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RUST INHIBITORS COMPRISING LITHIUM SALTS

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ABSTRACT OF THE DISCLOSURE

The lithium salts of hydrocarbon-substituted succinic anhydride, wherein the hydrocarbon substituent is an aliphatic hydrocarbon group having about 9 to about 30 carbon atoms, are effective as rust and corrosion inhibitors in lubricating oil compositions. These salts are rendered more oil-soluble by combining them with alkyl phenols.

Related application

This application is a continuation-in-part of copending application, Ser. No. 798,123, filed Feb. 10, 1969, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to new chemical compositions and to lubricating oil compositions containing the same. More particularly, it relates to a novel class of chemical compositions which act as rust and corrosion inhibitors in lubricating oils. Still more particularly, this invention relates to a lithium salt of a hydrocarbon-substituted succinic acid or anhydride having between 9 and 30 carbon atoms in the hydrocarbon substituent, in combination with an alkyl phenol solubilizer as a lubricant additive.

Description of the prior art

The prior art has taught the need for efficient rust inhibitors in lubricating oils. The need is especially prevalent in engines which are infrequently operated and particularly in engines which are subject to extended storage in humid climates. These engines experience excessive rusting of cylinder walls, wrist pins and other polished working surfaces. Such rusting can be explained by the fact that moisture accumulates within the engine, penetrates the lubricating film, and attacks ferrous surfaces. The attack is also aggravated by residues of chlorine compounds and bromine compounds left from the combustion of gasolines containing tetraethyl lead and a scavenging agent such as ethylene dibromide. The prior art has also shown the need for efficient corrosion inhibitors to prevent or reduce the deposition of lacquer or varnish-like coatings on the walls of the cylinders, piston rings, etc., and to prevent or reduce the corrosion of engine parts, bearings etc. An example of a specific purpose served by a corrosion inhibitors is the prevention of copper-lead bearing corrosion.

It is well known in the prior art that C_9–C_{30} alkenyl succinic anhydrides and acids are good ashless rust inhibitors for motor lubricants. But (in ashless formulation) they cause considerable copper-lead bearing weight loss.

It is also well known in the art that lithium salts of hydrocarbon-substituted succinic acids having at least about 50 aliphatic carbon atoms in the hydrocarbon substituent such as C_{50} polyisobutenyl succinic anhydride (conveniently designated PIBSA) are effective rust and corrosion inhibitors in lubricating compositions. (See U.S. Pat. No. 3,351,552.) However, this and other prior art references teach that, when using a salt of a hydrocarbon-substituted succinic acid, the size of the hydrocarbon substituent of the succinic compound appears to determine the effectiveness of the additive in lubricating oils. Thus, the prior art is replete with statements to the effect that it is critically important that said substituent be large; that is, that it have at least about 50 aliphatic carbon atoms in its structure that the molecular weight of the hydrocarbon substituent should be within the range of about 700 to about 10,000. Because such salts have high molecular weight hydrocarbon substituents, a relatively higher weight percent active ingredient content in oil is required than would be necessary if shorter chain hydrocarbon succinic acid salts could be used. However, as indicated, salts of the shorter chain aliphatic-hydrocarbon-substituted succinic acids have heretofore not been used in lubricating oils because they present oil solubility problems.

SUMMARY OF THE INVENTION

It has now been discovered that the lithium salts of C_9–C_{30} aliphatic-hydrocarbon-substituted succinic anhydrides and acids (conveniently designated ASA) can be made more soluble in lubricating oils by combining them with a C_5–C_{30} alkyl phenol. The hydrocarbon substituents will be either alkyl groups or alkenyl groups. The lithium salts thus modified are not only excellent rust inhibitors, but also show marked resistance to Cu-Cb corrosion. A particular advantage of the invention is that by making the lithium salts more oil-soluble, it is possible to prepare liquid oil concentrates, which greatly facilitates blending operations when making finished lubricating oil compositions.

