United States Patent Office 3,809,648
Patented May 7, 1974

3,809,648

MAGNESIUM PHENOXIDES AND LUBRICANTS CONTAINING THE SAME

Bruce W. Hotten, Orinda, Calif., assignor to Chevron Research Company, San Francisco, Calif.

No Drawing. Filed July 12, 1972, Ser. No. 271,324
Int. Cl. C10m 1/48
U.S. Cl. 252—32.7 E 10 Claims

ABSTRACT OF THE DISCLOSURE

Novel magnesium phenoxides are prepared by a two step process wherein an alkylated phenol is reacted with formaldehyde and a dialkanol amine in a first step to form a Mannich base and in a second step, the Mannich base is neutralized with magnesium methoxide. The magnesium phenoxides impart good hydrolytic stability to zinc dihydrocarbyl dithiophosphate containing lubricants.

This invention relates to novel stabilizers for lubricating compositions, more particularly this invention relates to stabilizers for zinc dithiophosphate containing lubricants.

BACKGROUND OF THE INVENTION

Additives are frequently incorporated into oils and greases to improve their lubricating properties. Typical additives currently employed include viscosity improvers, foam inhibitors, corrosion and rust inhibitors, anti-oxidants, etc. Although these additives are important and contribute to the overall performance of the lubricant, one class of additives is particularly important because of its ability to greatly increase machinery life. This class of additives is known as the anti-wear agents. Most of the conventional anti-wear agents contain elements such as chlorine, sulfur or phosphorus which react or complex with the exposed metal surfaces of the machinery. By attaching to the metal surfaces in such a manner, the anti-wear agents prevent or at least sharply reduce the wear at these surfaces and allow the machinery to operate under greater loads with less threat of wear or seizure.

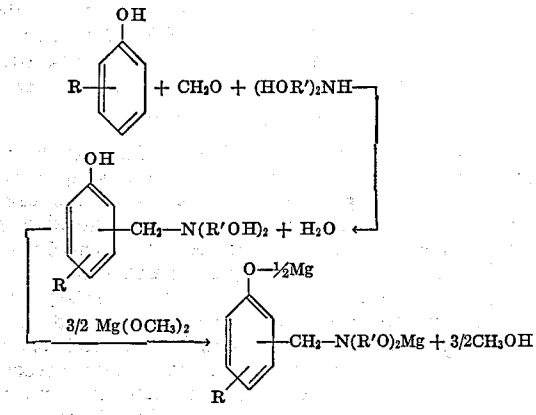
The zinc dithiophosphate anti-wear agents have experienced wide spread commercial success. These agents have been found to exhibit very good anti-wear properties as well as excellent corrosion inhibition and extreme pressure characteristics. The zinc dithiophosphates have also proven to be quite stable and endurable under low and moderate temperature conditions.

However, with the development of high speed and high temperature equipment, good performance at elevated temperatures is becoming more and more critical. Modern, more efficient engines are designed to operate at increasingly high temperatures and it is necessary that the lubricating oils and greases withstand these high temperatures with as little deterioration as possible.

This feature is particularly critical in the dithiophosphate additives since they have a tendency to decompose at high temperatures. Since the decomposition is auto-catalytic, decomposition of even a small amount of the dithiophosphate additive causes a rapid decomposition of the remaining material. Therefore, any means by which the initial decomposition can be lessened will have a highly beneficial effect on a lubricating composition. Since the zinc dithiophosphates have exceptional multi-functional properties, it is a considerable advantage to stabilize these compounds at the higher temperatures rather than develop a new anti-wear agent.

SUMMARY OF THE INVENTION

I have found that lubricants containing zinc dithiophosphates can be made having improved thermal stability by incorporating within the lubricant the reaction product of magnesium methoxide and a particular Mannich base. The Mannich base is prepared by condensing an alkylated phenol, formaldehyde and a dialkanol amine. The reaction and the reaction products can be illustrated by the following chemical equation:



In the above equation, R is a hydrocarbyl having from 8 to 35 carbons and preferably from 10 to 30 carbons; and R' is an alkylene having from 2 to 6 carbons and preferably from 2 to 4 carbons and most preferably 2 carbons.

As referred to herein hydrocarbyl is a monovalent organic radical composed essentially of hydrogen and carbon and may be aliphatic, aromatic or alicyclic or combinations thereof, e.g. aralkyl, alkyl, aryl, cycloalkyl, alkylcycloalkyl, etc. and may be saturated or ethenically unsaturated (one or more double bands conjugated or nonconjugated). The alkylene is a divalent saturated aliphatic hydrocarbon having its two free valences on different carbon atoms.

The above chemical equation represents a broad and simplified version of both the reaction between the Mannich base and the magnesium methoxide and the resulting magnesium phenoxide product. The reaction product is a mixture of various magnesium phenoxides forming dimers, trimers, etc. with the above aminophenolic groups. The above formula indicates that each hydroxyl unit on the Mannich base enters into a neutralization reaction with one half of the magnesium methoxide molecule. However, because the composition is a mixture of compounds, it should be recognized that a few of the molecules may have less than all the hydroxyl groups neutralized with the magnesium methoxide. Moreover, some of the metal atoms may be ionized and exist as cations within the product mixture. Also some molecules of magnesium methoxide may react with an hydroxyl unit on the phenolic group and with an hydroxy unit on the amino group of the same Mannich base molecule forming a heterocyclic ring. Thus, it is apparent that while the above chemical equation represents a general description of the reaction and the magnesium phenoxide product it should not be interpreted as limiting the invention to the exact structure as shown.

