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OIL SOLUBLE ALKALI AND ALKALINE EARTH METAL SALTS OF p-ACYLAMINO PHENOLS

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This invention relates to metal-containing compounds useful as additives for various solid and liquid organic compounds for improving one or more properties thereof. Particularly, it relates to metal salts of acyl p-amino phenols having improved solubility and other characteristics when used in various organic substances.

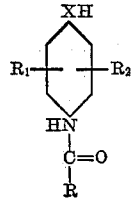
This application is a continuation-in-part of co-pending application Serial No. 285,304, filed April 30, 1952.

The class of compounds known as acyl p-amino phenols are outstanding oxidation inhibitors for many types of organic materials. They have found application in solid hydrocarbons such as waxes, synthetic rubbers, and the like, as anti-oxidants and thickeners for lubricating greases, etc. The acyl amino phenols, however, are substantially insoluble in some liquid organic materials, such as mineral lubricating oil compositions, at normal temperatures. Only the lower molecular weight compounds are soluble in synthetic lubricants. This difficulty has been observed even when the compound contains long chain acyl or alkyl groups that normally render related phenolic-type compounds soluble in mineral oil. Therefore, these compounds usually cannot be used per se as additives for certain materials, since they must exist in solution to impart oxidation inhibition properties thereto. In contrast, the acyl amino phenol may exist as a minute particulate dispersion in some solid materials to give oxidation resisting effects.

It has now been discovered that the metal salt derivatives of acyl amino phenols and related compounds are soluble in mineral oils and the like at a wide range of temperatures. This discovery is completely unexpected. Normally, metal derivatives are considerably less oil-soluble than the parent compounds. The reason for the increased oil solubility of the metal salts is not understood, but the extent of solubility of the parent material is in most cases increased several orders of magnitude when used as the metal salt. The increased solubility is also observed in synthetic lubricants, solid organic materials, and the like.

It has also been found that the metal acyl amino phenols retain the desirable oxidation inhibiting properties of the parent compound. In addition, they impart potent detergency and sludge dispersing properties to internal combustion engine lubricants. This is a valuable property in maintaining engine cleanliness. They also act as grease and wax thickeners and have other useful properties.

The compounds of the present invention may be described as the metal salts of N-acyl p-amino phenolic-type compounds having the following general formula:



wherein X is a non-metal of group VI of the periodic table, and R, R_1, and R_2 are selected from the group consisting of hydrogen and hydrocarbon radicals having in the range of 1 to 25 carbon atoms, and they may be alike or different. Hydrocarbon radicals such as alkyl, alkenyl, cycloalkyl, aralkyl, and other aliphatic, alicyclic and aromatic radicals may be used. R, R_1, and R_2 are preferably aliphatic radicals, more preferably straight or branched chain alkyl groups, the more highly branched alkyl groups being most useful in making salts of good oil solubility. Specific alkyl radicals include methyl, isopropyl, tert.-amyl, tert.-octyl, n-decyl, dodecyl, cetyl and the like. Alkenyl radicals include hexenyl, nonenyl, oleyl, etc. Alicyclic radicals include cyclohexyl, ethylcyclohexyl, n-butylcyclohexyl, and the like, as well as the unsaturated cycloaliphatic radicals. In some cases, the aryl and alkaryl radicals such as phenyl, methylphenyl, butylphenyl, diethyl phenyl and the like are useful, although they are less preferred than the aliphatic radicals because of their lower oil solubility.

R preferably has in the range of 6 to 20 carbon atoms to form materials having good oil solubility as well as effective antioxidant and sludge dispersing potency. R_1 and R_2 preferably have no more than a total of 30 carbon atoms.

X may be oxygen, sulfur, selenium and tellurium, although oxygen and sulfur are generally preferred from the standpoint of effectiveness, availability and cost of the compounds. Oxygen is particularly preferred since phenolic derivatives of the present invention are odorless and do not stain metals even at high temperatures. Thiophenolic derivatives have some disadvantages in this respect.

The N-acyl p-amino phenolic compound is readily prepared by mixing an organic acid or acid chloride with p-amino phenol, an alkylated derivative thereof, or the thiophenolic homologues and the like and heating the mixture to bring about reaction. The reaction progresses smoothly, splitting off water or hydrogen chloride, and yields the desired acylated amino phenol. The product may be purified by means known to the art, such as by distillation, crystallization, solvent extraction, etc.