DETAILED DESCRIPTION

The salts of this invention are prepared by reacting a C_9–C_{30} ASA with a lithium base such as lithium oxide, hydroxide, carbonate or alkoxide. The product can be the full or half salt of the ASA, both of which show excellent rust and corrosion inhibition.

The alkenyl-substituted or alkyl-substituted succinic acids and anhydrides used in forming the salts of this invention must have an aliphatic hydrocarbon substituent containing at least 9 and up to about 30 carbon atoms. Preferably, the substituent has 10 to 20 carbon atoms. Alkenyl-substituted acids and anhydrides are obtained by conventional methods known in the art which simply involve heating maleic anhydride and an olefinic material together, usually in about equal molar portions. By way of example, a C_{10}—C_{12} alkenyl succinic acid anhydride can be prepared by the condensation of maleic acid anhydride and a C_{10}—C_{12} fraction of propylene polymer by heating with agitation for 20 hours under pressure at a temperature of about 350 to 390° F. under gentle reflux. The reaction product is then allowed to cool and is fractionated under diminished pressure to remove unreacted polymer and low-boiling reaction products. The resulting alkenyl succinic acid anhydride can then be employed directly to produce certain of the salts hereinafter described. Alternatively, the anhydrides can be readily purchased as a commercial chemical commodity. In the present invention, either alkenyl succinic anhydrides or the corresponding acids can be used and it is to be understood that any general description involving the used of the anhydride is intended to encompass the use of the equivalent acid as well and vice versa. Among the alkenyl-substituted succinic acids and anhydrides which can be used according to the present invention are decenyl, tetradecenyl, hexadecenyl, octadecenyl, eicosenyl, hexaeicosenyl and octaeicosenyl succinic anhydride or acid, and mixtures thereof. A particularly preferred material is dodecenyl succinic anhydride (hereinafter referred to as DDSA) which can

eadily be prepared by the addition of tetrapropylene to naleic anhydride.

In place of the alkenyl succinic acid or anhydride, the orresponding saturated acid or anhydride, or mixtures of saturated and unsaturated materials, can be used. Conersion of the alkenyl group to the alkyl group is usually ccomplished by hydrogenation to saturate the double ond, using procedures well known in the art. See U.S. at. 2,682,489.

In the reaction herein between the ASA and the lithium ase, the reaction temperature can vary from about 50° o about 350° F., and preferably ranges from about 150° o about 300° F. Usually the stoichiometric amount of ithium base necessary to prepare at least the half salt f the dicarboxylic hydrocarbon-substituted succinic acid ill be used, although as much as twice the amount of ase needed to form the full salt can be employed, in hich case basic salts will be formed. Thus, the mole atios of lithium base to ASA can vary, and preferably ange anywhere from about 1:1 to about 4:1. In the ost preferred embodiments of this invention, the mole atios range from about 1:1 to about 2:1.

While it is possible to disperse the insoluble lithium alts of C_9–C_{30} alkenyl or alkyl succinic anhydrides or cids into lubricating oil compositions with the aid of ispersing agents, it is much preferred to work with oil oluble additives as opposed to oil dispersible additives. urthermore, as a practical matter, it is preferred and redominantly the practice to blend additives into lubriating compositions in concentrate form. Usually in a oncentrate, the weight percent of active ingredient anges from about 10 to about 80 weight percent, for here is no economic advantage in using concentrates aving less than 10 weight percent active ingredient. Howver, if one attempts to prepare concentrates wherein the eight percentage of oil insoluble lithium salt of ASA greater than 10, using dispersants, such cencentrates ill form solid gels at ambient temperatures, thus preenting a number of disadvantages in their handling in ubsequent blending operations.

Thus, it is a particular feature of the present invenion that by combining the lithium salts of C_9–C_{30} ASA ith a solubilizer, the said lithium salts are rendered oil oluble to the extent that liquid oil concentrates can be repared having as much as 50 weight percent of lithium alts.

