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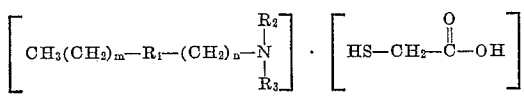
3,060,166

S-AMINE SALTS OF THIOGLYCOLIC ACID

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This invention relates to certain new S-amine salts of thioglycolic acid and to improved lubricating oil and gasoline fuel compositions containing the same. In particular, the amine salts of this invention can be represented by the structure,



wherein m is an integer from 0 to 17, n is an integer from 0 to 17, the sum of m and n is from 9 to 17, R_1 is selected from —CH=CH—, —CH_2—CH_2—, and sulfurized —CH=CH—, and R_2 and R_3 are selected from hydrogen and aliphatic radicals containing from 1 to 4 carbon atoms. The S-amine salts of thioglycolic acid of this invention, as defined above, are herein referred to as S-amine thioglycolates.

The S-amine thioglycolates of this invention are useful as additives for gasoline fuels to improve the anti-icing or de-icing properties thereof, and as additives for lubricating oils to improve the lubricating properties of the base stock oil. In particular, these new S-amine thioglycolates can be combined with certain other addition agents for hydrocarbon lubricating oils, which together cooperate with each other and the base stock oil to provide lubricating compositions having performance levels more than adequate to meet the extreme requirements of vehicle differentials having both hypoid-type gears and limited-slip mechanisms, as well as meeting the lubricating requirements for automatic transmissions.

Due to design, a conventional differential will always drive the wheel which offers the least resistance to turning. As a result, a vehicle equipped with a conventional differential, under adverse conditions, loses traction driving force as evidenced by wheel spinning when the traction wheels bounce over rough roads or non-uniform traction surface conditions such as ice and snow spots, wet and dry pavements, sand and gravel. There has recently been commercialized for use with passenger cars, station wagons, light trucks, and the like, a mechanism known as a locking differential or limited-slip differential, which mechanism permits an automotive axle to transmit the major driving force to the wheel with the better traction, thus minimizing the disadvantages of driving, under adverse conditions, a vehicle equipped with a conventional differential.

With the commercial advent of limited-slip differentials, the use of known hydrocarbon lubricating oils and hydrocarbon lubricating oil compositions containing additives has not proved adequate to meet the lubrication requirements of both the hypoid gears and the limited-slip differential mechanism. The non-effectiveness of said known oils and compositions is apparent in the case of a limited-slip differential, for example, from the stick-slip action (resulting in an objectionable "chatter" which may reach the proportion of "thumping") resulting when a vehicle provided with such a device makes a turn, thus instigating action in the limited-slip mechanism.

Various known lubricity agents have been added to gear lubricants in attempts to alleviate the stick-slip problem. In general, while these lubricity agents, such as

methyl oleate, glycerol mono-oleate, desulfurized degras and sulfurized sperm oil, help to alleviate the stick-slip problem, it was found that other properties which were "built" into the gear lubricants to meet the requirements of the hypoid gearing were deleteriously affected. Thus, for example, a hydrocarbon oil lubricant containing various multipurpose additives, which lubricant would meet the specifications of MIL-L-2105A, would not meet those specifications after the addition of one of these known lubricity agents in an amount sufficient to eliminate the stick-slip problem.

It is an object of this invention to provide a class of new compounds which, when combined with a hydrocarbon oil such as a mineral oil fraction of appropriate lubricating viscosity, are effective to improve the anti-wear and extreme-pressure lubricating characteristics of such oils. A further object is to provide improved lubricating compositions which alleviate the stick-slip problem associated with limited-slip differentials and also eliminate the undesirable disturbance in automatic transmissions known as "squawk" which occurs when the "bands" of such a transmission are engaged. It is also an object of this invention to provide a class of compounds which, when combined with certain other classes of oil addition agents, cooperate with each other and the base oil to provide hydrocarbon oil compositions which pass the MIL-L-2105A specification and, in addition, satisfactorily alleviate the stick-slip problem of limited-slip differential mechanisms.