Typical amino phenolic-type compounds that may be used in this reaction are as follows:

Para amino phenol
3-hexyl-4-amino phenol
3-hexyl-4-amino thiophenol
2-tert.-amyl-4-amino phenol
2-tert.-hexyl-4-amino thiophenol
2-tert.-octyl-4-amino phenol
2,6-di-tert.-octyl-4-amino phenol
3-pentadecyl-4-amino phenol
3-hexadecyl-4-amino thiophenol
2-isohexadecyl-4-amino phenol
C_{16}–C_{20} branched chain alkyl-4-amino phenol

The tellurium and selenium homologues of these compounds may be used. Specific organic acids that may be reacted with the amino phenols include fatty acids, highly branched Oxo acids, etc., such as formic, acetic, butyric, caprylic, capric, lauric, palmitic, stearic, undecylenic, oleic, linoleic, cyclohexylvaleric, 7,7,9,9-tetramethyl decanoic, and 6,8,8,10,10-pentamethyl undecanoic acids, as well as naphthenic acids, etc.

The Oxo acids, which may be reacted with the amino thiophenols, are derived from oxygenated organic compounds such as aldehydes or alcohols prepared by the well-known Oxo process in which these oxygenated organic compounds are synthesized from olefinic organic compounds and mixtures of CO and H_2 in the presence of a group VIII metal catalyst, usually cobalt. The primary

reaction product consists essentially of organic carbonyl compounds, mainly aldehydes, having one more carbon atom per molecule than the olefinic feed material. The oxygenated product may be then hydrogenated in a second catalytic stage to convert the aldehydes to the corresponding alcohols. Practically all types of organic compounds having an olefinic double bond, such as aliphatic olefins and diolefins, cyclo-olefins, aromatics with olefinic side chains, oxygenated organic compounds with olefinic double bonds, and the like, may be employed as starting materials. The metal catalyst may be present as a solid or in the form of a compound soluble in the olefinic feed stock. Suitable reaction conditions in the primary reaction include temperatures of about 150°–450° F., pressures of 100 to 300 and higher atmospheres, H_2 to CO ratios of about 0.5–2:1, liquid feed rates of about 0.1 to 5.0 v./v./hr., and gas feed rates of about 1000 to 45,000 standard cubic feet of gas mixture per barrel of liquid olefin feed.

Similar or higher temperatures and pressures, and hydrogenation catalysts such as nickel, copper, tungsten, oxides or sulfides of group VI and group VII metals, etc., may be employed in the second stage for hydrogenation of the carbonyl compounds to alcohols.

The Oxo acids may be produced by oxidizing the aldehydes formed in the Oxo process, for example, by oxidation of the aldehydes with air, followed by acidification of the reaction mixture to separate out the resultant Oxo acids. The Oxo acids may also be formed by a similar oxidation of the Oxo alcohols which are produced in the second stage (hydrogenation stage) of the Oxo process. In another method the Oxo alcohol may be reacted with an alkali metal hydroxide at a temperature in the range of about 275° C. to 325° C. for 0.5 to 10 hours to form the alkali metal salt of the corresponding Oxo acid, which can be then separated from the reaction mixture by water washing. The Oxo acid may then be separated by acidifying the water solution. Oxo acids are also produced as by-products of a Guerbet reaction carried out with an Oxo alcohol to produce as the main reaction product a primary monohydric alcohol having twice the number of carbon atoms per molecule as the original Oxo alcohol. In the Guerbet reaction, an alkali metal hydroxide may be employed in proportions of about 0.05 to 0.25 mole of alkali metal hydroxide per mole of Oxo alcohol and the reaction is carried out at a temperature in the range of about 200° C. to 250° C. for 5 to 50 hours. The product mixture includes about 10 to 30% by weight of an alkali metal salt of the corresponding Oxo acid, which may then be recovered from the mixture by water washing and subsequent acidification of the water solution.

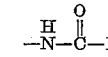
The acyl amino phenol is then converted to the metal salt derivative by reaction with a metal, metallic oxide, hydroxide, sulfide, alkoxide, hydride or carbide, a basic metal neutralizing agent being preferred. The reaction is usually carried out at an elevated temperature, such as in the range of about 80° C. to 200° C. The reaction proceeds smoothly when the phenol compound is first dissolved in a suitable inert solvent such as chloroform, isopropyl alcohol, and the like, the metal reagent added to the solution, and the material heated at reflux temperature for several hours until the reaction is completed. The material is then filtered to remove unreacted constituents and stripped free of solvent.

