-soluble)	1
Phenyl alpha-naphthylamine	0.2
Mineral lubricating oil	Balance

9. A heavy-duty lubricant having the following formula:

	Percent weight
Ca salt of octyl phenol-formaldehyde condensation product	1
Zn dihexyldithiocarbamate	0.4
Ca petroleum sulfonate (oil soluble)	1
Phenyl alpha-naphthylamine	0.2
Mineral lubricating oil	Balance

10. A heavy-duty lubricant having the following formula:

	Percent weight
Ca salt of octyl phenol-formaldehyde condensation product	1
Zn dialkyl dithiocarbamate (oil-soluble)	0.4
Ca petroleum sulfonate (oil-soluble)	1
Phenyl alpha-naphthylamine	0.2

and the balance consisting essentially of mineral lubricating oil.

11. A heavy-duty lubricant having the following formula:

	Percent weight
Ca salt of octyl phenol-formaldehyde condensation product	0.05–6
Zn dibutyl dithiocarbamate	0.1–5
Ca petroleum sulfonate (oil-soluble)	0.05–10
Phenyl alpha-naphthylamine	0.05–10
Mineral lubricating oil	Balance

12. A heavy-duty lubricant having the following formula:

	Percent weight
Ca salt of octyl phenol-formaldehyde condensation product	0.05–6
Zn dihexyl dithiocarbamate	0.1–5
Ca petroleum sulfonate (oil-soluble)	0.05–10
Phenyl alpha-naphthylamine	0.05–10
Mineral lubricating oil	Balance

13. A heavy-duty lubricant having the following formula:

	Percent weight
Ca salt of octyl phenol-formaldehyde condensation product	0.05–6
Zn dialkyl dithiocarbamate (oil-soluble)	0.1–5
Ca petroleum sulfonate (oil-soluble)	0.05–10
Phenyl alpha-naphthylamine	0.05–10

and the balance consisting essentially of mineral lubricating oil.

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