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LUBRICANT COMPOSITIONS CONTAINING METAL SALTS OF AROMATIC HYDROXY CARBOXYLIC ACIDS AS ANTIOXIDANTS

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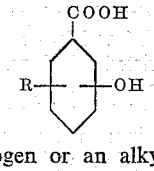
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This invention relates to the stabilization of organic materials normally subject to oxidative changes. Particularly, the invention relates to metal salts of aromatic hydroxy carboxylic acids and lubricant compositions containing said salts as antioxidants.

Lubricating oils, including synthetic as well as mineral oils which are quite inert chemically, are gradually oxidized in the presence of air or other oxygen-containing materials to produce acidic products, gums, sludge-forming materials, and other objectionable products which cause quality deterioration. When the lubricating oil is used in a grease, the grease structure tends to break down as the oil is oxidized, thus limiting the effective life of the composition. Both organic and inorganic materials have been proposed in the past for addition to, or treatment of lubricating oils and greases, to inhibit such oxidation and some of these have been quite successful. Unfortunately, many of the successful oxidation inhibitors contribute to other undesirable characteristics, such as corrosion of metals, reduction in viscosity index of lubricating oils, or softening of grease compositions, etc. Furthermore, a great many of the oxidation inhibitors hitherto used in lubricating oils are relatively expensive. It has now been found that the alkali metal salts of aromatic hydroxy carboxylic acids are excellent oxidation inhibitors. These materials are relatively inexpensive, may be prepared from readily available materials and overcome many disadvantages of the prior antioxidants.

The alkali metal salts of the invention are the mono- and disubstituted metal salts of a hydroxy aromatic acid of the general formula:



wherein R is hydrogen or an alkyl substituent, e.g., a C_1 to C_{15} alkyl group, while both the aromatic ring or the alkyl group can be still further substituted without adversely affecting the antioxidant properties of the salt. Specific examples of the above materials include the mono- and di-alkali metal salts of ortho, meta and para hydroxy carboxylic aromatic acids, e.g. monolithium salicylate, disodium salicylate, monosodium 2-hydroxy-4-diisobutyl benzoate, monolithium p-hydroxy benzoate and dilithium meta-hydroxy benzoate. While the salts are effective regardless of the position of the hydroxyl group relative to the carboxy group, the salts of the ortho-hydroxy carboxylic acids are preferred as they give the best results, apparently because of their higher water solubility. On the other hand, salts of the meta and para materials are less water soluble and are effective to a lesser extent. The metal salts of the above aromatic acids are readily formed by reacting between one and two moles of alkali metal base, i.e. a hydroxide or oxide, with one mole of the hydroxy carboxylic aromatic acid,

preferably followed by dehydration at elevated temperature. To achieve intimate mixing of the reactants, the hydroxy benzoic acid material may be dispersed in water, and then an aqueous solution of the alkali metal base added, followed by dehydration.

While the above type of salts have been found effective as antioxidants, particularly in greases, other somewhat related salts such as dilithium phthalate, dilithium terephthalate, sodium benzoate and lithium benzoate are not effective as antioxidants. Still other materials such as sodium and lithium phenates, while antioxidants, are not desirable for use in greases since they tend to destroy the grease structure.

The antioxidant additives of the invention may be used in either mineral lubricating oils, or synthetic lubricating oils. Thus, they can be used with such synthetic oils as: ester of tetraethylene glycol), complex esters, strs of C_8 Oxo acid), esters of dibasic acids (e.g., di-2-ethyl hexyl sebacate), esters of glycols (e.g., C_{13} Oxo acid diester of tetraethylene glycol), complex esters, esters of phosphoric acid, halocarbon oils, sulfite esters, silicone oils, carbonates, polyglycol-type synthetic oils, etc., or any mixture thereof.