There are a number of oxygen-containing compounds hich will solubilize lithium salts of aliphatic-hydrocaron-substituted succinic acids or anhydrides. Among ese are tall oil fatty acids and alcohols such as isoctanol and nonanol. However, all of these materials ave the disadvantage of reducing or destroying the copper-lead corrosion inhibiting properties of the lithium alts. Of all the oxygen-containing materials that were ound to be solubilizers, only the alkyl phenols made the thium salts soluble in lubricating oils without destroyng the copper-lead corrosion inhibiting properties of the alts and allowed the preparation of a stable liquid conentrate. The phenols used in the reaction mixture inlude alkyl phenols having a total of 5 to 30, and preferbly 8 to 26, carbon atoms in their alkyl side chains and ay be polyhydric phenols containing more than one ring ructure. The so-called bis phenols may be used, also cyl phenols, amino phenols, acetyl phenols and dialkyl henols. Thus, typical compounds include 2,2-bis-(2-ydroxy - 3 - tert - butyl - 5 - methylphenyl) - propane, iethylamino phenols, benzyl amino phenols, acyl amino henols, for example, N-propionyl-p-aminophenol, acetyl henol, and their homologues. Condensation products of uch phenols with aldehydes or ketones, e.g., formaldeyde and acetone, may also be used.

The preferred phenols are monoalkylated monohydroxy henols whose molecular weights are between 150 and 00. Especially preferred are monoalkylated phenols hav-ng 8 to 12 alkyl carbon atoms. Particularly effective compounds include p-octyl phenol, mixed nonyl phenols, mixed dodecyl phenols, and dihexyl phenol.

The phenol that is used to solubilize the ASA salts can be present when the lithium salt is made, or can be added later to the lithium salt. Reaction time of combining these components is not critical. The only requirement is that the phenol be present while the temperature of the mixture is at least as high as the melting point of the salt. Thus, the solubilization which must be carried out while the salt is in liquid phase can be effected at a temperature range of about 300° to about 500° F., and preferably at a temperature range of about 350° to about 450° F.

It is to be understood that the exact nature of the compositions formed upon the addition of the alkyl phenol has not been determined and, while they have been referred to as solubilized lithium salts, it is possible that a lithium phenate complex has been formed between the ASA, the lithium base, and the alkyl phenol or that some other undetermined compositional structure has resulted.

While experiments indicate that in the preferred embodiments of the invention the mole ratio of salt to phenol will range from about 8:1 to about 1:1, ratios ranging from about 15:1 to about 0.5:1 will in many cases also result in the desired oil soluble product.

It has also been found that if the C_9–C_{30} ASA is treated with sulfur before or after, but preferably before, neutralization and solubilization, the resulting product shows no deterioration of Cu-Pb (over a base case containing detergent-inhibitor alone) and has the unexpected advantage of having even greater solubility, thus allowing the manufacture of a 50% active ingredient concentrate with obviously improved ease of handling.

Preferably phosphorus pentasulfide is used to promote the reaction of the acid or anhydride and sulfur. Alternatively, other sulfides, such as P_2S_3, P_4S_3, and P_4S_7, may be employed if desired. The molar ratio of ASA to sulfur to be used can range between about 120:1 and about 0.2:1, and the presence of phosphorus sulfide in a molar ratio of ASA to phosphorus sulfide ranging from about 720:1 to about 1:1 will aid the reaction. Preferably the molar ratio of ASA to S will range from about 60:1 to about 0.5:1 and the molar ratio of ASA to phosphorus sulfide will range from about 150:1 to about 5:1. In the most preferred embodiments of this invention, the molar ratio of ASA to S will range from about 15:1 to about 1:1, and the molar ratio of ASA to phosphorus sulfide will range from about 75:1 to about 10:1. In the reaction herein between the anhydride, the sulfur and the phosphorus sulfide, the reaction temperature can vary from 100° to 450° F., preferably from 250° to 350° F., and the time can vary from 0.1 to 10 hours, preferably from 0.5 to 2 hours. The order of addition of P_2S_5 and sulfur is not important and P_2S_5 can be added first, S can be added first, or they can be added simultaneously.

