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HALOGEN CONTAINING EXTREME PRESSURE LUBRICANT STABILIZED WITH A POLYALKYLENE POLYAMINE

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The present invention relates to extreme pressure lubricants of improved stability against sedimentation. More particularly it relates to lubricating compositions comprising an extreme pressure halogen compound and a polyalkylene polyamine.

Halogen containing compounds, particularly chlorinated hydrocarbons, are commonly employed in lubricating compositions which are required to maintain lubrication of metal surfaces under high pressures such as are encountered for example in industrial heavy duty bearings and hypoid gears of automotive vehicles. While compounds of this class are very effective in producing lubricants of high load carrying capacity, they have a disadvantage in that they tend to hydrolyze with the liberation of halogen acid, which is undesirable because of its corrosiveness to metals. Furthermore, such halogen compounds tend to cause increased sedimentation or sludge formation in the lubricant on standing and in service which impairs both its appearance and its useful lubricating value.

It has been proposed heretofore to add to lubricating compositions comprising such halogenated compounds various types of materials, including amines, which have the property of repressing corrosion by neutralizing the acid formed. For example, McNulty et al. in U. S. 2,268,608, disclose that a number of different amines, including aliphatic amines, benzylamines, ethanolamines, etc., may be employed in extreme pressure lubricants containing halogen compounds, or both halogen compounds and sulfur or phosphorus-containing compounds. The use of various amines, including diphenylamine, hexamethylenetetramine and aniline in a lead soap gear lubricant containing both halogen and sulfur compounds is disclosed by Hilliker in U. S. 2,386,553.

However, it has been found that the problem of stabilizing a halogen bearing lubricant, such as a gear lubricant, against sedimentation is not effectively solved by the use of the amines of the prior art. It has further been found that, by the use of an amine selected from a particular small group of polyalkylene polyamines, such a lubricant is unexpectedly stabilized against sedimentation without impairment of its other desirable properties including extreme pressure characteristics.

In accordance with the invention, extreme pressure lubricants comprising halogen-containing compounds are stabilized by adding to them small amounts of compounds chosen from the class of polyalkylene polyamines having two primary amine groups attached to different aliphatic groups. Suitable compounds of this type may be represented by the general formula $NH_2R(NHR)_xNH_2$, where R is an alkylene group preferably containing from 1 to about 6 carbon atoms, and x is an integer preferably from 1 to about 5. For the sake of simplicity the term "alkylene" is used in this application to mean any bivalent aliphatic hydrocarbon group, including such hydrocarbon groups above ethylene wherein the available valences are terminal or located elsewhere than on adjacent carbon atoms. As examples of the above compounds may be mentioned trimethylene tetramine, diethylene triamine, pentamethylene hexamine, triethylene tetramine, tetraethylene pentamine, dibutylene triamine, tripropylene tetramine, and so forth. Tetraethylene pentamine has been found to be particularly suitable. Instead of a pure compound, mixtures of these compounds such as are obtained when dihalogen compounds are treated with ammonia, may be employed. It appears that the ability of these particular compounds to prevent sludging of the lubricant may be due to some specific action on inhibiting the formation of halogen acids as opposed to the neutralization thereof after formation.

Lubricating compositions in which the above compounds may be employed according to the invention are in general those containing or consisting of halogen-containing compounds having extreme pressure properties. Such halogen-containing compounds may be aliphatic, aromatic or alkylated aromatic compounds, such as for example halogenated derivatives of paraffin wax, petroleum fractions, polymeric materials, benzene, naphthalene, toluene, biphenyl, etc. The lubricating composition preferably comprises a hydrocarbon lubricating oil such as a mineral oil fraction containing one or more such compounds in relatively minor amount. In addition to the halogen-containing compounds, the lubricant may also contain various other additives of the usual type such as oxidation inhibitors, anti-foam agents, viscosity index improvers, thickening agents, etc. as well as other extreme pressure agents such as sulfur and/or phosphorus containing compounds.