It is a further object of this invention to provide a class of compounds which, when added to gasoline fuel compositions, inhibit the formation of ice or ice crystals, thereby providing gasoline fuels less adversely affected by climate conditions.

Referring to the structural formula for the S-amine thioglycolates of this invention, the aliphatic radicals from which R_2 and R_3 can be selected are preferably alkyl radicals containing from 1 to 4 carbon atoms, but can be other aliphatic radicals, such as hydroxyalkyl or haloalkyl radicals. Examples of such radicals are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert.-butyl, hydroxypropyl, hydroxyethyl, beta-chloroethyl, and the like.

Examples of amines which can be used to prepare the S-amine thioglycolates of our invention are dodecylamine, dodecenylamine, sulfurized dodecenylamine, tridecylamine, tridecenylamine, sulfurized tridecenylamine, tetradecylamine, N,N-2-hydroxypropyl octadecenylamine, N,N,N-di-2-hydroxypropyl octadecenylamine, N,N-hydroxylethyl octadecenylamine, N,N-hydroxybutyl octadecenylamine, tetradecenylamine, sulfurized tetradecenylamine, pentadecylamine, pentadecenylamine, sulfurized pentadecenylamine, hexadecylamine, hexadecenylamine, sulfurized hexadecenylamine, heptadecylamine, heptadecenylamine, sulfurized heptadecenylamine, octadecylamine, octadecenylamine, sulfurized octadecenylamine, nondecylamine, nondecenylamine, sulfurized nondecenylamine, eicosylamine, eicosylnylamine, sulfurized eicosyenylamine, methyldodecylamine, dimethyldodecylamine, diisopropyl pentadecylene amine, diethyl octadecenylamine, methylethyl octadecylamine, methylbutyl sulfurized octadecenylamine, and dimethyl eicosylamine. By "sulfurized," as used herein (for example, sulfurized dodecenylamine), we mean that sulfur has been introduced into an olefinic bond, although the precise chemical structure of the resulting product is uncertain. The sulfurization of the compounds disclosed herein can be accomplished by methods known to the art.

The S-amine thioglycolates of this invention can be prepared by methods known to the art. As non-limiting examples of the preparation of such compounds, the following are illustrative. Parts are parts by weight unless otherwise stated.

EXAMPLE 1

To a suitable reaction vessel there are charged 144 parts of 9,10-octadecenylamine, such as is commercially available as a product sold by Armour and Company under the trademark "Armeen O." Forty-six parts of thioglycolic acid are added to the amine while agitating the mixture, causing the temperature of the mixture to rise to about 60° C. The resulting compound, the S-octadecenylamine salt of thioglycolic acid, is a clear viscous liquid having an amber color and is readily soluble in hydrocarbon oils of lubricating viscosity.

EXAMPLE 2

Into a suitable reaction vessel there are charged 430 parts of 9,10-octadecenylamine. After heating the amine to about 125° C., 48 parts of sulfur are slowly added, after which the mixture is maintained at about 120–125° C. for about 8 hours. Analysis of the product, sulfurized octadecenylamine, shows the presence of about 5.7% sulfur.

EXAMPLE 3

About 125 parts of sulfurized octadecenylamine, as prepared in Example 2, and 37.5 parts of thioglycolic acid are charged into a suitable reaction vessel and thoroughly mixed, causing some H_2S foaming. The product, the sulfurized S-octadecenylamine salt of thioglycolic acid, is similar to the product of Example 1, except for being of higher viscosity as compared to the unsulfurized S-octadecenylamine salt of glycolic acid.

