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VISCOUS HYDROCARBON OILS

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This invention relates to viscous hydrocarbon oils and particularly to lubricants having high film strength, under conditions of thin film lubrication, and to stabilized lubricating oils.

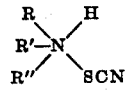
The main function of a lubricating oil is to prevent seizure and wear of parts which are in motion relative to each other, frequently under conditions of heavy pressure and high temperatures. In such circumstances, lubricants frequently fail to maintain a film between the moving parts with resultant seizure and breakdown of mechanical parts. Under conditions of service such as are found in modern automotive engines, the lubricating oils tend to absorb oxygen and break down to form sludge and acidic products which are deleterious to satisfactory performance. When the oils oxidize, the oxidation products frequently become insoluble in the oil and settle out. Likewise insoluble material may appear in the oils in the form of road dust, carbon from incompletely burned fuel, and minute metal particles from the wear of moving parts. These insoluble materials may be deposited in oil holes, on bearing surfaces, or in oil lines whereby flow of the oil to the moving parts is restricted and may even be prevented.

Many materials have been proposed for addition to the viscous hydrocarbon oils for solving these various problems. Usually it has been necessary to add an agent to improve the film strength, to add another agent to inhibit the absorption of oxygen and formation of sludge, and to add a still further agent to prevent deposition of insoluble materials. For example, sulfurized fish oils, chlorinated hydrocarbons, phosphates and the like have been proposed for addition to lubricating oils to impart improved film strength thereto. Such agents may effect a marked improvement in the film strength of the lubricant, but they have no, or substantially no, beneficial effect toward inhibiting oxidation, sludge formation and the deposition of insoluble materials. Also certain compounds, such as phenolic compounds, aromatic tin derivatives, aromatic amines and the like, have been proposed for stabilizing the oils against oxidation and sludge formation. These materials may have such stabilizing action but generally do not improve the film strength of the oils or inhibit the deposition of insoluble materials. Soaps have frequently been added to lubricating oils to disperse the insoluble materials and to prevent the deposition thereof on metallic surfaces. However, such soaps generally have little or no effect on the film strength or on the stability of the oils.

It is an object of the present invention to provide lubricants having incorporated therein agents for maintaining a lubricating film under severe operating conditions and particularly to improve the film strength. Another object is to provide lubricants having incorporated therein compounds which will improve the resistance of the oils to oxidative degradation as well as to improve the film strength. It is a further object to provide lubricants having incorporated therein compounds which will improve the resistance of the oils to deposition of insoluble sludge-like materials on metal surfaces as well as to improve the film strength and stability of such oils. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with my invention which comprises incorporating in a viscous hydrocarbon oil a salt of an aliphatic amine with thiocyanic acid. I have found that such salts, when incorporated in the oils, impart improved film strength to the oils, substantially inhibit the absorption of oxygen by the oils and hence the formation of oxidized products in the oils and tend to disperse in the oils insoluble sludge-like materials and inhibit the deposition of such materials on surfaces in contact with the oils.

The aliphatic amine salts of thiocyanic acid, which may be employed in accordance with my invention, may be represented by the formula:



wherein each of R, R' and R'' represents an aliphatic radical or hydrogen and at least one of R, R', and R'' represents an aliphatic radical. In other words, the salts of my invention are derived from primary, secondary and tertiary aliphatic amines. By the term 'aliphatic" I mean that the compound, amine or radical, is strictly aliphatic and does not contain any benzene ring or other aromatic group. The aliphatic radicals may be saturated, unsaturated or cyclic aliphatic groups. Also the aliphatic groups may contain interrupting atoms selected from divalent sulfur, oxygen, and trivalent nitrogen. Also the aliphatic groups may carry substituents selected from nitro, amino, amide, hydroxy, carboalkoxy, carboxy, sulfonamide, and halogen groups.

Preferably, the salts of my invention are de-

rived from aliphatic amines which contain a total of at least eight carbon atoms and particularly from twelve to eighteen carbon atoms. Also preferably, the aliphatic amine, except for the amino nitrogen atoms, consists of carbon and hydrogen. Of these, the mono-amines are preferred. By a mono-amine, I mean an amine which contains only one amino group. Also for the best results, the aliphatic amine should be a primary aliphatic mono-amine and particularly a primary a-cyclic aliphatic mono-amine containing from twelve to eighteen carbon atoms in the chain.