The amount of the polyamine inhibitor employed depends upon the amount of halogen in the lubricant composition and upon the instability of the halogen-containing compound. In general the amount will range from about 0.01 to about 1 per cent by weight of the lubricant. For halogen-containing extreme pressure lubricants of the usual type the inhibitor is suitably employed in amounts of from about 0.05 to about 0.5 per cent, and preferably from about 0.1 to about 0.3 per cent.

A particularly valuable application of the invention is found in the production of heavy duty lubricants which contain in addition to halogenated compounds appreciable amounts of metal salts, such as oil-soluble salts of copper, mercury, lead, etc., which are commonly added to compounded lubricating oils and fluid greases to further improve their load carrying properties. In such compositions the dissociation or hydrolysis of the halogenated organic compounds to form free halogen acid is especially objectionable because it leads to excessive sludging, which is due largely to the formation of insoluble metal salts by reaction between the halogen acid and the metal compound.

The effectiveness of the stabilizing agents has been demonstrated in the production of a very superior halogen-containing lubricant of the above type. This is a hypoid gear lubricant containing a lead-chlorine-sulfur additive combination, which was found to impart very superior extreme pressure and other desirable lubricating characteristics to lubricant compositions with the exception that an excessive amount of sludge, consisting chiefly of lead chloride, was formed in service and in laboratory tests at elevated temperatures. As shown by the following examples, compositions of very satisfactory stability as well as high load carrying capacity were obtained by adding small amounts of the stabilizing agents to lubricants comprising this combination of additives in varying proportions in different types of lubricating oils. The stability of the compositions was determined by measuring the amount of sediment occurring at elevated temperatures of the order of those developed in oils in service under extreme pressure conditions. The test was carried out by placing a 100 ml. sample of the lubricant in a graduated centrifuge tube in a constant-temperature oven at 250° F., for periods of 4 and 30 hours, then cooling and centrifuging at room temperature at 6000 R. P. M. for 45 minutes. The amount of sediment formed was determined from the graduations on the tube.

EXAMPLE 1

A lubricant was prepared by blending as the essential constituents the following materials in the proportions indicated:

	Per cent
Lead naphthenate	10.0
Chlorinated paraffin wax	3.0
Sulfur chlorinated sperm oil	10.0
Mineral lubricating oil	Remainder

The mineral lubricating oil employed in the above composition was a blend in approximately a ½ ratio of a paraffinic residuum having an API gravity of 21.9, a flash point, COC, of 570 and an SUS viscosity at 210° F. of 195.2, and a paraffinic distillate oil having an API gravity of 29.4°, a flash point, COC, of 450° F. and an SUS viscosity at 210° F. of 54.4.

The lead naphthenate, which was prepared from lubricating oil naphthenic acids, had a lead content of 21.0% and an unsaponifiable content of 22.8%.

The chlorinated wax was a commercial product sold under the name of "Anglamol 40" by Lubrizol Corporation. It had a chlorine content of 44.0% and contained a small amount of phenoxy propylene oxide as a corrosion inhibitor.

The sulfur chlorinated sperm oil was a commercial product sold under the name of "Sulchlor 55" by Carlisle Chemical Works, Inc. It contained 6.73% of chlorine and 6.76% of sulfur.

To portions of the above lubricant small amounts of various amines including diethylene triamine were added and the compositions tested according to the stability test described. The following results were obtained:

Table I

STABILITY TEST
[4 hours at 250° F.]

Additive:	Sediment, Percent by volume
None	0.8
0.5% triethanolamine	0.8
1.0% diphenyl amine	0.8
0.5% high molecular weight aliphatic amine[1]	1.5
1.0% high molecular weight aliphatic amine[1]	0.8
0.5% diphenyl amine	0.8
1.0% diphenyl amine	1.0
0.5% phenyl alphanaphthylamine	1.0
1.0% phenyl alphanaphthylamine	0.6
0.1% diethylene triamine	0.3
0.5% diethylene triamine	0.3

[1] Sold commercially under the trade name "Armeen C."