The above magnesium phenoxide can be employed directly in the lubricating oil to stabilize the zinc dithiophosphates. However I have found that by carbonating the magnesium phenoxide the oil solubility of the compound can be beneficially improved. The carbonation can be performed by simply contacting the compound with carbon dioxide under elevated temperatures and pressures. Carbonation generally takes place with the magnesium atom on the phenoxy group, however, some carbonation of the magnesium on the amino groups may also occur and in some instances may be present in major quantities. The carbonation of the magnesium phenoxide

does not reduce the effectiveness of the compound in thermally stabilizing the zinc dithiophosphate lubricants.

DESCRIPTION OF THE INVENTION

The magnesium phenoxide stabilizers of this invention can be prepared by a series of reaction steps. In a first step, a Mannich base is prepared by a condensation reaction of an alkylated phenol, formaldehyde and a dialkanol amine. This condensation product is thereafter neutralized with magnesium methoxide in a second step to produce the magnesium phenoxide. In an optional third step, the magnesium phenoxide is subjected to carbonation to produce a carbonated magnesium phenoxide. These three steps are discussed separately hereinafter.

Mannich condensation step

The Mannich condensation intermediate can be prepared by either a continuous or batch processing scheme. However, in either processing scheme, the reaction can be conducted non-catalytically by merely contacting the alkylated phenol with formaldehyde and dialkanol amine. For the purposes of illustrating the preparation, the following is a brief discussion of an exemplary batch process. The alkylated phenol, formaldehyde, dialkanol amine and an inert mutual solvent having good solvency for the three reactants are charged to a suitable reaction vessel. The reaction is allowed to proceed at a temperature from 70 to 250° F. and preferably from 90 to 200° F. The reaction is exothermic and hence cooling is normally required to maintain the temperature within the desired range. The reaction pressure is not critical except that it is preferred to apply sufficient pressure on the system to maintain the reactants and mutual solvent in the liquid phase. Generally, the pressure employed ranges from 1 to 5 atmospheres with atmospheric pressure being preferred. The reaction time required to complete the condensation reaction varies depending upon the reaction temperature, the particular reactants selected, the processing scheme employed, etc. However, the reaction time usually varies from 1 to 20 hours and preferably from 2 to 15 hours.

At the end of the reaction period, the mutual solvent and any water of reaction are stripped from the system and an inert auxiliary diluent is charged to the vessel. The diluent is employed to reduce the viscosity of the Mannich base to within a range suitable for pumping. The amount of auxiliary diluent which may be employed generally ranges from 40 to 80 weight parts of diluent per part of Mannich base, however greater or less amounts may be used.

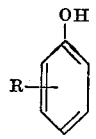
The amount of the various reactants charged to the reaction vessel will normally be stoichiometric or substantially stoichiometric quantities. The concentration of the reactants within the mutual solvent, on the other hand, will normally be within the range set forth in the following Table 1.

TABLE 1

Reactant concentration in Mannich step

	Weight percent	
	Broad range	Preferred range
Component:		
Mutual solvent	0–80	40–60
Alkylated phenol	20–90	40–80
Formaldehyde	5–30	10–20
Dialkanol amine	5–30	15–25

The alkylated phenols useful in the practice of this invention are of the formula:

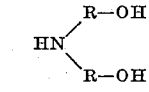


wherein R may be a straight or branched chain alkyl having from 4 to 35 carbon atoms and preferably from 7 to 30 carbon atoms. The R groups or alkyl groups may be present on any of the sites around the phenolic ring, i.e. ortho, meta or para. That is, less than 40% of the R groups will be in the ortho position and preferably less than 15% in the ortho position. A particularly preferred alkylated phenol is a polypropenylphenol having from 9 to 20 carbons in the polypropenyl group and located mainly in the para position.

Examples of suitable alkyls include octyl, decyl, dodecyl, ethylhexyl, triacontyl, etc.; radicals derived from petroleum hydrocarbons such as white oil, wax, olefin polymers (e.g. polypropylene, polybutylene, etc.) may be employed. While one specific structure is indicated by the above formula, it should be recognized that mixtures of alkylated phenols can be successfully employed in this invention.

Formaldehyde is one of the reactants in the subject process, and is preferably in the form of paraformaldehyde. Although it is preferred to carry out the reaction with stoichiometric quantities of each of the reactants, in some instances it is advantageous to employ an excess of the formaldehyde reactant. In these instances, a molar excess of 5 to 15 percent over that stoichiometrically required may be employed.