This invention contemplates the use of 0.01 to 50 weight percent of the products of the present invention in oil compositions. As stated above, the lithium salts of the present invention, in combination with an alkyl phenol, are useful as antirust additives in lubricating oils and when combined with a lubricating oil will form homogeneous liquid lubricating oil compositions which are stable at ambient temperatures. When used as antirust additives, they can be incorporated in lubricating oil compositions in concentrations within the range of from about 0.01 to about 10 weight percent active ingredient, but will ordinarily be used in concentrations of from about 0.01 to about 5 weight percent. Preferably, they will be used in concentrations ranging from about 0.1 to about 1 weight percent active ingredient.

The lubricating oils to which the additives of the invention can be added include not only mineral lubricating oils, but synthetic oils also. The mineral lubricating oils may be of any preferred types, including those derived

from the ordinary paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods. The synthetic oils include synthetic hydrocarbon lubricating oils, as well as dibasic acid esters such as di-2-ethyl hexyl sebacate, carbonate esters, phosphate esters halogenated hydrocarbons, polysilicones, polyglycols, glycol esters such as C_{13} oxo acid diesters of tetraethylene glycol, and complex esters, as for example the complex ester formed by the reaction of 1 mole of sebacic acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethyl hexanoic acid.

While the lubricant compositions herein described are primarily designated as internal combustion engine crankcase lubricants, the additives of the invention may also be employed in other oil compositions, including turbine oils, various industrial oils, gear oils, hydraulic fluids, transmission fluids and the like.

It is within the contemplation of this invention to prepare easily handled liquid additive concentrates in which the concentration of additives is greater than would normally be employed in a finished lubricant. These concentrates may contain in the range of from 10 to 50% of additive on an active ingredient basis, the balance being mineral oil. Such concentrates are convenient for handling the additive in the ultimate blending operation into a finished lubricating oil composition. The additive concentrates can be made up simply by combining the lithium salts and alkyl phenol of the present invention in a suitable mineral oil medium. The additive package can also include other additives that are intended for use along with the additives of the invention in a finished lubricant. Such additives include, for example, detergents and dispersants of the ash-containing or ashless type, oxidation inhibiting agents, viscosity index improving agents, pour point depressants, extreme pressure agents, color stabilizers and antifoam agents. Typical examples of additives serving these purposes are known to those skilled in the art.

Alternatively, although not preferably, the alkyl phenol and the lithium salt can be combined in any aliphatic or aromatic hydrocarbon with a boiling point of about 400° F. or higher, e.g., ortho-cresol or cetane, which, can then be boiled off to leave a readily soluble additive in solid form.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples will serve to illustrate methods of preparing the compositions of this invention and include preferred embodiments of said invention.

EXAMPLE 1

Part A

A solution of 90.4 grams of DDSA (dodecenyl succinic anhydride) in 540 grams of a solvent-refined naphthenic oil having a viscosity at 210° F. of 37 SUS (hereinafter referred to as Oil A) is heated at 320° F. and a solution of 16.8 grams of lithium hydroxide monohydrate dissolved in 40 grams of boiling water is added over a one-hour period with mixing. The product, having a lithium to DDSA molar ratio of about 1:1; solidifies on cooling into a loose grainy grease.

Part B

The product of Part A is reheated to 380° F. and 20 grams of mixed nonyl phenols are added with mixing. The product having an ASA to alkyl phenol molar ratio of about 3.4:1 is allowed to cool and is observed to remain in liquid form. The mixed nonyl phenols are prepared by alkylating phenol with tripropylene to produce a product comprising about 65 to 70 weight percent nonyl phenol and 30 to 35 weight percent dinonyl phenol. The mixture is hereinafter referred to as nonyl phenol .

From Examples 1(A) and 1(B) it can be seen that an alkyl phenol will solubilize an otherwise soluble lithium salt of DDSA and that an 18% concentrate of lithium salt and phenol complex in oil can be prepared by this procedure.