EXAMPLE 2

A lubricant was prepared by blending as the essential constituents the following materials in the proportions indicated.

	Per cent
Lead naphthenate	7.0
Chlorinated paraffin wax	3.0
Sulfur chlorinated sperm oil	7.0
Sulfurized sperm oil	6.5
Mineral lubricating oil	Remainder

The mineral lubricating oil employed in the above composition was the same as that employed in the lubricant of Example I.

The sulfurized sperm oil was a commercial product sold under the name of "S/V 28 Base" by Socony Vacuum Oil Company. It comprised chiefly a sulfurized derivative of cetyl oleate and analyzed 9.48% sulfur.

The other additives were the same as those employed in the lubricant of Example I.

To portions of the above lubricant small amounts of various amines including diethylene triamine were added and the compositions tested according to the stability test described. The following results were obtained:

Table II

STABILITY TEST
[4 hours at 250° F.]

Additive:	Sediment, Percent by volume
None	2.0
0.5% triethanolamine	1.0
1.0% triethanolamine	1.0
0.5% high molecular weight aliphatic amine[1]	0.8
1.0% high molecular weight aliphatic amine[1]	0.5
0.5% diphenyl amine	1.3
0.5% phenyl alpha naphthylamine	1.0
1.0% phenyl alpha naphthylamine	0.6
0.1% diethylene triamine	0.4
0.5% diethylene triamine	0.3

[1] Sold commercially under the trade name "Armeen C."

EXAMPLE 3

A lubricant was prepared by blending as the essential constituents the following materials in the proportions indicated:

	Per cent
Lead naphthenate	10.0
Chlorinated paraffin wax	1.0
Sulfur chlorinated sperm oil	10.0
Sulfurized sperm oil	5.0
Mineral lubricating oil	Remainder

The mineral lubricating oil was a blend in approximately equal proportions of an asphaltic residuum having an API gravity of 17.0°, a flash point, COC, of 645° F. and an SUS viscosity at 210° F. of 764, and an asphaltic distillate oil having an API gravity of 25.3°, a flash point, COC, of 335° F. and an SUS viscosity at 210° F. of 38.7.

The additives employed were the same as those of Examples 1 and 2.

To separate portions of the above lubricant small amounts of various amines including typical compounds of the invention were added and the stability of the resulting compositions determined by the stability test described. The following results were obtained:

Table III

STABILITY TEST
[4 hours at 250° F.]

Additive:	Sediment, Per cent by volume
None	0.8
0.1% p-phenylene diamine	0.5
1.0% p-phenylene diamine	1.0
0.1% hexamethylene tetramine	2.5
1.0% hexamethylene tetramine	2.0
0.1% diethylene triamine	0.5
0.5% diethylene triamine	0.4
0.1% triethylene tetramine	0.3
0.5% triethylene tetramine	0.4
0.1% tetraethylene pentamine	0.1
1.0% tetraethylene pentamine	0.1

EXAMPLE 4

A lubricant was prepared by blending as the essential constituents the following materials in the proportions indicated:

	Per cent
Lead naphthenate	10.0
Chlorinated paraffin wax	3.0
Sulfur chlorinated fat	7.0
Sulfurized sperm oil	6.5
Mineral lubricating oil	Remainder

The mineral lubricating oil was a solvent refined, clay contacted and lightly acid treated paraffinic wax distillate having an API gravity of 27.5, a flash point, COC, of 490 and an SUS viscosity at 210° F. of 78.6.

The extreme pressure additives were the same as those employed in the lubricants of the previous examples.

To portions of the above lubricant small amounts of tetraethylene pentamine were added and the compositions tested according to the stability test described for periods of 30 hours. The following results were obtained:

Table IV

STABILITY TEST
[30 hours at 250° F.]

