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METAL SALTS OF REACTION PRODUCT OF AN ALKYL PHENOL AND AN ETHYLENEAMINE

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ABSTRACT OF THE DISCLOSURE

Organic compositions are provided containing as improving agents metal salts of the reaction product of an alkyl phenol and an ethyleneamine. These metal salts act as antiscreen clogging agents and smoke suppressants for fuel oils and as stabilizers for lubricating oils and greases. A method for the preparation of these metal salts is also provided.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a division of my copending application Ser. No. 654,327 filed July 19, 1967, now U.S. Pat. No. 3,493,508.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to organic compositions and, in one of its aspects, relates more particularly to improved organic compositions in the form of liquid and solid hydrocarbons which, in the form of fuel oils, normally cause screen clogging or emit smoke upon combustion or, when in the form of lubricating oils or greases, are subject to oxidative deterioration. Still more particularly, in this aspect, the invention relates to improved organic compositions in the form of petroleum distillate hydrocarbon fuels, lubricating oils or greases which, in their uninhibited state, tend to result in the above-described deleterious conditions in the course of use or storage.

(2) Description of the prior art

It is well known that certain types of organic compositions in the form of liquid hydrocarbon fuels normally cause screen clogging or can emit smoke upon combustion. Furthermore, it is also known that organic compositions, when employed in the form of lubricating oils or greases containing such oils as vehicles, are subject to oxidative deterioration in the course of their functional environments, thus clearly indicating the necessity for incorporating into such organic compositions effective improving agents.

SUMMARY OF THE INVENTION

It has now been found that the aforementioned screen clogging, smoke emission or oxidative deterioration properties of organic compositions, particularly in the form of fuels and lubricants, can be effectively overcome by incorporating therein small amounts of a metal salt of the reaction product of an alkyl phenol and an ethyleneamine.

In general, the present invention in its preferred applications contemplates organic compositions of the above-described types which contain a small amount of the aforementioned metal salts, usually from about .001 percent to about 10 percent, by weight, and preferably from

about .01 percent to about 0.5 percent, by weight, of the total of such compositions.

The organic compositions improved in accordance with the present invention may comprise any materials that are normally susceptible to the above-described screen clogging, smoke emission or oxidative deterioration characteristics. A field of specific applicabilty is the improvement of liquid hydrocarbons boiling from about 75° F. to about 1000° F. Of particular significance is the treatment of petroleum distillate fuel oils having an initial boiling point from about 75° F. to about 135° F. and an end boiling point from about 250° F. to about 750° F. It should be noted, in this respect, that the term "distillate fuel oils" is not intended to be restricted to straight-run distillate fractions. These distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight-run distillate fuel oils, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well-known commercial methods, such as acid or caustic treatment, hydrogenation, solvent-refining, clay treatment and the like.

The distillate fuel oils are characterized by their relatively low viscosity, pour point and the like. The principal property which characterizes thes hydrocarbons, however, is their distillation range. As hereinbefore indicated, this range will lie between about 75° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower boiling range, falling nevertheless within the above-specified limits. Likewise, each fuel oil will boil substantially, continuously throughout its distillation range.

Particularly contemplated among the fuel oils are Nos. 1, 2 and 3 fuel oils, used in heating and as diesel fuel oils, gasoline, turbine oil, and the jet combustion fuels. The domestic fuel oils generally conform to the specifications set forth in ASTM Specification D396–48T. Specifications for diesel fuels are defined in ASTM Specification D975–48T. Typical jet fuels are defined in Military Specification MIL–F–5624B. In addition, as previously indicated, hydrocarbon lubricating oils of varying viscosity and pour points, falling both within the aforementioned range and as high as 1000° F. or higher, may also be effectively treated through the use of the aforementioned metal salts.