As hereinbefore stated, the amine portion of the S-amine thioglycolate of our invention can be saturated, unsaturated or sulfurized. Saturated amines are available commercially, but can also be prepared by hydrogenation of unsaturated amines by methods known to the art, as, for example, by hydrogenation using a nickel catalyst. Sulfurized amines can be prepared from unsaturated amines by known methods, such as, for example, by the slow addition of sulfur to unsaturated amines at a temperature of about 125° C.

The S-amine thioglycolates of the present invention can be employed in any lubricating oil or lubricating oil composition. Thus, for example, our additives can be employed in hydrocarbon oil lubricants, including the so-called "heavy-duty" types of lubricants containing various functional additives. Suitable base stocks include, for example, mineral oils and synthetic oils. An example of a mineral oil is a petroleum fraction of lubricating viscosity. Examples of synthetic oils are those obtained by the polymerization of olefins, cracking coal tar fractions, animal, vegetable or fish oils or their hydrogenated products, and mixtures thereof with mineral oils. The viscosity of the oil may vary, depending upon the intended application of the finished lubricant, from about 1 to about 10,000 centistokes at 100° F. Particularly preferred for use in this invention, i.e., in the hypoid gears of automotive vehicles, are hydrocarbon oils having viscosities from about 10 to about 1,500 centistokes at 100° F. The oil should, of course, also be selected on the basis of suitable pour point and viscosity index characteristics for the specific purpose intended, it being understood that the desired characteristics of the finished lubricant may be obtained by the addition of lubricating oil additives to provide the desired properties in the oil.

In addition to the foregoing, we contemplate using the S-amine thioglycolates of our invention in combination with certain other preferred types of additives in hydrocarbon oils to provide a lubricating composition which will provide a level of performance hereinafter described. These preferred types of additives, which are referred to as Types A, B and C, are as follows:

Type A.—A chlorinated aliphatic material or a chlorinated aliphatic material in which part of the chlorine has been replaced with a thiocarbonate group. Suitable

aliphatic materials in either case are those containing from 5 to about 24 carbon atoms.

When a chlorinated aliphatic material is to be used, the higher carbon content materials are preferred, especially petroleum wax or similar material, and chlorination is carried to the level where the average amount of chlorine substituted is about 30% to 70% of the theoretical maximum, and preferably to about 40% to 50% of the theoretical maximum, in order to obtain maximum benefit of such an additive without a serious decrease in solubility, which normally occurs when a highly chlorinated material is used.

When a chlorinated aliphatic material-thiocarbonate reaction product is used, it is usually preferable to use aliphatic materials having from about 5 to about 15 carbon atoms, since the extremely short-chain and extremely long-chain materials are more difficult to react and are less efficient in their effect upon the final formulation. Preferably, a kerosene containing about an average of 10 carbon atoms and having a boiling range of from about 150° C. to about 275° C. is used.

The thiocarbonate group which is used to replace a part of the chlorine is derived from an alkali (Na, K, Li) or alkaline earth (Ca, Sr, Ba) metal salt of a thiocarbonic acid, preferably an alkyl thiocarbonic acid. The thiocarbonate radical can be a mono-, di- or trithiocarbonate, but, in general, preference is given to the dithiocarbonate (xanthate) compounds, characterized by the divalent group (OCS_2). The trithiocarbonate type of compounds, characterized by the divalent group (CS_3), have also been prepared and have been found to form effective extreme-pressure agents in combination with the chlorinated aliphatic material, but from the standpoint of odor and cost, we prefer products in which the thiocarbonate constituent is a xanthate group.

A procedure which may be followed in synthesizing this material involves substantial chlorination of an aliphatic compound or a predominantly aliphatic material, such as a petroleum naphtha, followed by reaction of the chlorinated material with an alkali or alkaline earth metal salt of an alkyl thiocarbonic acid in such proportions and under such conditions that only part of the chlorine is replaced by the alkyl thiocarbonate.