EXAMPLE 2

There is added 20 grams of octyl phenol to a solution of 45.2 grams of DDSA in 540 grams of Oil A. A solution of 16.8 grams of lithium hydroxide monohydrate dissolved in 40 grams of water is then added over a 45 minute period with mixing at a temperature of 280° F. until essentially all the water is boiled off. The temperature is then elevated over a 30-minute period to 400° F. to melt the salt. Upon cooling, the product, a 10% concentrate of lithium salt and phenol complex in oil, is obtained as a clear viscous liquid. The lithium salt has a lithium to DDSA molar ratio of about 2:1.

EXAMPLE 3

The procedure of Example 2 is repeated, substituting, for dodecenyl succinic anhydride, dodecyl succinic anhydride obtained by hydrogenating the dodecenyl succinic anhydride.

EXAMPLE 4

A solution of 90.4 grams of C_{28} ASA (prepared by heating maleic anhydride and octaeicosenyl alpha olefin) in 540 grams of Oil A is heated to 320° F. and a solution of 8.4 grams of lithium hydroxide monohydrate dissolved in 40 grams of boiling water is added over a 30-minute period with mixing. The temperature is raised over a 45-minute period to 400° F. and 10 grams of nonyl phenol is added with mixing. The product on cooling remains in liquid form, and is an additive concentrate suitable for lubricating oil blending operations.

EXAMPLE 5

A solution of 90.4 grams of C_{20} ASA (prepared from maleic anhydride and eicosenyl alpha olefin) in 540 grams of Oil A is heated at 320° F. and a solution of 11.2 grams of lithium hydroxide monohydrate dissolved in 40 grams of boiling water is added over a one-hour period with mixing. Thereafter, 20 grams of C_{16} alkyl phenol is added with mixing and the temperature is raised over a 30-minute period to 380° F. Upon cooling the product concentrate appears as a clear viscous liquid.

EXAMPLE 6

A solution of 123 grams of DDSA in 730 grams of Oil A is heated to 300° F. and a solution of 23 grams of lithium hydroxide monohydrate dissolved in 40 grams of boiling water is added over a 45-minute period with stirring. The temperature is raised to 375° F. and 25 grams of mixed nonyl phenol is mixed into the solution. The solution is cooled to 350° F. and 27 grams of sulfur is added with vigorous mixing over a 15-minute period. The solution is then blown with nitrogen for 10 minutes and allowed to cool. The product analyzes 0.76% sulfur.

EXAMPLE 7

After 95 grams of DDSA has been heated to 280° F., one gram of sulfur is added over a 15-minute period, followed by the addition of one gram of P_2S_5 with mixing over a 30-minute period. After reheating the resulting product to 280° F., 125 grams of Oil A and 18 grams of lithium hydroxide monohydrate dissolved in 40 grams water are added over a one-hour period with mixing. Then 20 grams of nonyl phenol is added and the temperature is raised over a one-hour period to about 400° F. The product is stirred until it is a uniform liquid. The product upon cooling needs no filtering and is observed to be a red brown, clear, viscous liquid.

EXAMPLE 8

A blended base oil was prepared by blending at 140° F. (1) 2.87 weight percent of an oil composition comprising 70% of an amide condensate of polyisobutenyl propionic acid and triethylene pentamine (see preparation in Example 1, U.S. Pat. 3,364,130); (2) 0.95 weight percent of an oil composition consisting of 25 weight percent of a hydrocarbon lubricating oil and 75 weight percent of

. zinc dialkyl dithiophosphate prepared from a mixture of 65% isobutyl alcohol and 35% primary amyl alcohols; (3) 76.94 weight percent of a high viscosity index, phenol-extracted, solvent-dewaxed lubricating oil distillate having a viscosity at 100° F. of 325 SUS; and (4) 9.24 weight percent of a dewaxed, deasphalted paraffinic esidual bright stock.