As previously indicated, the aforementioned metal salts of the present invention may also be incorporated as anti-oxidants in grease compositions. Such greases may comprise a combination of a wide variety of lubricating vehicles and thickening or gelling agents. Thus, greases in which the aforementioned metal salts are particularly effective, may comprise any of the conventional hydrocarbon oils of lubricating viscosity, as the oil vehicle, and may include mineral or synthetic lubricating oils, aliphatic phosphates, esters and di-esters, silicates, siloxanes and oxalkyl ethers and esters. Mineral lubricating oils, employed as the lubricating vehicle, may be of any suitable lubricating viscosity range from about 45 SSU at 100° F. to about 6,000 SSU at 100° F., and, preferably, from about 50 to about 250 SSU at 210° F. These oils may have viscosity indexes varying from below 0 to about 100 or higher. Viscosity indexes from about 70 to about 95 are preferred. The average molecular weights of these oils may range from about 250 to about 800. The lubricating oil is employed in the grease composition in an amount sufficient to constitute the balance of the total grease composition, after accounting for the desired quantity of the thickening agent, and other additive components to be included in the grease formulation.

As previously indicated, the oil vehicles employed in the novel grease formulations of the present invention, in which the aforementioned metal salts are incorporated as anti-oxidative or anti-corrosive agents, may comprise min-

eral or synthetic oils of lubricating viscosity. When high temperature stability is not a requirement of the finished grease, mineral oils having a viscosity of at least 40 SSU at 100° F., and particularly those falling within the range from about 60 SSU to about 6,000 SSU at 100° F., may be employed. In instances where synthetic vehicles are employed rather than mineral oils, or in combination therewith, as the lubricating vehicle, various compounds of this type may be successfully utilized. Typical synthetic vehicles include: polypropylene, polypropylene glycol, trimethylol propane esters, neopentyl and pentaerythritol esters, di(2-ethyl hexyl) sebacate, di(2-ethyl hexyl) adipate, di-butyl phthalate, fluorocarbons, silicate esters, silanes, esters of phosphorus-containing acids, liquid ureas, ferrocene derivatives, hydrogenated mineral oils, chain-type polyphenyls, siloxanes and silicones (poly-siloxanes), alkyl-substituted diphenyl ethers typified by a butyl-substituted bis (p-phenoxy phenyl) ether, phenoxy phenyl ethers, etc.

The lubricating vehicles of the aforementiond improved greases of the present invention containing the above-described metal salts as additives are combined with a grease-forming quantity of a thickening agent. For this purpose, a wide variety of materials may be employed. These thickening or gelling agents may include any of the conventional metal salts or soaps, which are dispersed in the lubricating vehicle in grease-forming quantities in such degree as to impart to the resulting grease composition the desired consistency. Other thickening agents that may be employed in the grease formulation may comprise the non-soap thickeners, such as surface-modified clays and silicas, aryl ureas, calcium complexes and similar materials. In general, grease thickeners may be employed which do not melt and dissolve when used at the required temperature within a particular environment; however, in all other respects, any material which is normally employed for thickening or gelling hydrocarbon fluids for forming grease can be used in preparing the aforementioned improved grease in accordance with the present invention.

The metal salts of the present invention may be prepared, in general, by reacting an alkyl phenol, an ethyleneamine and a metal oxide at a temperature from about 50° C. to about 250° C., and preferably at a temperature from about 150° C. to about 250° C., to produce a reaction product which is incorporated as an improving agent in the aforementioned organic compositions. The mechanism of the reaction or the structure of the reaction product produced is not known. During the reaction, it is found that water is evolved. It is theorized that the metal may possibly be present in a chelate form in the final product.

The alkyl phenol reactant may be of any type or chain length, either substituted or unsubstituted. Thus, the alkyl phenol may include such compounds as didodecylphenol, monododecylphenol, monopolybutylene alkylated phenol and monononylphenol.

The ethyleneamine reactant may be of any type or chain length, either substituted or unsubstituted. Thus, the ethyleneamine may include such compounds as ethylenediamine, N-hydroxyethylethylene diamine, triethylene tetramine, tetraethylene pentamine, tetrahydroxyethyl diamine and N-dodecyldiethylene triamine.