By viscous hydrocarbon oils, I mean to include fuel oils, particularly Diesel engine fuel oils, especially those used in high speed engines, as well as the usual lubricating oils, employed in automotive engines, and greases. Preferably, the oils are those derived from petroleum. They may be solvent extracted oils or conventionally refined lubricating oils obtained from various base crude oils. The amount of amino thiocyanate employed will be determined by the effect desired, but in general will be from about 0.1% to about 5.0% by weight based on the oil. Preferably I employ from about 0.2% to about 2.0% of the compound based on the oil. The compounds may be incorporated in the oils by various means, such as simple mixing and heating, where solubility characteristics permit, or by the use of more vigorous means, such as grinding or passage through a colloid mill, where the solubility characteristics of the compound are low. Also where the solubilities are low, blending agents or suitable auxiliary solvents may be employed.

The methods of preparing the amine salts of thiocyanic acid are well-known and follow conventional organic methods. The preparation of a few representative amine thiocyanates is given by way of illustration, in which the quantities are given as parts by weight.

Example I

Preparation of oleylamine thiocyanate

One hundred six and eight-tenths parts of oleylamine and 30.4 parts of ammonium thiocyanate were mixed and allowed to stand fifteen hours. A considerable evolution of ammonia took place. The mixture was then warmed on a steam bath two hours, following which it was dissolved in benzene and filtered. Upon removal of the solvent under reduced pressure, 115 parts of a viscous yellow fluid was obtained which was soluble in hydrocarbon solvents and which, on vigorous shaking with an aqueous solution of a ferric salt, yielded the characteristic red color of ferric thiocyanate. The compound contained 9.83% sulfur and, on standing several days, solidified to a grease-like solid.

Example II

Preparation of di(2-ethylhexyl) amine thiocyanate

Thirteen parts of di(2-ethylhexyl) amine and 3.8 parts of ammonium thiocyanate were mixed and warmed on a steam bath for an hour, then allowed to stand 15 hours. The mixture was dissolved in benzene, filtered, and the benzene removed under reduced pressure. A reddish semi-solid was obtained which weighed 14 grams and which showed appreciable solubility in a number of mineral oils. It also showed a strongly positive test for thiocyanate ion when shaken with aqueous ferric chloride.

Example III

Preparation of amine thiocyanates from reduced petroleum nitrogen bases

Twenty parts of nitrogen bases, which had been obtained during the refining of crude petroleum and which had been catalytically reduced, were mixed with 20 parts of ammonium thiocyanate and warmed slightly on the steam bath. After evolution of ammonia had ceased, the mixture was worked up in the usual way, yielding 25 grams of a deep-red liquid which gave a positive test for the thiocyanate radical. The reduced nitrogen bases, used in this preparation, had the following characteristics: boiling range, 177–230° C.; neutralization value, 316 mg. H_2SO_4/gm.; apparent molecular weight, 155; color, water-white.

Example IV

Preparation of dodecylamine thiocyanate

Fifteen and two-tenths parts of ammonium thiocyanate were added to 37 parts of dodecylamine. After evolution of ammonia ceased, the mixture was heated at 112° C. for 1 hour. The product was washed with low-boiling naphtha and filtered, yielding 45 parts of a white crystalline waxy solid. On analysis, this product showed 23.15% SCN, the theoretical value being 23.77%.

In a manner similar to the above examples, an amine thiocyanate mixture was prepared from a mixture of amines obtained from alcohols derived by the catalytic reduction of coconut oil and containing an average of 12 carbon atoms in the amine molecule. The amine thiocyanate mixture was a brown soft grease-like material. This amine thiocyanate mixture is hereinafter referred to as "Lorol" amine thiocyanate. The amine thiocyanate from tributylamine was a deep red liquid.

The effect of these compounds, on the film strengths of lubricating oils, was determined on the Cornell friction tester. This machine consists essentially of a steel pin, held in place by a brass shear pin, which rotates between the flat surfaces of two cylindrical steel blocks. These blocks serve as part of a jaw mechanism which is drawn together at a uniform rate by means of a ratchet and screw during operation, thus applying a continuously increasing load between the steel pins and blocks. The point at which the lubricating film breaks down sufficiently to permit seizure is indicated either by the development of a "squeal" or by the shearing of the brass pin. In the following table, the jaw load at point of seizure is given in pounds for various compounds.

Table I

Cornell film strength tests

[Using a naphthenic base SAE-30 oil]

Compound	Concentration, per cent by weight	Load at seizure, pounds
None—control		750
Dodecylamine thiocyanate	0.5	950
	1.0	2,375
Oleylamine thiocyanate	0.5	2,250
Tributylamine thiocyanate	1.0	2,125
"Lorol" amine thiocyanate	1.0	2,250
Amine thiocyanate from reduced petroleum nitrogen bases	1.0	2,500
Di(2-ethylhexyl)amine thiocyanate	1.0	2,250

In addition to improving film strength, these

compounds serve to inhibit oxygen absorption by mineral oils. This effect was demonstrated in the following manner: 25 grams of a water-white mineral oil was placed in a 250 cc. flask containing a tube charged with soda-lime. The flask was filled with oxygen, stoppered tightly, placed in an oil bath at 160° C. and connected to a mercury manometer. The time for oxygen absorption to begin, as noted by rise of mercury in the manometer tube, was recorded as the induction period. The effect of amine thiocyanates, on prolonging the period until oxygen absorption began, is shown in the following table.