The base oil, and compositions consisting of the base oil to which different weight percent active ingredient mounts of lithium salts were added, were tested for rust nhibition and corrosion of copper-lead bearings. For rust nhibition a variation of the General Motors MS test eries was used, employing a sequential MSIIA+2 engine nerit test. The MSIIA+2 engine test entails running the egular MSIIA low temperature cycle plus 2 hours of he MSIIIA high temperature cycle, then disassembling nly the parts to be rust rated. The engine crankcase s then drained, filled with new test oil (plus dummy rust est parts) and run to flush the system of all the oil and esidue from the first run. Then, new parts and fresh est oil are placed in the engine for the next run. An ASIIB+2 test was also employed which entails running he regular MSIIB cycle plus 2 hours of the MSIIIB ycle. The MSA series of test is described in ASTM pecial Technical Publication 315C and the MSB series s described in ASTM Special Technical Publication 15X. To test corrosion the standard sequential L-38 Cu-Pb bearing mg. weight loss test was employed. The ollowing Table I shows the data obtained. Except as oted below, the various lithium salts were added as oncentrates, however, the weight percentages in the following tables are on the basis of percent active ingredient n the total composition. The notation Li/2 signifies a alf lithium salt, and Li/2 PIBSA signifies a half lithium alt of polyisobutenyl succinic anhydride, wherein the olyisobutenyl group had an average of 50 carbon atoms.

TABLE I.—FULL-SCALE ENGINE TEST DATA

dditive	Active ingredient, weight percent	MSIIA+2 rust merit	L-38 Cu-Pb BWL (mg.)
one		5.4	65
DSA	0.5	8.7	454
i/2 PIBSA	1.8	9.1	
i/2 PIBSA	1.0	7.5	32
i/2 DDSA [1]	0.3		162
i/2 DDSA [1]	0.2	8.8	138
i/2 DDSA [1]	0.15	7.3	59
i DDSA+C_9 phenol [2]	0.3	8.0	165
i/2 DDSA+C_9 phenol [3]	0.15	7.8	57
i/2 P_2S_5-S-DDSA+C_9 phenol [4]	0.5	9.0	60
		(MSIIB+2)	

[1] Product of Example 1, Part A.
[2] Product of Example 2.
[3] Product of Example 1, Part B.
[4] Product of Example 7.

The data presented in Table I show that the oil soluble combinations of lithium salt and alkyl phenol are as ood rust and corrosion inhibitors as the oil insoluble thium half salts of DDSA, which were incorporated into ne oil compositions for testing purposes through heating, igorous mixing and the use of a dispersant (an amide ondensate of polyisobutenyl propionic acid and tetrathylene pentamine; see British Pat. 1,075,121). This emonstrates that none of the desirable porperties of the thium salts of C_9–C_{30} alkenyl succinic acids or anhydrides re impaired by rendering them oil soluble in accordance ith the present invention. The data in Table I show lso that, while the lithium salts of PIBSA are good rust nd corrosion inhibitors, these higher molecular weight thium salts undergo a marked decrease in rust inhibition as the concentration of active ingredient is reduced to one percent. The lithium salts of PIBSA have been found to be unacceptable as rust inhibitors at concentrations below one percent. Thus, the lithium salts of this invention can be used at much lower concentrations than are required with the prior art higher molecular weight lithium salts in order to obtain satisfactory oil compositions.

It is also to be noted that, while 0.5 wt. percent of DDSA causes a copper-lead weight loss of over 440 mg., the use of the same concentration of a lithium salt of the dodecyl succinic acid treated with sulfur and P_2S_5 shows no increase in copper-lead weight loss over that found in the base oil without any antirust additive.

EXAMPLE 9

Laboratory multiple oxidation tests (LMOT) were run on the blended base oil described in Example 8 and on the base oil plus various additives to test the effect of these additives on oxidation. In this test, 40 gram samples were prepared consisting of the base oil into which different weight percentages of different additives had been incorporated. Then, 2.5° grams of iron filings, a 19" piece of No. 14 gauge copper wire and a sanded aluminum strip (12" x ¼" x 1/16") were added to each composition as catalysts. Air at the rate of 25 cc. per minute was bubbled through the sample, whose temperature was maintained at 300° F. At the end of five days, the neutralization number (ASTM–D–974) of the used, i.e., oxidized, oil was determined. Table II shows the ASTM–D–974 total acid number data obtained from these tests.