Tetraethylene pentamine, per cent:	Sediment, Per cent by volume
None	1.0
0.05	0.5
0.10	0.5
0.20	Trace
0.30	None
0.40	None
0.50	None

The following data were obtained on the load carrying properties of the above lubricants. Lubricant A of Table V below is that of Example 1, lubricant B is that of Example 2, and lubricant C is that of Example 3.

Table V

LOAD CARRYING PROPERTIES

Lubricant	Additive	Timken Test	
		OK, lbs.	p. s. i.
A	None	90	37,750; 42,500
	0.1% Diethylene triamine	85	36,500; 42,000
B	None	90	28,500; 43,750
	0.1% Diethylene triamine	90	31,500; 33,000
C	None	85	35,500; 38,500
	0.1% Diethylene triamine	75	34,500; 27,250
	0.1% Triethylene tetramine	65	37,000; 38,000
	0.1% Tetraethylene pentamine	85	41,000; 41,000

The data given in the above tables show that stable lubricating compositions comprising ordinarily unstable halogen compounds are obtained by use of the stabilizing compounds of the invention. The data given in Tables I, II and III show that the compounds are outstandingly superior in stabilizing such compositions as compared with other amines which have been proposed heretofore for this purpose. Table V shows furthermore that the load carrying properties of the halogen-containing lubricant are not appreciably impaired by the compounds in the small amounts required to impart satisfactory stability to the composition.

In the production of lubricating compositions of the type described in the examples it is to be understood that compounds of similar nature may be substituted for the extreme pressure agents employed. Thus instead of lead naphthenate, other lead salts such as lead oleate, lead menhadenate or lead resinate may be employed. In place of chlorinated paraffin wax, other halogenated compounds having extreme pressure properties including halogenated aliphatic, aromatic, heterocyclic and oxygen-containing organic compounds such as fatty acids, esters and fatty oils may be employed. The halogen compound is preferably a highly chlorinated aliphatic material, containing from about 20 to 45 per cent of chlorine. In place of sulfurized and sulfur chlorinated sperm oil, suitable additives of this type may be obtained by sulfurizing and sulfur chlorinating other oils such as lard oil, lanolin, corn oil, cottonseed oil, menhaden oil, etc. Also, various types of lubricating oils may be employed, preferably comprising mineral oil fractions obtained by the usual refining methods. The finished composition suitably comprises about 3 per cent to about 15 per cent by weight of lead naphthenate or other lead soap, about 1 to 7 per cent of halogenated extreme pressure agent such as chlorinated paraffin wax, about 3 to 10 per cent of sulfurized fatty oil and about 5 to 15 per cent of sulfur chlorinated fatty oil. Small amounts of other additives such as oxidation inhibitors, corrosion inhibitors, anti-foam agents, extreme pressure agents, and so forth may also be present.

While the stabilizing agents of the invention are employed with particular advantage in the production of lubricants of the above type, the invention is not to be construed as limited to this application, since it is obvious that these compounds may be employed in a wide variety of lubricating compositions containing ordinarily unstable halogen compounds.

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.

What is claimed is:

1. A lubricant composition consisting essentially of a mineral lubricating oil containing about 1–7% by weight of chlorinated paraffin wax, about 3–10% by weight of sulfurized sperm oil, about 3–15% by weight of sulfur chlorinated sperm oil, about 3–15% by weight of lead naphthenate and about 0.05–0.5% by weight of tetraethylene pentamine.

2. A lubricant composition consisting essentially of a hydrocarbon lubricating oil containing a minor amount of an oil-soluble organic halogen containing compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, and about 0.01 to about 1 per cent by weight of a polyalkylene polyamine represented by the general formula

$NH_2R(NHR)_xNH_2$, where R is a bivalent aliphatic hydrocarbon group containing from 1 to 4 carbon atoms and x is an integer from 1 to 4.