TABLE II

Oxygen absorption tests in a water-white oil

Compound	Concentration	Induction
	Per cent by weight	Per min.
None—control		25
Dodecylamine thiocyanate	0.50	Above 330
Di(2-ethylhexyl)amine thiocyanate	0.25	Above 300
Oleylamine thiocyanate	0.25	368
Dodecylamine	0.50	28
Dodecyl thiocyanate	0.50	23

Dodecylamine and dodecyl thiocyanate have been included in the above table to show that the stabilizing action resides in the combination of amine and thiocyanate radicals and not in either radical individually and separately.

Similar oxygen absorption tests were performed on a naphthenic base SAE 30 oil, using, as a criterion of stabilizing action, the time required to absorb oxygen equivalent to six inches of mercury.

TABLE III

Oxygen absorption tests in a naphthenic base SAE 30 oil

Compound	Concentration, per cent by weight	Minutes to 6 inches mercury rise
None—control		415
Oleylamine thiocyanate	0.25	490
None—control		515
Dodecylamine thiocyanate	0.25	[1] Above 655

[1] Mercury had risen 3.7 inches at this time.

Since mineral oils must operate in the presence of metals and frequently become contaminated with metal soaps, an oxygen absorption test at 160° C. was made on the naphthenic base SAE 30 oil containing 60 parts per million of iron as iron oleate. The effectiveness of an amine thiocyanate is shown in the data in Table IV.

TABLE IV

Oxygen absorption tests in naphthenic base SAE 30 oil using iron catalyst

Compound	Concentration, per cent by weight	Minutes to 6 inches mercury rise
None—control		125
Dodecylamine thiocyanate	0.25	380

A similar series of tests at 160° C. was conducted using a paraffin base SAE 30 oil, the data being summarized in Table V.

TABLE V

Oxygen absorption tests in paraffin base SAE 30 oil

Compound	Concentration, per cent by weight	Minutes to 6 inches mercury rise
No catalyst		
None—control		225
Dodecylamine thiocyanate	0.25	450
Catalyst—60 parts per million iron (as oleate)		
None—control		95
Oleylamine thiocyanate	0.25	240

The ability of an amine thiocyanate to prevent deposition of oil insoluble sludge was tested in the following manner: a standard amount of a benzene extract of motor oil engine sludge, obtained during engine testing of various oils, was added to the oil under test containing 2% of the amine thiocyanate and 2% of naphthenic acid. After agitation at 150° C., samples of this mixture were diluted with an equal volume of standard naphtha, centrifuged, and the volume of precipitated sludge measured. Results were expressed as per cent dispersion compared with the control containing no additive. In this test, 2% of oleylamine thiocyanate resulted in 99% sludge dispersion when tested in a naphthenic base SAE 20 oil.

Other amine thiocyanates, which are suitable for use in this invention, are listed below:

Dimethylamine thiocyanate
Diethylamine thiocyanate
Tripropylamine thiocyanate
Diamylamine thiocyanate
Hexylamine thiocyanate
Trihexylamine thiocyanate
Cyclohexylamine thiocyanate
Dicyclohexylamine thiocyanate
Tricyclohexylamine thiocyanate
Cyclopentylamine thiocyanate
Dicyclopentylamine thiocyanate
Tricyclopentylamine thiocyanate
Octylamine thiocyanate
Dioctylamine thiocyanate
Butyl cyclohexylamine thiocyanate
Octadecyl cyclohexylamine thiocyanate
Dioctadecylamine thiocyanate
Ethyl decahydronaphthylamine thiocyanate
Propyl decahydronaphthylamine thiocyanate
Diethyl cyclohexylamine thiocyanate
Dimethylaminoethylamine thiocyanate
Diethanolamine thiocyanate
Triethanolamine thiocyanate
Morpholine thiocyanate
Furfurylamine thiocyanate
Tetrahydrofurfurylamine thiocyanate
Decylamine thiocyanate
Undecylamine thiocyanate
Methyl butylamine thiocyanate
Methyl octadecylamine thiocyanate
Ethyl cyclohexylamine thiocyanate
Dimethyloctadecylamine thiocyanate
Hexamethylenediamine di-thiocyanate
Decamethylenediamine di-thiocyanate
Propylenediamine di-thiocyanate
Ethylenediamine di-thiocyanate
3-nitropropylamine thiocyanate
5-carbomethoxyamylamine thiocyanate
5-carbamidoamylamine thiocyanate
Diethylaminoethylthioethylamine thiocyanate
p-Ethoxycyclohexylamine thiocyanate
p-Propylthiocyclohexylamine thiocyanate