As to the substituents in the thiocarbonate or exanthate groups which are substituted in the chlorinated aliphatic material, it is preferable that such substituents be derived from aliphatic compounds of relatively low molecular weight, e.g., methyl, ethyl, propyl and butyl. There is no particular advantage to be gained by having a long-chain alkyl group in the xanthate or thiocarbonate substituent from the standpoint of solubility, etc., and the lower molecular weight alkyl groups give a finished product in which the content of the chlorine and characterizing divalent thiocarbonate groups (O_2CS, OCS_2 or CS_3) is somewhat more highly concentrated.

Examples of the thiocarbonate or xanthate materials which can be reacted with chlorinated aliphatic materials to provide extreme-pressure agents of the type discussed are sodium or potassium methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, octyl, decyl or dodecyl xanthates or the corresponding mono- or trithiocarbonates.

It is desired that the proportions of reactants used and the conditions of reaction be controlled so that the final product contains both chlorine and thiocarbonate characterizing groups in chemical combination with the aliphatic hydrocarbon material. The relative amounts of chlorine and sulfur or, more specifically, of chlorine and thiocarbonate characterizing groups in the finished product may be varied over a relatively wide range, but, in general, it may be said that the finished product should preferably be one which contains from about 25% to 40% of chlorine and from about 7% to 15% of sulfur. Expressing the sulfur content as the equivalent amount of characterizing thiocarbonate groups present in the product, such preferred products are more accurately identified

as containing from about 10% to about 22% characterizing dithiocarbonate or xanthate (divalent OCS_2) groups or from about 7% to about 17% characterizing trithiocarbonate (divalent CS_3) groups. For general purposes, it may be said that the characterizing thiocarbonate group content is preferably from about 7% to about 22%.

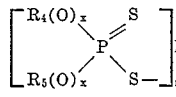
A specific non-limiting example of the preparation of a chlorinated aliphatic-thiocarbonate reaction product is given below. Parts are in parts by weight.

EXAMPLE A

A chlorinated naphtha is first prepared by chlorinating petroleum naphtha (Stoddard solvent) until it contains about 54% by weight of chlorine. Two hundred parts of the chlornaphtha are then dissolved in about 500 parts of acetone and placed in a reaction vessel heated by a water jacket and equipped with a stirrer and reflux condenser. To this solution, 120 parts of potassium isopropyl xanthate are added and the mixture held at its boiling temperature with stirring under reflux for about 2 hours. The resulting mixture is cooled to room temperature, filtered, and the filtrate subjected to distillation to remove the acetone. After removal of the acetone, the product is washed to remove potassium salts and is dried and filtered. The finished reaction product obtained by the foregoing procedure is a dark brown liquid containing about 11% sulfur, or, more specifically, about 16% of the characterizing xanthate (divalent OCS_2) group, and 34% chlorine.

Variation in xanthate and chlorine content of the reaction product can be obtained by varying the degree of chlorination of the naphtha, by varying the amount of alkali xanthate used, and by varying the hydrocarbon substituent in the alkali xanthate. Thus, products of widely varying chlorine and xanthate content are readily possible.

Type B.—A metal salt of a dithio acid of phosphorus represented by the structure,



where M is a metal selected from Zn, Ba, Mg and Ca, but preferably Zn, n is the valence of M, x is one or zero, when x is one, R_4 and R_5 are each selected from acyclic, alicyclic, aromatic and substituted aromatic hydrocarbon radicals, and when x is zero, R_4 and R_5 are selected from substituted and unsubstituted aromatic hydrocarbon radicals.

Examples of acyclic radicals are propyl, butyl, isobutyl, sec.-butyl, amyl, isoamyl, hexyl, isohexyl, 2-ethylamyl, octyl, iso-octyl, 2-ethylhexyl, decyl, dodecyl, tetradecyl and hexadecyl; of alicyclic radicals are cyclopentyl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, amylcyclohexyl; of aromatic radicals and substituted aromatic radicals are those radicals having six or more carbon atoms, such as phenyl, methylphenyl, ethylphenyl, propylphenyl, isobutylphenyl, amylphenyl, nonylphenyl, chlorophenyl and cyclohexylphenyl, di-tert.-butylphenyl, tolyl, xylyl, dichlorophenyl, trichlorophenyl, paraffin wax-substituted phenyl, chlorinated biphenyl, naphthyl, and lauryl phenyl; as well as other radicals which are isomers and homologues of those named.