3. A lubricant composition consisting essentially of a hydrocarbon lubricating oil containing a minor amount of an oil-soluble halogenated aliphatic compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, and about 0.01 to about 1 per cent by weight of a polyalkylene polyamine represented by the general formula

$$NH_2R(NHR)_xNH_2$$

where R is an ethylene group and x is an integer from 1 to 3.

4. A lubricant composition consisting essentially of a hydrocarbon lubricating oil containing a minor amount of an oil-soluble chlorinated aliphatic hydrocarbon compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, and about 0.05 to about 0.5 per cent by weight of a polyalkylene polyamine represented by the general formula $NH_2R(HNR)_xNH_2$, where R is an ethylene group and x is an integer from 1 to 3.

5. A lubricant composition consisting essentially of a hydrocarbon lubricating oil as the major component, containing a minor amount of an oil-soluble halogenated aliphatic compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, a minor amount sufficient to impart improved load carrying properties to the said composition of a lead soap, and about 0.01 to about 1 per cent by weight of a polyalkylene polyamine represented by the general formula $NH_2R(NHR)_xNH_2$, where R is a bivalent aliphatic hydrocarbon group containing from 1 to 4 carbon atoms and x is an integer from 1 to 4.

6. A lubricant composition consisting essentially of a hydrocarbon lubricating oil containing about 1 to about 7 per cent by weight of an oil-soluble chlorinated aliphatic hydrocarbon compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, about 3 to about 15 per cent by weight of a lead soap, and about 0.01 to about 1 per cent by weight of a polyalkylene polyamine represented by the general formula $NH_2R(NHR)_xNH_2$, where R is an ethylene group and x is an integer from 1 to 3.

7. A lubricant composition consisting essentially of a hydrocarbon lubricating oil as the major component, containing a minor amount of an oil-soluble organic halogen containing compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, a minor amount of an organic sulfur containing compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, a minor amount sufficient to impart improved load carrying properties to the said composition of a lead soap, and about 0.01 to about 1 per cent by weight of a polyalkylene polyamine represented by the general formula $NH_2R(HNR)_xNH_2$, where R is a bivalent aliphatic hydrocarbon group containing from 1 to 4 carbon atoms and x is an integer from 1 to 4.

8. A lubricant composition consisting essentially of a hydrocarbon lubricating oil as the major component, containing about 1 to about 7 per cent by weight of an oil-soluble halogenated aliphatic compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, about 3 to about 10 per cent by weight of a sulfurized fatty oil, about 5 to about 15 per cent by weight of a sulfur halogenated fatty oil, about 3 to about 15 per cent by weight of a lead soap, and about 0.01 to about 1 per cent by weight of a polyalkylene polyamine represented by the general formula $NH_2R(NHR)_xNH_2$, where R is an ethylene group and x is an integer from 1 to 4.

9. A lubricant composition consisting essentially of a hydrocarbon lubricating oil as the major component, containing a minor amount of an oil-soluble organic halogen containing compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, a minor amount sufficient to impart improved load carrying properties to the said composition of a lead soap, and about 0.01 to about 1 per cent by weight of a polyalkylene polyamine represented by the general formula $NH_2R(NHR)_xNH_2$, where R is an ethylene group and x is an integer from 1 to 4.

10. A lubricating composition consisting essentially of a hydrocarbon lubricating oil as the major component, containing a minor amount of an oil-soluble organic halogen containing compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, a minor amount of an organic sulfur containing compound having extreme pressure properties and which is normally corrosive to metals at elevated temperatures and pressures, a minor amount sufficient to impart improved load carrying properties to the said composition of a lead soap, and about 0.01 to about 1 per cent by weight of a polyalkylene polyamine represented by the general formula $NH_2R(NHR)_xNH_2$, where R is an ethylene group and x is an integer from 1 to 4.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,268,608	McNulty et al.	Jan. 6, 1942