The metal oxide reactant may be employed in the form of a monoxide, dioxide and higher oxides, hydroxides, hydroxide monohydrates and other oxides. The term "metal oxide" is intended to denote not only the oxide, per se, but other forms of oxygen-containing compounds of the type described. The metal of these oxides may include a wide variety of metallic elements, and preferably those selected from the group consisting of calcium, zinc, barium, lithium and potassium.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The following data and examples will serve to illustrate the preparation of the novel metal salts of the present invention and their efficacy as improving agents in organic compositions. It will be understood, however, that it is not intended the invention be limited to the particular metal salts or the particular organic compositions containing these salts, as described. Various modifications of these metallic salts and organic compositions, as previously indicated, can be employed and will be readily apparent to those skilled in the art.

EXAMPLE 1

215 grams (0.5 mol) or didodecylphenol, 215 grams of a diluent comprising a 100" refined pale paraffin oil, 18.5 grams (0.25 mol) calcium hydroxide and 15 grams (0.25 mol) of ethylene diamine were stirred at a temperature of approximately 75–80° C. for a period of about two hours, and then slowly heated to a tempreature of about 250° C. to produce a hydrocarbon soluble product which contained, by weight, 1.7% nitrogen and 1.0% calcium.

EXAMPLE 2

131 grams (0.5 mol) of monododecylphenol, 131 grams of the diluent employed in Example 1, 18.5 grams (0.25 mol) of calcium hydroxide and 27 grams (0.25 mol) of N-hydroxyethylethylene diamine were slowly heated with stirring to a temperature of about 175° C. over a period of about six hours. Upon analysis, the resulting product was found to contain, by weight, 2.0% nitrogen and 3.64% calcium.

EXAMPLE 3

262 grams (1 mol) of monododecylphenol, 200 grams of the diluent employed in Example 1, 37 grams (0.5 mol) of calcium hydroxide, 36.5 grams (0.25 mol) of triethylene tetramine and 4 grams of water were stirred at a temperature of about 95° C. for a period of about ten hours and then slowly heated to a temperature of about 225° C. Upon analysis, the resulting product was found to contain, by weight, 2.8% nitrogen and 2.5% calcium.

EXAMPLE 4

131 grams (0.5 mol) of monododecylphenol, 135 grams of the diluent employed in Example 1, 18.5 grams (0.25 mol) of calcium hydroxide, 18.9 grams (0.1 mol) of tetraethylene pentamine and 2 grams of water were slowly heated with stirring to a temperature of about 250° C. over a period of about six hours. Upon analysis, the resulting product was found to contain, by weight, 2.5% nitrogen and 3.22% calcium.

EXAMPLE 5

131 grams (0.5 mol) of monododecylphenol, 151 grams of the diluent employed in Example 1, 47.35 grams (0.25 mol) tetraethylene pentamine, 18.5 grams (0.25 mol) calcium hydroxide and 4 grams of water were stirred at a temperature of 90° C. for a period of about two hours and then slowly heated to a temperature of about 200° C. Upon analysis, the resulting product was found to contain, by weight, 5.5% nitrogen and 2.45% calcium.

EXAMPLE 6

131 grams (0.5 mol) of monododecylphenol, 131 grams of the diluent employed in Example 1, 18.5 grams (0.25 mol) of calcium hydroxide and 60 grams (0.25 mol) of tetrahydroxyethyl ethylene diamine were slowly heated with stirring to a temperature of about 250° C. Upon analysis, the resulting product was found to contain, by weight, 2.0% nitrogen and 2.93% calcium.

EXAMPLE 7

210 grams (0.8 mol) of monododecylphenol, 32 grams (0.43 mol) of calcium hydroxide, 230 grams (0.85 mol)

of N-dodecyldiethylene triamine and 20 grams of water were stirred at a temperature of 90° C. for a period of about four hours and then slowly heated to a temperature of about 225° C. Upon analysis, the resulting product was found to contain, by weight, 8% nitrogen and 2.86% calcium.