A non-limiting example of the preparation of a metal salt of a dihydrocarbon dithio acid of phosphorus, where x is 1, is the following:

EXAMPLE B

To a suitable reaction vessel are added and intimately mixed approximately 4 molecular proportions of methyl isobutyl carbinol and approximately one molecular proportion of phosphorus pentasulfide. The mixture is heated at 90–100° C. for about three hours employing a pressure slightly below atmospheric. Thereafter the reaction product (a dithiophosphoric acid) is decanted from the unreacted phosphorus pentasulfide and admixed with a small amount of water and zinc oxide in excess of that theoretically required. The mixture is heated at about 60° for about three hours, cooled and filtered. The dark oily zinc salt of di(1,3-dimethylbutyl) dithiophosphoric acid so obtained analyzes approximately, in weight ratio, one part of phosphorus and approximately 2.2 parts of sulfur per one part of zinc.

A non-limiting example of the preparation of a metal salt of a dihydrocarbon dithio acid of phosphorus, where x is 0, is the following:

EXAMPLE C

In a suitable reaction vessel, a mixture of 222 parts of P_2S_5, 136 parts of zinc chloride and 133 parts of aluminum chloride is slowly added with stirring to 600 parts of sec.-amyl benzene which is kept at a temperature in the range of 40–60° C. Thereafter the temperature of the mass is raised, with continual stirring over a period of about one hour, to about 130° C. and maintained in the temperature range of 130–140° C. for about four hours. After allowing the resulting brownish-colored mixture to cool, 250 ml. of benzene is added and the whole mass is poured with stirring into cold water. The mixture is then filtered, and the benzene layer isolated from the filtrate and concentrated to yield a viscous red oil, which is the substantially pure zinc salt of di-(sec.-amylphenyl) phosphinodithioic acid, containing, by weight, about 12% sulfur, 7.5% phosphorus and 3% zinc.

Type C.—A phosphorized-sulfurized dicyclic terpene is obtained by reacting a dicyclic terpene, such as carene, pinene, camphene, fenchene and similar terpenes containing one double bond in the molecule and comprising two-ring systems, with a phosphorus sulfide at a temperature of about 100–160° C. While any phosphorus sulfide, such as P_2S_5, P_3S_6, P_4S_6, P_4S_3, P_4S_7, etc., can be employed in the preparation of said reaction products, the preferred reaction products are those obtained employing phosphorus pentasulfide (P_2S_5). While the proportions of these reactants will vary depending upon the oil-solubility and oil-improvement properties desired, the preferred product is that obtained by the reaction of about one mol of a phosphorus sulfide with about four mols of a dicyclic terpene at a reaction temperature in the range of about 100–160° C.

As a non-limiting example of the preparation of an oil-soluble sulfurized- and phosphorized-dicyclic terpene, the following is illustrative. Parts are parts by weight.

EXAMPLE D

A mixture of 245 parts of pinene (substantially 1.8 mol) and 220.5 parts of mineral oil (SAE–10 grade motor oil) is charged into a suitable reaction vessel and is heated to 110–115° C. While stirring, 100 parts of phosphorus pentasulfide (substantially 0.45 mol) are added slowly while maintaining the temperature at 110–120° C. The temperature of the mixture is then increased to about 150° C. and stirred at that temperature for one hour. After partial cooling of the reaction mixture, there is added a small amount of clay and the mixture filtered. The filtered product is a clear red viscous oil having a specific gravity of 1.02 at 15.6/15.6° C., a Saybolt viscosity of 145 at 210° F., analyzing about 4.7% phosphorus and about 13% sulfur and containing 43% by weight mineral oil.