TABLE II

LMOT oxidation tests 5 days/300° F., Cu, Fe, Al catalysts, air 25 cc./min.

Additive	Weight percent	Total acid number/5 days (ASTM–D–974)
None		4.7
DDSA	0.3	6.3
Li/2 DDSA [1]	0.3	4.9
Li/2 DDSA [1]	0.15	3.7
Li/2 DDSA+C_9 phenol [2]	0.3	2.8

[1] Product of Example 1, Part A.
[2] Product of Example 1, Part B.

Table II illustrates that the additives of this invention do not increase thermal oxidation at extreme temperatures and, in fact, the lithium salt and the alkyl-phenol-modified salt actually reduce oxidation as measured by the total acid number.

An additional advantage of this invention is that even the P_2S_5-S-treated lithium salt of DDSA, for instance, has a much lower ash level when used in an amount sufficient to give good rust protection that does a corresponding conventional overbased calcium sulfonate. Said overbased calcium sulfonate which is one of the most accepted rust inhibitors in use today in motor oils is used in the form of a mineral oil concentrate of overbased calcium sulfonate prepared from synthetic alkyl aromatics of about 420 molecular weight and contains about 30% calcium sulfonate and about 25% calcium carbonate and has a Total Base Number of about 300 (mg./KOH/g.).

It is estimated that about 3.5 wt. percent of this concentrate would be necessary in order to give the same level of performance in the MSIIB+2 test as did 0.5% AI of Li/2 P_2S_5-S-DDSA+C_9 phenol. The difference between the ask levels of these two additives is compared in Table III.

TABLE III

Additive	Metal	Percent ash	Percent sulf. ash	Blend: Weight percent add. conc.	Blend: Percent ash	Blend: Percent sulf. ash
Overbased calcium sulfonate	12.0% Ca	17	40	3.5	0.600	1.400
Li/2 P_2S_5-S-DDSA+C_9 Phenol [1]	1.2% Li	2.6	9.7	1.0	0.026	0.096

[1] Product of Example 7.

While particular embodiments of this invention are shown in the examples, it will be undertsood that the invention is obviously subject to the variations and modifications disclosed above without departing from its broader aspects. Accordingly, it is not intended that the invention be limited to the specific modifications which have been given above for the sake of illustration, but only by the appended claims.

What is claimed is:

1. An oil-soluble composition comprising:
   (a) a corrosion inhibiting proportion of a lithium salt of an aliphatic-hydrocarbon-substituted succinic acid having from about 9 to about 30 carbon atoms in the aliphatic hydrocarbon radical; and
   (b) an oil-solubilizing proportion of an alkyl phenol having a total of about 5 to about 30 alkyl carbon atoms.

2. The composition of claim 1 wherein the molar ratio of lithium to hydrocarbon succinic acid in component (a) ranges from about 1:1 to about 4:1 and the molar ratio of component (a) to (b) ranges from about 15:1 to about 0.5:1.

3. The composition of claim 1 wherein the aliphatic hydrocarbon substituent of said substituted succinic acid has from about 10 to about 20 carbon atoms and said alkyl phenol has from about 8 to about 26 alkyl carbon atoms.

4. The composition of claim 3 wherein said hydrocarbon substituent is dodecenyl and wherein said alkyl phenol is nonyl phenol.

5. A lubricating oil composition comprising:
   (a) a major proportion of an oil of lubricating viscosity;
   (b) a minor corrosion inhibiting proportion of a normally oil insoluble lithium salt of an aliphatic-hydrocarbon-substituted succinic acid having from about 9 to about 30 carbon atoms in the aliphatic hydrocarbon radical; and
   (c) a minor proportion of an alkyl phenol in an amount sufficient to render said lithium salt soluble in said oil.