The product may be prepared directly in an oil base stock to produce a concentrate of the additive. Thus, the acyl amino phenol is added to oil at a sufficiently high temperature to cause at least some of the phenol to go into solution. The basic reagent is added slowly; the resulting metal salt stays in solution. The reactants may be stirred to insure complete reaction. The oil concentrate, containing as high as in the range of about 15 to 50% by weight or higher of the metal salt derivative, is then filtered and may be stored, transported and sold in that form as a lubricant additive. In making a finished lubricant, a sufficient amount of the concentrate is added to the base stock to give the desired active ingredient content.

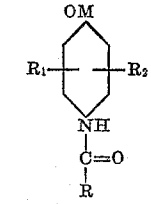
Anti-foaming agents such as higher alcohols including stearyl, lauryl, or cetyl alcohols, wool fat alcohols, etc., may be added to the reaction mixture when salts are formed in lubricant base stocks. The alcohol reduces foaming and acts as an auxiliary solvent for the final product. Sufficient alcohol to give a concentration of about 3% to 15% based on the final additive concentration will generally give good results.

The salts may be of mono-valent metals such as the alkali metals including sodium, potassium, lithium, etc. Such salts are less preferred as lubricant additives than those of polyvalent metals, since they are soluble in water to some extent and may be leeched out of lubricants containing them. The alkali metal salts, however, are generally most suitable as thickening agents and are useful as antioxidants where sludge dispersing properties are not needed. Desirable polyvalent metals include barium, calcium, strontium, aluminum, copper, cobalt, antimony, zinc, tin, iron, nickel, and other heavy metals. Salts of these metals form valuable oil-soluble additives. Divalent metal salts are preferred such as those of calcium, strontium, and particularly barium. These salts are readily prepared and have outstanding detergency as well as oxidation inhibition characteristics.

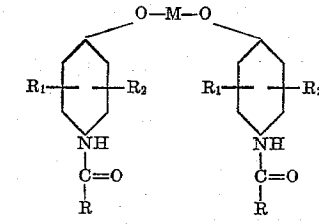
In forming the metal derivative, the metal replaces the hydrogen of the —XH radical, the hydrogen in the



radical being unreactive. The amount of metal reagent to employ will depend to a large extent on the metal content desired in the finished product. Thus, substantially equimolar quantities of phenol and monovalent metal reagent such as sodium hydroxide will form the normal metal salt having the formula:

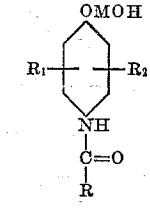


The normal metal salt of a divalent metal, formed by reaction of the phenol with lime, barium hydroxide octahydrate, etc., may have the formula:

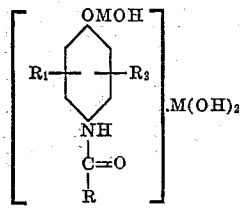


in which the ratio of metal to acyl amino phenol is 0.5:1.

If the detergency characteristics of the additive are to be emphasized, the phenol compound is treated with an amount of metal reagent in excess of that required to form the normal salt. Thus, for divalent metals, formulas for metal phenates having a metal to acyl amino phenol ratio of 1:1 and 2:1 may be



and



Metal phenate derivatives having intermediate ratios of metal to acyl amino phenol of 0.8:1, 1.5:1, and the like, may be prepared. In these cases mixtures of the above types are usually present. Metal salts containing more than the normal amount of metal required for neutralization may be termed "basic" salts.

Mixed metal salts of the acyl amino phenols are desirable for some uses. They may be prepared by treating the phenol with two or more basic neutralizing agents. For example, the acyl amino phenol may be treated with lime in an amount sufficient for neutralization purposes and then further treated with barium hydroxide to form the mixed calcium-barium "basic" salt.

In some cases, it is preferred to prepare the heavy metal salts from alkali metal salts of the acyl amino phenol by double decomposition. Thus, the sodium derivative may be treated with barium hydroxide pentahydrate or lime. The calcium salts are also conveniently prepared by reacting the phenol compound with calcium methylate or other calcium alcoholate.