Due to the precipitate-forming characteristics of the phosphorized-sulfurized dicyclic terpene while in storage, it may be desirable to incorporate in the composition of this invention a small amount (e.g., 2% to 10% by weight based on the weight of the phosphorized-sulfur-

ized dicyclic terpene) of an oil-soluble alkali metal or alkaline earth metal hydrocarbon sulfonate such as sodium, barium or calcium wax-alkylated benzene sulfonates or petroleum sulfonates.

In general, in the preferred lubricating compositions of this invention, the weight ratio of the metal dihydrocarbon dithiophosphate (or dithiophosphinate) to the phosphorized- and sulfurized-dicyclic terpene will be approximately 1 to 9 parts of the former to 1 part of the latter, and the weight ratio of the chlorinated aliphatic material to the metal dihydrocarbon dithiophosphate (or dithiophosphinate) is approximately 0.5 to 3 parts of the former to 1 part of the latter, and the total weight percent based on the mineral oil base is in the range of about 4% to 20%. Optimum results, however, are obtained when the weight ratio of the metal dihydrocarbon dithiophosphate (or dithiophosphinate) to the phosphorized-sulfurized dicyclic terpene is about 4 to 6.5 parts of the former to 1 part of the latter and wherein the weight ratio of the chlorinated aliphatic material, in which part of the chlorine has been replaced with a thiocarbonate group, to the metal dihydrocarbon dithiophosphate (or dithiophosphinate) is approximately 1 to 1.5 parts of the former to 1 part of the latter. Generally, we employ the aforedescribed three components so that their total weight is in the range of about 8% to 15% by weight based on the hydrocarbon oil.

In order to demonstrate the effectiveness of the compounds described above in fulfilling the objects hereinbefore stated, the following tests were utilized:

High-Speed Axle Test

This test is a research technique for determining load-carrying and extreme-pressure lubrication characteristics of universal gear lubricants in axles under conditions of high speed and shock loading. All tests were performed according to the procedure established by the Coordinating Research Committee (CRC) and given the designation L–42–458. This test differs from CRC test L–19–645 in that the peak torques are approximately two to three times those obtained in the L–19 procedure. Results of the L–42 test are stated as "pass" or "fail," a pass being equivalent to the performance which is obtained with CRC Reference Gear Oil (R60)–110–57.

Limited-Slip Test

This is a test devised to enable evaluation of the effectiveness of various additives in hydrocarbon oils in alleviating the stock-slip problem. The test is as follows: The apparatus to be used is assembled as required for a high-speed and shock-loading test (CRC designation L–42). In our tests we used a Spicer Model 44–1 rear axle equipped with gears having a 47:12 ratio (as required for the L–42 test), which had incorporated therein a limited-slip or locking differential device manufactured by the Dana Corporation. The clutch plates in the differential (which are part of the slip-limiting mechanism) are arranged for the milder setting (i.e., two splined plates between two tonged plates, giving three friction surfaces). The field current on the right dynamometer (i.e., the dynamometer occupying the position of the right rear wheel if the test equipment were a vehicle) is adjusted to give a 65-pound load at 100 r.p.m., and the field current on the left dynamometer is adjusted to give a 15-pound load at 100 r.p.m. The carburetor idle screw is adjusted to give a 30-wheel r.p.m. at no load (i.e., no differentialing). After completing the above, maximum axle differentialing is obtained, using second gear of a four-speed transmission, by accelerating to 100-wheel r.p.m. using a 10-inch manifold vacuum. Differentialing and noises due to the action of the clutches are observed. The above cycle is repeated once using a 10-inch manifold vacuum and twice using a 5-inch manifold vacuum. The complete evaluation of the additive undergoing test is accomplished using the following dynamometer load combinations:

Rating	Right	Left
1	65	15
2	165	15
3	265	15
4	365	15
1	15	65
2	15	165
3	15	265
4	15	365