The antioxidants of the invention are also useful in any compositions containing a substantial amount of lubricating oil, e.g., lubricating greases. Thus, lubricating greases generally comprise a major proportion of a lubricating oil and about 3.0 to 35.0 wt. percent, e.g., 3 to 20 wt. percent, based on the total weight of the composition, of a salt, soap, or a mixed-salt or soap-salt complex thickener, or a polymeric thickener such as polyethylene, or inorganic thickeners such as graphite, carbon black, clays, etc. Such salt and soap thickeners are generally metal salts of monocarboxylic acids, such as fatty acids, although sulfonic acids are also frequently used. The soap-salt and mixed-salt thickeners are generally complex thickeners which are prepared by the coneutralization of a high molecular weight fatty acid, and/or an intermediate molecular weight fatty acid, and a low molecular weight fatty acid, with metal bases, generally alkali or alkaline earth metal bases.

The high molecular weight fatty acids or aliphatic monocarboxylic acids useful for forming the soaps, soap-salt complexes and mixed-salt complexes, include naturally-occurring or synthetic, substituted and unsubstituted, saturated and unsaturated, mixed or unmixed fatty acids having about 12 to 30, e.g., 16 to 22, carbon atoms per molecule. Examples of such acids include stearic, hydroxy stearic, such as 12-hydroxy stearic, di-hydroxy stearic, polyhydroxy stearic and other saturated hydroxy fatty acids, arachidic, oleic, ricinoleic, hydrogenated fish oil and tallow acids.

Intermediate molecular weight fatty acids include those aliphatic, saturated or unsaturated, unsbustituted, monocarboxylic acids containing 7 to 12 carbon atoms per molecule, e.g., capric, caprylic and lauric acids.

Suitable low molecular weight acids include saturated and unsaturated, substituted and unsubstituted aliphatic monocarboxylic acids having about 2 to 6 carbon atoms. These acids include fatty acids such as acetic, propionic, and similar acids including their hydroxy derivatives such as lactic acid. Acetic acid is preferred.

The metal component of the soaps, salts or soap-salt complex thickeners can be any soap-forming metal such as aluminum, but generally is an alkali metal such as lithium, potassium, and sodium; or an alkaline earth metal such as calcium, strontium, barium and magnesium.

When desired, the soaps, soap-salt or mixed-salt grease thickeners can be prepared by neutralizing the carboxylic acid with metal base in situ in the lubricating oil, followed by heating the resultant composition for a time

and at a temperature sufficient to dehydrate the mixture and to form the soap and/or salt materials. Thus, simple salts and soaps or mixtures thereof, are generally formed on heating to about 300° to about 430° F., while heating to about 430° to about 600° F. is usually necessary to form the complexes.

The hydroxy benzoates of the invention can be added to the lubricant in amounts of 0.01 to 15.0, e.g., 0.1 to 5.0 wt. percent, based on the total weight of the composition. The lubricant in turn can be either a lubricating oil composition or a lubricating grease. If the lubricant contains other metal containing compounds, such as metal soap as a thickening agent in the case of a grease, then it is sometimes desirable that the metal portion of the hydroxy benzoate be the same metal that is already present in the lubricant. For example, it is preferred to use a lithium hydroxy benzoate in a lithium soap grease, while a sodium hydroxy benzoate is preferred for a sodium soap grease. The reason for this, is that there is a tendency for a metal exchange to take place between the hydroxy benzoate and certain other metal containing compounds. While this metal exchange does not interfere with the antioxidant properties of the hydroxy benzoate, it can, in some instances, have a deleterious effect upon the grease. Thus, lithium greases have excellent water resistance, while sodium greases have poor water resistance. However, by using a sodium hydroxy benzoate as the antioxidant in a water resistant lithium soap grease, some lithium hydroxy benzoate will eventually form as well as some sodium soap thickener. Now the lithium hydroxy benzoate will still be a good antioxidant, however the sodium soap thickener will lower the water resistance of the grease. Of course, in lubricants containing no other metal component, this possibility does not arise.