The metal salts of the present invention are most advantageously blended with lubricant oils of either mineral or synthetic base, or mixtures of these, in concentrations between the approximate limits of 0.02% and 15.0%, preferably about 0.1 to 5.0% by weight. The exact amount used will depend on the particular product used, the nature of the lubricant base stock, the operating conditions in the engine using the oil, and other factors. The metal salts may also be used advantageously in greases, although amounts up to about 20% by weight may be needed.

In another aspect of the present invention, the normal or basic metal salts of the present invention may be reacted with a sulfurizing agent or phosphosulfurizing agent. The resulting products have improved corrosion inhibition properties making them useful as lubricant additives. Furthermore, they exhibit desirable properties in promoting engine cleanliness, improving oil film strength properties, etc. The introduction of sulfur or sulfur and phosphorus into the metal acyl amino phenate molecule also provides a material having extreme pressure properties.

Sulfurizing agents for the above purpose include elemental sulfur, mixtures of elemental sulfur and phosphorus, sulfides of phosphorus such as P_2S_5, P_4S_3, P_4S_7, sulfur halides, such as sulfur chloride, and the like. The reaction may be carried out at a temperature in the range of about 100° C. to 250° C. employing in the range of about 2 to 25% by weight of sulfurizing agent based on the metal salt. The reaction is preferably conducted in a lubricant base stock.

In the following examples are described various preparations of products in accordance with this invention and the results obtained on testing them in various lubricants and greases. These examples are given for illustrative purposes only, and are not to be construed as limiting the scope of the invention in any way.

EXAMPLE I.—PREPARATION OF PRODUCTS

(*A*) *Preparation of* N-*acyl p-amino phenols*

A series of preparations were carried out in which either p-amino phenol or alkylated p-amino phenols were acylated with various carboxylic acids. In these preparations, equal molar quantities of the amino phenol and acid were dissolved in toluene (used as solvent) and heated at refluxing temperature for about 8 to 14 hours. By-product water was removed as a water-toluene azeotrope. Toluene and unreacted amino phenol and acid were removed by vacuum stripping. Product yields of about 85% were obtained. A small amount of boric acid catalyst was found to be helpful in some of the preparations.

The "Oxo" acids used in the preparations were prepared as follows.

Preparation of C_8 *Oxo acids.*—390 g. of C_8 Oxo alcohol and 140 g. of sodium hydroxide pellets were charged to a 2 liter rocking bomb and heated at 315° C. for 5½ hours. The cooled reaction mixture was dissolved in 50% methanol, washed three times with one-third of its volume of hexane, and the hexane washes discarded. The aqueous solution was acidified with sulfuric acid to a Congo red endpoint, the C_8 Oxo acid layer removed by washing three times with one-fourth volume of hexane, the hexane solution washed repeatedly with one-sixth volume of water until the water was neutral to Congo red, and the hexane solution was then dried over sodium sulfate, filtered, and evaporated on a steam bath. The yield was 399 g. of Oxo acid concentrate. The product from four similar preparations was combined and distilled in a short path vacuum still. One percent distilling up to 70° C. at 1.5 mm. was discarded, 71% distilled at 70°–72° C., and 27% distilled at 72°–77° C. The residue was discarded. The two main fractions appeared to have a purity of 99% or better when titrated as C_8 Oxo acids.

Preparation of C_{13} *Oxo acids.*—692 g. of C_{13} Oxo alcohol and 160 g. of sodium hydroxide pellets were mixed in a rocking bomb and heated to 310° C. for 4¼ hours. The product was handled similarly to the above preparation. The C_{13} Oxo acid concentrate amounted to 683 g. Ninety-two percent distilled at 124°–140° C. at 2.5 mm. and by titration was 97% C_{13} Oxo acid.

The "Oxo" alcohols employed in making the above acids were prepared by the well-known "Oxo" process. The C_8 Oxo alcohol, for example, may be prepared as described in U. S. Patent 2,637,746 and more specifically may be prepared under the conditions set forth in that patent in column 5, line 70, to column 6, line 25. The C_{13} Oxo alcohol may be prepared by the "Oxo" process from a C_{12} olefin polymer, such as tetra-propylene, in substantially the same manner.

(*B*) *Preparation of metal* N-*acyl p-amino phenates*

The salts were generally prepared by dissolving the N-acyl p-amino phenol in chloroform, adding the desired amount of metal as a hydroxide, and heating the mixture at refluxing temperature for a time sufficient to complete the reaction (usually about 5 to 6 hours). By-product water was removed during the reaction period. The product was then filtered through both paper and a diatomaceous filter aid to remove solids. Chloroform or other solvent was then stripped off. The products are generally tacky viscous liquids at room temperature.