The test composition is given a two-number rating, which rating is dependent upon the load conditions at which the first reproducible noise is observed. Thus, if under "right turn" conditions a reproducible noise (as a grind or chatter) occurred at 265–15, and under "left turn" conditions, at 15–165, the additive would be rated 3–2. If no noise is observed under any of the test conditions, an additive would be rated 5–5. The temperature of the hydrocarbon oil composition within the axle is maintained between 150° C. and 200° C. As a precautionary measure, a break-in and warm-up period for each composition is provided by running at speeds not greater than 100-wheel r.p.m., under conditions resulting in differentialing, first in one direction and then in the other. For a more stringent test, the clutch plates are arranged to provide five friction surfaces (i.e., by alternating the splined and tonged plates). In expressing the results, the average of a rating is usually expressed. Thus, a 5–3 rating (or a 4–4 rating) would be expressed as a 4 rating. The significance of the ratings is as follows:

5, pass—No chatter under any of the test conditions.
4, pass—Some chatter under severe test conditions.
3, borderline—Chatter under severe test conditions.
2 or 1, fail—Chatter under mild test conditions.

The results observed in the latter three tests are tabulated below. The percent additive is percent by weight based on the weight of the hydrocarbon oil.

Spl. No.	Test Composition	Weight Percent of Additive	LSD Test	L–42
1	Gear Oil "A"		2	Pass.
2	"A" plus octadecenylamine salt of thioglycolic acid.	0.25	5	Pass.
		0.125	3	
3	"A" plus sulfurized octadecenylamine salt of thioglycolic acid.	0.25	5	Pass.

The amount of the new S-amine thioglycolates of our invention used with a hydrocarbon oil or hydrocarbon oil composition can vary over a range dependent to some extent upon the particular application in which said oil is to be used. Generally, not over about 10% by weight is sufficient. When these additives are used in combination with other additives in a hydrocarbon oil designed to give performance sufficient to pass the L–19 and L–42 tests, the amount which is used will generally be from about 0.1% to about 1.5% by weight, based upon the amount of said oil, although we prefer to use from about 0.25% to about 1% by weight, based upon the oil content.

As is seen from the above results, the base composition (Gear Oil "A") used would pass the L–42 test, but would not pass the LSD test (sample 1). Gear Oils "A," "B" and "C" contained the aforedescribed preferred additives in quantities falling within the specified ranges for such additives and, more particularly, had the following composition.

GEAR OIL "A"

Ingredient:	Percent by weight of composition
Solvent-refined Mid-Continent SAE 90 oil	90.1
Reaction product of Example A	4.3
Reaction product of Example B	4.3
Reaction product of Example D	1.3
Total	100.0

The additives used to make the base oil composition can be varied within the prescribed limits for those additives while maintaining performance levels adequate to pass the L–42 test. However, for purposes of showing the performance results of the S-amine thioglycolates of our invention, the base oil composition was not varied.

In addition to the aforedescribed, the S-amine thioglycolates of our invention are suitable for use in hydrocarbon oils of lubricating viscosity which, although not "built" to a level which will give a performance capable of passing the L–42 test, can be used for applications where only a performance level as defined by the L–19–645 test is needed. Examples of such compositions are those containing about 2% to about 15% by weight of those preferred additives designated as Type A and about 1% to about 5% by weight of those preferred additives designated as Type B. Such compositions can also contain a small amount of an oil-soluble alkali metal or alkaline earth metal hydrocarbon sulfonate as previously described. More particular examples of such compositions which also contain an additive of our invention are as follows. Percentages are by weight, based upon the hydrocarbon oil content.