The lubricating oils and greases to be protected may, of course, contain other additive materials. Thus, viscosity index improvers, such as polyisobutylene; corrosion inhibitors, such as sorbitan monooleate; pour depressants; dyes; and the like are frequently used in preparing finished lubricants. The antioxidants of the invention, can also be supplemented with other antioxidants, e.g. phenyl-α-naphthylamine.

The invention will be further understood by the following examples, which include preferred embodiments of the invention:

EXAMPLE I

A. 1.0 wt. percent of finely powdered (about 100 mesh) anhydrous dilithium salicylate was mixed with 99.0 wt. percent of a lubricating oil having a viscosity at 100° F. of 601.2 SSU and a viscosity index of 93. The dilithium salicylate was prepared by dispersing powdered salicylic acid (1 mole) in water, adding lithuim hydroxide (2 moles), then heating to dehydrate. The dehydrated salt was dissolved in a 50/50 mixture of ethanol and water and then recrystallized in order to purify the salt. The anhydrous salt was recovered and ground to a 100 mesh powder.

B. A composition was prepared in the same manner as Example I–A, except that 1.0 wt. percent of anhydrous disodium salicylate was used.

The above compositions, along with the uninhibited base oil, were tested for oxidation resistance as follows:

100 grams of the oil composition to be tested in a 400 ml. beaker are heated for 500 hours in an oven maintained at 300° F. At the end of this time, the oil is examined for various physical changes. The results of the above tests are summarized in the following table:

Table I

SUMMARY OF OXIDATION RESULTS
[500 hours at 300° F.]

			I–A	I–B
Mineral Lubricating Oil	100%	100%	99.0%	99.0%.
Antioxidant	None	None	1.0% dilithium salicylate.	1.0% disodium salicylate.
	Before Test	After Test	After Test	After Test
Inspections:				
Viscosity at 100° F., SSU	601.2	657	678	699.
Viscosity at 210° F., SSU	67.9			
Viscosity Index	93.0			
Color—				
ASTM Color Scale	1	8	6	3.
Visual	Yellow	Black	Red	Orange.
Neutralization No	<0.03	.86	<0.03	0.24.
Sludge	Nil	Heavy deposit.	Trace	Nil.

As seen from Table I, the base oil without additive had substantially deteriorated at the end of 500 hours at 300° F. as shown by the darkening of the oil, the increase in neut. No., and the heavy sludge formation. By use of the dilithium and disodium salicylates, the oil became much more resistant to oxidation as shown by color, neut. No., and lack of sludge.

The effectiveness of the antioxidants of the invention in greases is illustrated by the following example:

EXAMPLE II

One weight percent of the antioxidant to be tested in the form of a finely divided powder (100 mesh or finer) was mixed with 99 weight percent of a base grease. This base grease consisted of 88 wt. percent of mineral lubricating oil having a viscosity at 100° F. of about 200 SUS and a V.I. of 90, thickened with 12 wt. percent of a mixed lithium-calcium soap of 12-hydroxy stearic acid having a weight ratio of lithium to calcium of 20/80. The resulting grease mixture was then subjected to oxidation tests as follows:

A. 10 grams of the inhibited grease composition, smeared on a watch glass, were placed in an oven maintained at 300° F. The appearance of the grease composition was then observed at varying time intervals.

B. Since one of the major drawbacks to some oxidation inhibitors is the fact that they tend to form insoluble carbonates when exposed to elevated temperatures, the effect of CO_2 on the material of the invention was investigated. In this test, powdered solid CO_2 was sprinkled on the inhibited grease, which was then sealed in a vented container. The closed container was allowed to stand for 16 hours in a saturated carbon dioxide atmosphere and then opened. Five grams of this CO_2 exposed grease were then packed into a steel bearing and hung in an oven at 300° F. for 24 hours. At the end of this time, the grease was examined for color change.