The normal sodium salts were prepared by treating one mol of the N-acyl-p-aminophenol with one mol of sodium hydroxide. The normal lithium salts were likewise prepared using equal molar quantities of the acyl amino phenol and lithium hydroxide.

The normal calcium, barium, and strontium salts were prepared by treating two mols of the N-acyl p-aminophenol with one mol of metal hydroxide. In the case of the calcium salt, however, isopropyl alcohol was used in place of chloroform as solvent.

A basic barium salt was prepared by treating one mol on N—C_{13} Oxo acyl p-aminophenol with one mol of barium hydroxide octahydrate.

In the range of 500 to 1000 ml. of solvent were used during the preparations.

In another procedure the barium salt of N-lauroyl-3-pentadecyl-4-aminophenol was prepared in a lubricant base stock having an S. S. U. viscosity at 210° F. of

43. The phenolic compound was stirred in the oil at a temperature of about 280° F., at which temperature some of the acyl aminophenol went into solution. Barium hydroxide octahydrate was added with stirring until reaction was completed. The filtered product consisted of a 17% concentrate of the normal barium salt in oil. The metal salt was soluble in the oil at room temperature.

A comparison of actual and theoretical inspections of a typical barium salt are shown below. This salt was formed by heating 190 g. of "C_8 Oxo acyl"-3-pentadecyl-4-amino phenol (dissolved in one liter of chloroform) with 68 g. of $Ba(OH)_2.8H_2O$ at reflux temperature, filtering, and stripping off solvent.

Inspection	Actual	Theoretical
Molecular Weight	1,058	1,027
Barium, Wt. Percent	13.04	13.39
Nitrogen, Wt. Percent	2.68	2.73
Hydrogen, Wt. Percent	9.37	9.74
Carbon, Wt. Percent	67.01	67.90

EXAMPLE II.—SOLUBILITY OF PRODUCTS IN OILS

The maximum solubility at room temperature of the various acyl p-aminophenols and of their metal salt derivatives in mineral and synthetic lubricating oils was determined. The mineral lubricating oil was a Mid-Continent base stock having an S. S. U. viscosity at 210° F. of 50 and a viscosity index of 50. The synthetic lubricant employed was a complex ester formed by the interaction of 2 mols adipic acid, one mol 1,3-butanediol and 2 mols C_8 Oxo alcohol; this ester was prepared by conventional procedures. The data are shown in Table I, below:

TABLE I

	Compound Tested	Maximum Solubility in Oil, Weight Percent	
		Mineral Oil	Synthetic Oil
1	N-"C_8 Oxo acyl"-4-aminophenol	0	0.5
	Lithium Salt	2.7	1.5
2	N-"C_{13} Oxo acyl"-4-aminophenol	0	0.25
	Sodium Salt	1.7	0.8
	Lithium Salt	3.4	2.2
	Basic Barium Salt	17.8	4.4
3	N-"C_8 Oxo acyl"-3-pentadecyl-4-amino-phenol	0.15	0
	Normal Barium Salt	45.0	12.0
4	N-"C_{13} Oxo acyl"-3-pentadecyl-4-amino-phenol	0.18	0
	Normal Barium Salt	50.0	15.0
5	N-Lauroyl-4-aminophenol	0	0.2
	Normal Barium Salt	5.0	2.0
	Normal Calcium Salt	2.5	1.5
	Normal Strontium Salt	44.0	18.0

EXAMPLE III.—CORROSION TEST

The effect of the normal barium salt of "C_{13} Oxo acyl"-3-pentadecyl-4-amino phenol for preventing the corrosion of a copper-lead alloy when in contact with an oil containing it was determined. A solution of an S. A. E. 20 grade oil containing 1.0% by weight of the barium salt and a sample of the unblended base oil were tested as follows:

500 cc. of the oil to be tested were placed in a glass oxidation tube (13" long and 2⅝" diameter) fitted at the bottom with a ¼" bore air inlet tube perforated to facilitate air distribution. The oxidation tube was immersed in a heated bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. To increase the severity of the test, the bearings were washed and weighed at the end of each four hour period and then polished and reweighed before continuing for another four-hour period.