D. SAE–90 oil plus
- 7.5% chlorinated wax (about 40% chlorination)
- 2.5% zinc dihexyl dithiophosphate
- 3.35% S-octadecenylamine salt of thioglycolic acid

E. SAE–90 oil plus
- 5.0% reaction product of chlorinated kerosene (containing about 10 carbon atoms) and sodium ethyl xanthate
- 4.2% zinc dihexyl dithiophosphate
- 0.35% S-octadecenylamine salt of thioglycolic acid

As mentioned above, the S-amine thioglycolates of this invention are particularly useful in gasoline fuels as a carburetor anti-icer, that is, to eliminate icing in carburetors which results in stalling commonly encountered when operating a gasoline engine under idling conditions when the air is moist and cool. The S-amine thioglycolates, as additives for gasoline fuels, are compatible with other conventional gasoline additives such as lead alkyl anti-detonants, dyes, gum inhibitors, oxidation inhibitors, and the like, and the gasoline compositions of this invention can include such additives.

In addition to preventing carburetor icing, the S-amine thioglycolates of this invention prevent icing in other mechanisms where the presence of moisture is not dependent upon atmospheric moisture. For example, almost all gasoline engine-powered vehicles are normally provided with filters, such as filter screen or micronic filters, in the fuel supply system so as to prevent the passage of solid contaminants, e.g., rust particles, into the engine. When ice is formed in the gasoline used, it will often plug the filters, thus stopping the flow of fuel to the engine. In the case of vehicles operating upon the ground or water surface, this is at least inconvenient; but in aircraft, such stoppage involves a grave risk to human life. Because of this danger, most aircraft are provided

with an automatic filter by-pass. However, upon the opening of the by-pass, the ice is passed into injector mechanism and the like, which contain parts having close and critical tolerances. Here the ice can also cause difficulties, including malfunctioning of these mechanisms, so that a dangerous condition may still exist.

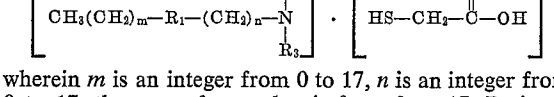
When employing the S-amine thioglycolates as additives for gasoline fuels, the specific amount to be added will depend, to some extent, upon the composition of the base fuel. Thus it is known that carburetor icing is governed to some extent by the volatility of the fuel, in addition to the weather conditions of the area where the fuel is to be used. Thus, the S-amine thioglycolates must be employed in an effective amount sufficient to overcome anticipated icing problems. Generally, it has been found that the use of S-amine thioglycolates in an amount of from about 0.01% to about 1.0% by weight of the base fuel is adequate for conditions encountered in the continental United States.

Examples of base fuels in which the S-amine thioglycolates of this invention can be used are those defined in specifications MIL–F–5572 of the United States Armed Forces for aviation use, and MIL–G–3056 for automotive use, as well as Fuel M as defined in United States Federal Specification VV–M–561*a* for regular and premium grades of gasoline in Classes A, B and C.

Other modes of applying the principles of this invention will be apparent to those skilled in the art. Accordingly, while this invention has been described with reference to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it may be variously practiced within the scope of the following claims.

What is claimed is:

1. S-amine salts of thioglycolic acid represented by the structure,



wherein m is an integer from 0 to 17, n is an integer from 0 to 17, the sum of m and n is from 9 to 17, R_1 is selected from —CH=CH—, —CH_2—CH_2—, and sulfurized —CH=CH—, and R_2 and R_3 are selected from hydrogen, alkyls, hydroxyalkyls and haloalkyls containing from 1 to 4 carbon atoms.

2. The amine salts of claim 1 wherein R_2 and R_3 are hydrogen.

3. The amine salts of claim 2 where R_1 is

—CH=CH—

4. The amine salts of claim 2 where R_1 is sulfurized —CH=CH—.

5. The amine salts of claim 2 where R_1 is

—CH_2—CH_2—

6. The amine salts of claim 2 wherein m is 8 and n is 7.

7. The amine salts of claim 6 wherein R_1 is sulfurized —CH=CH—.

8. S-octadecenylamine salt of thioglycolic acid.

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