The materials tested and the results of the above tests are summarized in Table II, which follows:

Table II

EVALUATION OF OXIDATION INHIBITORS IN GREASE

Inhibitor in Grease [1]	Conc. percent	Change in Color and Consistency at 300° F.				Color after 24 hrs. in an oven at 300° F. after CO_2 treat.
		24 hours	70 hours	166 hours	330 hours	
None			Black and Fluid			Brown, beginning to fluidize.
Monolithium Salicylate	1		Tan	Light Brown	Light Brown	
Dilithium Salicylate	1	White	Light Tan	Tan	Tan	White to light tan.
Dilithium Phthalate	1		Black fluid			
Dilithium Terephthalate	1		do			
Alpha-phenylnaphthylamine	1		Brown	Dark Brown	Black fluid	
Commercial Grease Antioxidant [2]	1		do	do	do	

[1] 12 wt. percent calcium-lithium 12-hydroxystearate soap dispersed in a mineral oil of 200 SSU viscosity at 100° F., and 90 V.I. Original color of grease was white.
[2] Mixture of substituted diphenylamine and zinc dithiocarbamate.

As seen from Table II, the mono and dilithium salicylates were quite effective in preventing oxidation breakdown of the grease. The dilithium phthalate and dilithium terephthalate had little or no effect. The phenyl-alpha-naphthylamine and the substituted diphenylamine-dithiocarbamate material, both of which are conventional antioxidants for grease, while having some effect, were decidedly inferior to the salicylate inhibitors of the invention.

EXAMPLE III

Several more grease compositions containing the inhibitors of the invention were prepared and tested. The test was carried out by packing 5 grams of the grease composition into a weighted open single roll ball-bearing which was then hung in an oven maintained at 300° F. The bearing was periodically removed, re-weighed, and the weight loss of the grease was determined. The compositions tested and the results of these tests are summarized in Table III.

Table III

Inhibitor in grease [1]	Percent Wt. Loss at 330° F.	
	168 hours	330 hours
None	29	39
1.0 wt. percent monosodium salicylate	24	32
1.0 wt. percent disodium salicylate	18	30

[1] Grease consisted of 84 wt. percent mineral lubricating oil having a viscosity at 100° F. of 300 SUS and a V.I. of 70, and 16 wt. percent of sodium stearate.

To further illustrate the invention, a synthetic oil composition can be prepared by dispersing 5.0 wt. percent of a monosodium 2-hydroxy-4-diisobutyl benzoate in 95.0 wt. percent of di-(2-ethylhexyl) sebacate.

In summary, the invention relates to compositions normally subject to oxidation which are inhibited by an alkali metal salt of a substituted or unsubstituted hydroxy benzoic acid. While the inhibitors of the invention have been shown as particularly useful in lubricants, they can also be used as oxidation inhibitors in plastics, rubbers, and other compositions where oxidation occurs. Also, the antioxidants of the invention are compatible with other antioxidants. Thus, the calcium-lithium 12-hydroxy stearate base grease of Example II shows a NLGI spindle life at 250° F. of 223 hours; the addition of 1.0 wt. percent of dilithium salicylate increased the spindle life to 1,790 hours; while a mixture of 1 wt. percent dilithium salicylate and 1.0 wt. percent of phenyl-alpha-naphthylamine added to 98% of the base grease gave a spindle life in excess of 2,350 hours.

What is claimed is:

1. A lubricating composition comprising lubricating oil and an oxidation inhibiting amount of a di-alkali metal salt of a hydroxy benzoic acid.

2. A lubricant composition according to claim 1, wherein said lubricant is a grease and contains a thickening amount of a grease thickener.

3. A lubricant composition according to claim 1, wherein said oil is a mineral oil.

4. A lubricant composition comprising mineral lubricating oil and about 0.1 to 15.0 weight percent of a di-alkali metal salt of salicylic acid.

5. A lubricant composition according to claim 4, wherein said salt is selected from the group consisting of sodium and lithium salicylates.

6. A lubricant composition according to claim 4, wherein said lubricant also contains a grease thickening amount of a grease making metal soap.

7. A lubricating grease according to claim 6, wherein the metal component of said grease making soap is the same as the metal component of said salicylate.

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