The blend containing the barium salt gave a bearing weight loss of only 7 mg. after 24 hours, whereas the base stock gave a weight loss of 19 mg. during the same period.

EXAMPLE IV.—CARBON BLACK DISPERSION TEST

A carbon black dispersion test was carried out to measure the comparative effectiveness of various metal salts of this invention as agents for dispersing sludge in lubricating oil. In this test 6% by weight of activated carbon was added to the oil blend containing the additive and was thoroughly dispersed in the oil by stirring with an "egg beater" type mixer for 15 minutes while the temperature of the oil was maintained at 250° F. 250 cc. of the blend was then placed in a 250 cc. graduated cylinder and allowed to settle for 24 hours while the temperature was maintained at 200° F. If an additive is not a dispersing agent, the carbon black settles rapidly at this point leaving clear oil at the top in an hour or two. A very effective disperser will maintain the carbon black in suspension so that no change in the opaque slurry is apparent even after a 24-hour period. With all but the most potent dispensers stratification occurs with a black layer at the bottom (high concentration of carbon black) and a blue opaque layer at the top (reduced carbon black concentration). Cases of this type, known as "blue line" separations, are only detectable in reflected light. The base oil used for the test was a solvent extracted Mid-Continent oil of 52 seconds Saybolt viscosity at 210° F. The results of the test when applied to blends containing 0.75% of the barium and strontium salts of this invention in the base oil showed no settling of the carbon black during the 24-hour period. A similar test of the base oil alone showed a volume of 40 cc. of supernatant oil at the end of the test period. The calcium salt gave almost perfect dispersion. The sodium and lithium salts were somewhat less effective than the polyvalent metal salts.

EXAMPLE V.—GREASE OXIDATION TESTS

A grease composition was prepared having the following formulation:

	Percent
Rapeseed oil	29.00
Sodium hydroxide	5.92
Petroleum sulfonate	1.00
Barium salt of "C_{13} Oxo acyl"-3-pentadecyl-4-amino phenol	1.00
Coastal distillate having a viscosity (Saybolt) at 210° F. of 55 seconds	63.08

A portion of the lubricating oil was mixed with the fatty material in a grease kettle having a steam jacket. The sodium hydroxide was added with stirring while heating to about 400°–420° F. The remaining lubricating oil and the additive material was added, the heating discontinued, and the grease was pan cooled.

A similar composition was prepared in which the grease contained no additive. In another case, the grease contained 1.0% by weight of N-lauroyl-p-aminophenol.

The Norma-Hoffman oxidation bomb test was then used to evaluate the greases. This oxidation test is described in the patent literature and involves subjecting a given sample of a grease to a constant temperature, usually 100° C., under an oxygen pressure of 110 p. s. i. The loss in oxygen pressure is a function of the oxidation resistance of the grease, that is to say, a grease that is highly resistant to oxidation will show a small pressure drop after an extended period of test time. The results

of the tests on these experimental greases are shown in Table II below.

TABLE II

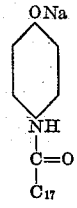
Pressure Drop, Lbs./Sq. In.	5	10	30
Additive in Grease	Time Required to Attain Pressure Drop, Hours		
None	46	52	78
N-Lauroyl-p-aminophenol (1% by weight)	144	250	(*)
Barium salt of N-"C_{13} Oxo acyl"-3-pentadecyl-4-aminophenol (1% by weight)	240	360	(*)

*Not determined.

Although the acyl aminophenol is quite effective as an antioxidant, the barium salt was considerably more effective. This is probably due chiefly to the increased solubility, and hence availability, of the metal salt in the grease.

EXAMPLE VI.—THICKENING PROPERTIES

Sodium N-stearoyl-p-aminophenate having the formula



was prepared substantially by the procedure described in Example I. This material was tested as a thickening agent. A wax having a melting point of 110° F. and a dropping point of 50° F. had blended with it 2% by weight of the above sodium salt. The resulting blend had a dropping point of 255° F.