EXAMPLE 8

410 grams (0.4 mol) of monopolybutylene alkylated phenol, 28 grams (0.5 mol) of calcium hydroxide, 30 grams (0.5 mol) of ethylenediamine and 10 grams of water were stirred at a temperature of 90° C. for a period of about three hours and then slowly heated to a temperature of about 225° C. Upon analysis, the resulting product was found to contain, by weight, 3.0% nitrogen and 0.6% calcium.

EXAMPLE 9

220 grams (1 mol) of monononylphenol, 73 grams (0.5 mol) of triethylene tetramine, 21 grams (0.25 mol) of zinc oxide and 220 grams of xylene as a diluent were stirred at a temperature of 100° C. for a period of about four hours and then at 140° C. for a period of about three hours. Upon analysis, the resulting product was found to contain, by weight, 5.0% nitrogen and 3.2% zinc.

EXAMPLE 10

220 grams (1 mol) of monononylphenol, 73 grams (0.5 mol) of triethylene tetramine, 42 grams (0.25 mol) of barium dioxide and 15 grams of water were stirred at a temperature of 105° C. for a period of about six hours and then slowly heated to a temperature of about 175° C. 220 grams of xylene as a diluent were added. Upon analysis, the resulting product was found to contain, by weight, 5.1% nitrogen and 6.7% barium.

EXAMPLE 11

220 grams (1 mol) of monononylphenol, 73 grams (0.5 mol) of triethylene tetramine and 20 grams (0.5 mol) of lithium hydroxide monohydrate were stirred at a temperature of about 105–110° C. for a period of about four hours. Upon analysis, the resulting product was found to contain, by weight, 9.0% nitrogen and 0.63% lithium.

COMPARATIVE EXAMPLES

In order to illustrate the specific criticality of the ethyleneamine component in the reaction mixture for producing the novel metal salts of the present invention, the following comparative data was obtained.

EXAMPLE 12

1 mol of monododecylphenol, 0.33 mol of dipropylene triamine (iminobispropylamine) and 0.5 mol of calcium hydroxide were stirred to a temperature of about 200° C. It was found that no reaction product was formed and the calcium hydroxide remained unreacted.

EXAMPLE 13

An attempt was made to react calcium hydroxide in varying amounts with alkyl phenols in the absence of ethyleneamine compounds. No reaction was found to occur.

EXAMPLE 14

An attempt was made to react a cyclic ethyleneamine, viz. piperazine, with dodecylphenol and calcium hydroxide. No reaction was found to occur.

EXAMPLE 15

An attempt was made to react 1,3 propanediamine with dodecylphenol and calcium hydroxide. No reaction was found to occur.

The anti-screen clogging characteristics of organic compositions in the form, for example, of fuel oils having incorporated therein the novel metal salts of the present invention were determined from a standard screen clogging test, as described in U.S. Pat. 3,296,130, issued Jan. 3, 1967. In general, this test is conducted using a Sundstrand V3 or S1 home fuel oil burner pump with a self-contained 100-mesh monel metal screen. About 0.05 percent, by weight, of naturally-formed fuel oil sediment, composed of fuel oil, water, dirt, rust and organic sludge is mixed with 10 liters of the fuel oil. This mixture is circulated by the pump through the screen for 6 hours. Then, the sludge deposit on the screen is washed off with normal pentane and filtered through a tared Gooch crucible. After drying, the material in the Gooch crucible is washed with 50–50 (volume) acetone-methanol mixture. The total organic sediment is obtained by evaporating the pentane and the acetone-methanol filtrates. Drying and weighing the Gooch crucible yields the amount of inorganic sediment. The sum of the organic and inorganic deposits on the screen can be reported in milligrams recovered or converted into percent screen clogging.

The metal salts prepared in accordance with the foregoing Examples 1 through 10 were individually blended in test fuel oils comprising a blend of 60 percent distillate stock obtained from continuous catalytic cracking and 40 percent straight-run distillate stock, having a boiling range of between about 320° F. and about 640° F., and typical of No. 2 fuel oils. Each blend was subjected to the above-described screen clogging test. The test results obtained are set forth in the following Table I.