Cyclohexanolamine thiocyanate
o,o'-Dihydroxydicyclohexylamine thiocyanate
Methallylamine thiocyanate
Dimethallylamine thiocyanate
Allylamine thiocyanate
Isobutylamine thiocyanate
Diisobutylamine thiocyanate
Ethoxyethoxyethylamine thiocyanate
Ethylthioethylamine thiocyanate

Mixtures of amine thiocyanates or amine thiocyanates derived from mixed amines may be used. Amines, derived from fatty acids obtained from vegetable, animal or fish oils, as well as those derived from acids obtained by oxidation of paraffin or other petroleum fractions or by oxidation of alcohols obtained during hydrogenation of carbon oxides, may be used in making the amine thiocyanates. Naphthenylamine thiocyanates are very suitable for use in this field.

It will be understood that the above examples and tests have been given for illustrative purposes only. It will be readily apparent to those skilled in the art that many variations and modifications can be made in the compounds employed, the proportions, the conditions and the like. For example, the amine thiocyanates of my invention may be employed in conjunction with other additives such as fatty acid esters, organic phosphates, organic phosphites, halogenated aromatic compounds, pour point depressants, viscosity index improving agents, or anti-ring sticking agents. They may be employed in greases or in specially compounded oils, such as those containing lard oil, fish oil, or castor oil. They may be employed in fuel oils for the purpose of improving the lubrication of the pumps or other moving parts through which the fuel oil passes.

Mineral oil compositions of the type described herein may be used in the lubrication of internal combustion engines, for bearings subjected to high speeds and high pressures, for gear lubrication of the hypoid, spiral, or bevel types, for railroad rolling stock, and in marine engines. They may be used as bases for greases and as protective coatings for steel or other metal surfaces. They may be used as a component of Diesel-engine fuel oils.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid.

2. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine contains a total of at least 8 carbon atoms.

3. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine contains from 12 to 18 carbon atoms.

4. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine, except for amino nitrogen atoms, consists of carbon and hydrogen.

5. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine contains a total of at least 8 carbon atoms and, except for amino nitrogen atoms, consists of carbon and hydrogen.

6. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine contains from 12 to 18 carbon atoms and, except for amino nitrogen atoms, consists of carbon and hydrogen.

7. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a monoamine.

8. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a monoamine containing a total of at least 8 carbon atoms.

9. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a monoamine and, except for the nitrogen of the amino group, consists of carbon and hydrogen.

10. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a monamine containing a total of at least 8 carbon atoms and, except for the nitrogen of the amino group, consists of carbon and hydrogen.

11. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a monoamine containing from 12 to 18 carbon atoms and, except for the nitrogen of the amino group, consists of carbon and hydrogen.

12. A viscous hydrocarbon oil having incorporated therein a small proportion, sufficient in amount to substantially inhibit absorption of oxygen by the oil, of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a primary aliphatic monoamine containing at least 8 carbon atoms and, except for the nitrogen of the amino group, consists of carbon and hydrogen.

13. A viscous hydrocarbon oil having incorporated therein from about 0.2% to about 2.0% of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a primary a-cyclic aliphatic monoamine containing from 12 to 18 carbon atoms and, except for the nitrogen of the amino group, consists of carbon and hydrogen.

14. A viscous hydrocarbon oil having incorporated therein from about 0.2% to about 2.0% of oleylamine thiocyanate.

15. A viscous hydrocarbon oil having incorporated therein from about 0.2% to about 2.0% of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a primary acyclic unsaturated aliphatic monoamine containing at least 8 carbon atoms and, except for the nitrogen of the amino group, consists of carbon and hydrogen.

16. A viscous hydrocarbon oil having incorporated therein from about 0.2% to about 2.0% of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a primary acyclic saturated aliphatic monoamine containing at least 8 carbon atoms and, except for the nitrogen of the amino group, consists of carbon and hydrogen.

17. A viscous hydrocarbon oil having incorporated therein from about 0.2% to about 2.0% of an aliphatic amine salt of thiocyanic acid, in which the aliphatic amine is a primary cyclic aliphatic monoamine containing at least 8 carbon atoms and, except for the nitrogen of the amino group, consists of carbon and hydrogen.

18. A viscous hydrocarbon oil having incorporated therein from about 0.2% to about 2.0% of dodecylamine thiocyanate.

19. A viscous hydrocarbon oil having incorporated therein from about 0.2% to about 2.0% of aliphatic amine salts of thiocyanic acid, in which the aliphatic amines are reduced petroleum nitrogen bases.

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