EXAMPLE VII.—RUBBER OXIDATION TESTS

Barium N-lauroyl-p-aminophenate was tested as an additive for synthetic rubbers. In one case, the rubber tested was Paracril rubber prepared by emulsion copolymerization of butadiene and acrylonitrile using conventional procedures. Conventionally prepared GR–S rubber (emulsion copolymerized butadiene and styrene) was also tested. In these tests, the synthetic rubber, with 1% by weight of the barium salt blended therein and the unblended materials were placed in an oven and heated at 160° F. in the presence of air for 14 days. The percent gel (toluene insolubles) was then determined on each sample. The percent gel is a measure of the hardening and cross linking tendencies of the rubber in air. The results are shown in Table III, below:

TABLE III

Rubber tested:	Gel after 14 days, percent
Paracril	63
Paracril plus 1.0% barium salt	17
GR–S (60 Mooney viscosity)	77
GR–S plus 1.0% barium salt	21

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, alphaltic or mixed base crudes, or if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides or carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils, or their hydrogenated or voltolized products, may be employed, either alone or in admixture with mineral oils.

Other synthetic lubricants useful as a base for the improved compositions of this invention include long chain esters of monobasic acids, polybasic acids, mono and polyhydroxy alcohols, polymerized esters, ethers, ether esters, ester ethers, and the like. Of these various types of synthetic lubricants, the synthetic esters, either simple or complex, are usually preferred.

The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of diesel service, particularly with high speed diesel engines, and in aviation engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used in the lubricants such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fatty oils or fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc.

The lubricant grease compositions of this invention may be prepared by dispersing any of the common grease making soaps in a lubricating oil, using sufficient quantities of the desired soaps to form grease compositions of varying consistencies. Any of the various alkaline earth or alkali metals such as calcium, strontium, barium, potassium, sodium, or lithium may be used to form the soaps of any of the well-known grease making acidic materials, exemplified by hydrogenated fish oil acids, stearic acid, hydroxy stearic acid, oleic acid, palmitic acid, lauric acid, tallow, coconut oil, the saturated or unsaturated glycerides of the various fatty acids or mixtures of these in any proportion.

The oil base in which the above-mentioned soaps is to be dispersed may be selected from the natural occurring mineral oil distillates treated by any of the modern refinery techniques, synthetic lubricating oils of the above-named type, and the like. Such grease compositions may be prepared by any of the procedures known to the art of grease manufacture.

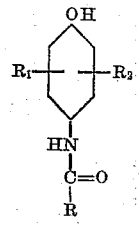
In addition to being employed in crankcase lubricants and greases, the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, general machinery oils, process oils, and rust preventive compositions. Also their use in motor fuels, diesel fuels, and kerosene is contemplated. A particular application in this regard is their use in motor fuels containing tetraethyl lead or other anti-knock agents, the additives of the present invention serving not only as antioxidants for the fuel but also as stabilizers for the antiknock agent itself. Since these additives exhibit anti-oxidant properties and thickening properties, they may be employed in asphalts, road oils, waxes, fatty oils of animal or vegetable origin, soaps, and plastics. Similarly, they may be used in natural and synthetic rubber compounding as vulcanization assistants, antioxidants, and mill release agents, and generally they may be used in other non-gaseous organic materials subject to deterioration by atmospheric oxygen.

The present invention is not to be considered as limited by any of the examples described herein which are given

by way of illustration only, but it is to be limited solely by the terms of the appended claims.

What is claimed is:

1. As a new composition of matter, the metal salt of a compound having the general formula



wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl radicals having in the range of 1 to 25 carbon atoms and R is an alkyl radical having in the range of 1 to 25 carbon atoms, and wherein said metal is selected from the group consisting of alkali metals and alkaline earth metals.

2. A composition as in claim 1 wherein said metal is an alkaline earth metal.

3. A composition as in claim 1 wherein at least one of the R_1 and R_2 groups is hydrogen.

4. A composition as in claim 1 wherein the acyl group of said compound is the acyl group of an Oxo acid.

5. A composition according to claim 4 wherein said metal salt is barium N-"C_{13} Oxo acyl"-4-aminophenate.

6. A composition according to claim 4 wherein said metal salt is barium N-"C_{13} Oxo acyl"-3-pentadecyl-4-aminophenate.

7. As a new composition of matter, strontium-N-lauroyl-4-amino-phenate.

8. As a new composition of matter, sodium-N-stearoyl-p-amino-phenate.

9. As a new composition of matter, barium N-lauroyl-4-aminophenate.

10. As a new composition of matter an oil soluble metal salt of an N-lauroyl-4-aminophenate, wherein said metal is selected from the group consisting of alkali metals and alkaline earth metals.

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