TABLE I.—SCREEN CLOGGING TEST

Additive	Concentrate lbs./1,000 bbls.	Screen clogging, percent
Uninhibited fuel blend	0	100
Uninhibited fuel blend plus Example 1	50	18
Uninhibited fuel blend plus Example 2	50	19
Uninhibited fuel blend plus Example 4	50	21
Uninhibited fuel blend plus Example 6	50	18
Uninhibited fuel blend plus Example 8	50	25
Uninhibited fuel blend plus Example 9	50	35
Uninhibited fuel blend plus Example 10	50	15
Uninhibited fuel blend plus Example 11	50	32

In order to evaluate the metal salts of the present invention as stabilizers for lubricating oils, and for subsequent incorporation of the latter into grease formulations, these metal salts were subjected to a Catalytic Oxidation Test. This test determines the effectiveness of an additive in preventing the catalytic oxidation of the oil sample under oxidizing conditions. The test procedure is conducted as follows: in a 200 mm. x 25 mm. test tube is placed a 25 gram sample of the test oil having immersed therein (a) 15.6 sq. in. of sand-blasted iron wire, (b) 0.78 sq. in. of polished copper wire, (c) 0.87 sq. in. of polished aluminum wire and (d) 0.167 sq. in. of a polished lead specimen. The oil sample is heated to a temperature of 325° F. and maintained at this temperature while dry air is placed therethrough at the rate of 5 liters per hour for a period of 40 hours. The change in neutralization number and kinematic viscosity before and after the oxidation are recorded, and the weight loss of the lead specimen is obtained. In the following Table II are shown the effects of the additives of some of the foregoing examples of the present invention compared with the uninhibited lubricant which comprises a furfural refined neutral mineral oil SUS 130" at 100° F.

TABLE II.—CATALYTIC OXIDATION TEST

Additive	Concentrate, weight percent	ΔN.N.	Viscosity increase, percent	Lead loss, mg.	Sludge
Uninhibited oil		19.3	460	220	Medium.
Example 1	4	0.53	60	55	Nil.
Example 2	4	4.28	83	90	Nil.
Example 3	4	3.4	67	82	Nil.
Example 4	2	0.5	4.5	4.0	Nil.
Example 5	4	1.7	79	71	Nil.
Example 6	4	2.1	73	52	Nil.
Example 7	4	9.0	92	54	Nil.
Example 8	4	0.9	12	26	Nil.
Example 9	4	2.7	37	56	Nil.
Example 10	4	2.7	44	51	Nil.
Example 11	4	8.1	52	60	Nil.

As is apparent from the data of Tables I and II, the metal salts of the present invention are effective as improving agents in various types of organic compositions, such as exemplified by their use as anti-screen clogging agents in fuel oils, or as stabilizers for lubricating oils, or lubricating oils employed as vehicles in grease formulations. In this respect, it will also be seen that these additives are effective as improving agents with respect to other specific types of organic compounds, such as fuel oils in the form of gasolines, and more specifically, to the treatment of such hydrocarbons as petroleum distillate fuels. They are also effective as stabilizers for hydrocarbon and synthetic lubricants of various types.

Although the present invention has been described with preferred embodiments, it will be understood that modifications and variations thereof may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily appreciate.

I claim:

1. A metal salt of the reaction product of an alkyl phenol selected from the group consisting of monododecylphenol, didodecylphenol, monopolybutylene alkylated phenol and monononylphenol, an ethyleneamine selected from the group consisting of ethylene diamine, N-hydroxyethylethylene diamine, triethylene tetramine, tetraethylene pentamine, tetrahydroxyethyl ethylene diamine and N-dodecyldiethylene triamine, and a metal oxide wherein the metal of said metal oxide is selected from the group consisting of calcium, zinc, barium, lithium and potassium.

2. The method for producing a metal salt as defined in claim 1 which comprises stoichiometrically reacting the alkyl phenol, ethyleneamine and metal oxide at a temperature from about 50° C. to about 250° C.

3. The method for producing a metal salt as defined in claim 1 which comprises reacting the alkyl phenol, ethyleneamine and metal oxide at a temperature from about 150° C. to about 250° C.

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