6. The composition of claim 5 wherein the molar ratio of lithium to hydrocarbon-substituted succinic acid ranges from about 1:1 to about 4:1, the molar ratio of component (b) to (c) ranges from about 0.5:1 to about 15:1 and the combination of components (b) and (c) represents about 0.01 to about 5 wt. percent of the total lubricating composition.

7. The composition of claim 5 wherein the hydrocarbon substituent of said hydrocarbon succinic acid has from about 10 to about 20 carbon atoms and said alkyl phenol has from about 5 to about 30 alkyl carbon atoms.

8. The composition of claim 7 wherein said hydrocarbon substituent is dodecenyl and wherein said alkyl phenol is nonyl phenol.

9. A process for preparing an oil-soluble composition comprising:
   (a) contacting a lithium salt of an aliphatic-hydrocarbon-substituted succinic acid having from about 9 to about 30 carbon atoms in the hydrocarbon radical with an alkyl phenol in an amount sufficient to render said lithium salt soluble in oil; and
   (b) heating the mixture to a temperature at least as high as the melting point of the lithium salt.

10. The process of claim 9 wherein said temperature is in the range of about 300° F. to about 500° F. and the molar ratio of the lithium salt to the alkyl phenol is from about 0.5:1 to about 15:1.

11. The process of claim 9 wherein the hydrocarbon radical has from about 10 to about 20 carbon atoms and the alkyl phenol has about 5 to about 30 alkyl carbon atoms.

12. The process of claim 11 wherein said hydrocarbon radical is dodecenyl and wherein said alkyl phenol is nonyl phenol.

13. The process of claim 9 comprising the additional subsequent step of adding sulfur wherein the molar ratio of hydrocarbon-substituted succinic acid to sulfur ranges from about 120:1 to about 0.2:1 and said combination with sulfur takes place at a temperature in the range of about 100° F. to 450° F.

14. The process of claim 9 wherein the lithium salt is the salt of an alkenyl succinic acid which, prior to salt formation, has been reacted with from about $\frac{1}{120}$ to about 5 moles of sulfur per mole of said acid or anhydride thereof at a temperature in the range of about 100° F. to 450° F.

15. The process of claim 14 wherein the combination of alkenyl succinic anhydride or acid and sulfur has been carried out in the presence of a phosphorus sulfide, the molar ratio of alkenyl succinic acid to S ranges from about 15:1 to about 1:1 and the molar ratio of alkenyl succinic anhydride or acid to phosphorus sulfide ranges from about 720:1 to about 1:1.

16. A process for preparing an oil-soluble composition comprising:
   (1) contacting (a) an aliphatic-hydrocarbon-substituted succinic anhydride or acid having from about 9 to about 30 carbon atoms in the alkenyl radical, with (b) an alkyl phenol; and then
   (2) combining the product of step (1) with (c) a lithium base, at a temperature in the range of about 300° F. to 500° F.

17. The process of claim 16 wherein the molar ratio of component (a) to component (b) ranges from about 0.5:1 to about 15:1 and the molar ratio of component (c) to component (a) ranges from about 1:1 to about 4:1.

18. The process of claim 16 wherein the hydrocarbon radical has from about 10 to about 20 carbon atoms and the alkyl phenol has about 5 to about 30 carbon atoms.

19. The process of claim 18 wherein said hydrocarbon radical is dodecenyl and wherein said alkyl phenol is nonyl phenol.

20. A lubricating oil composition as in claim 5 wherein component (b) has been reacted with sulfur wherein the molar ratio of hydrocarbon-substituted succinic acid to sulfur ranges from about 120:1 to about 0.2:1 and said combination with sulfur takes place at a temperature in the range of about 100° F. to 450° F.

References Cited

UNITED STATES PATENTS

2,733,235	1/1956	Gross et al.	252—32.7 X
2,980,615	4/1961	Morway et al.	252—41
3,351,552	11/1967	Le Suer	252—41
3,485,858	12/1969	Gee et al.	260—485 X

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252—33.6, 389; 260—125, 137