The dialkanol amines useful in the practice of this invention have the following structure:



wherein R is a straight or branch chained alkylene having from 2 to 6 carbon atoms. Exemplary dialkanol amines include diethanol amine, di-n-propanol amine, diisopropanol amine, dibutanol amine, di-sec-butanol amine, di-n-butanol amine, dipentanol amine, dihexanol amine, etc. The preferred dialkanol amines are diethanolamine and diisopropanol amine and more preferably diethanolamine.

The mutual solvent employed in this step can comprise any stable organic solvent which is inert to the reactants, Mannich base and auxiliary diluent and which provides good solvency for all three reactants. With this medium, phase separation is avoided along with the resultant distribution of reactants in the two phases. An exemplary mutual solvent found most suitable in this invention is isopropyl alcohol. Other suitable mutual solvents include the C_1 to C_6 alkanols such as methanol, ethanol, propanol, butanol, isobutyl alcohol, etc. The reaction may, alternatively, be conducted without a solvent, but in these instances more vigorous stirring and longer reaction times may be required.

The auxiliary diluent employed in the subject invention can comprise any C_6 to C_{30} aliphatic or aromatic hydrocarbon, such as hexane, octane, nonane, benzene, toluene, naphthelene, ethyl cyclohexane, etc., halogenated hydrocarbons, hydrocarbon esters, hydrocarbon ether, hydrocarbon amides, etc. each having from 2 to 20 carbons.

In a specific embodiment of this invention, the diluent is a mineral lubricating oil obtained from paraffinic, naphthenic asphaltic or mixed based crudes and/or mixtures thereof having a flash point above about 350° F. In this embodiment, the diluent is compatible with or comprises the base stock for the lubricant composition. The diluent serves to reduce the viscosity of the Mannich base and the magnesium phenoxide to make them more readily transferable by pumping operations and the like.

Neutralization step

The magnesium phenoxides are prepared by neutralizing the Mannich base prepared by the above procedure with magnesium methoxide. This process may be performed by simply contacting, under strong agitation, the Mannich base and magnesium methoxide within a suitable reaction vessel under conditions conducive for the reaction. Generally, the reaction temperature may vary from 20° C. to

200° C. and preferably from 50° C. to 150° C. The pressure on the system is not critical except that liquid phase conditions should be maintained. In one convenient embodiment the pressure is maintained at a sufficient level so as to allow by-product methanol to be continuously stripped from the system during the reaction.

It is also preferred to conduct the reaction in the presence of the auxiliary diluent of the type employed in the Mannich condensation step. In this manner, the reaction may proceed within a low viscous liquid reaction medium without forming a semi-solid or gelled phase. The time required to complete the neutralization varies depending upon the reactants chosen, the reaction temperature, etc. Usually the time varies from 2 to 10 hours and preferably from 2 to 8 hours.

The amount of magnesium methoxide employed in the reaction is preferably maintained at stoichiometric amounts; however, it is recognized that in some instances it might be advantageous to employ slightly excess amounts of magnesium methoxide to force the neutralization reaction to completion.

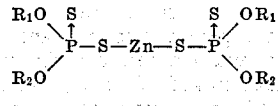
The magnesium methoxide is preferably introduced into the reaction medium within a liquid solution and preferably a liquid methanol solution. By introducing the magnesium methoxide into the reaction medium in this manner, increased intimacy of the reactants is achieved. Good results can be obtained with concentrations of magnesium methoxide in a methanol solution ranging from 5 to 12 weight percent.

The particular concentration of the Mannich base and magnesium methoxide within the auxiliary diluent during the reaction is not critical to the practice of the invention. However, I have found that a concentration of 10 to 50 weight percent of Mannich base and 5 to 15 weight percent of magnesium methoxide results in a good conversion to the magnesium phenoxide product without experiencing high viscosity problems. The reaction is preferably conducted under anhydrous or substantially anhydrous conditions since water has a deleterious effect on the reaction.

Carbonation step

The carbonation of the magnesium phenoxide improves the oil-solubility of the compound without detracting from its thermal stabilizing properties. The compound is carbonated by simply passing carbon dioxide through the magnesium phenoxide solution prepared in the above neutralization step. The carbonation temperature is generally maintained between about 50 and 100° C. and preferably from 60° to 80° C. and the reaction pressure is preferably maintained from 1 to 50 atmospheres and preferably from 1 to 10 atmospheres. The reaction time varies depending on its temperatures and pressures and degree of carbonation desired; however, it usually ranges from 30 minutes to 10 hours and preferably from 2 to 8 hours. Generally, from 1 to 2 mols of carbon dioxide are employed per mol of magnesium phenoxide prepared in the neutralization step.

The magnesium phenoxides of this invention are capable of stabilizing zinc dithiophosphate esters having the formula:



Where R_1 and R_2 are the same or different aliphatic or aromatic radicals having from 3 to 30 carbon atoms. Exemplary zinc dithiophosphate esters include zinc salts of dialkyldithiophosphates, such as, dibutyldithiophosphate, dihexyldithiophosphate, diamyldithiophosphate, dioctyldithiophosphate, butylamyldithiophosphate, etc.; diaryldithiophosphates, such as, diphenyldithiophosphate, di(tetrapropenylphenyl)dithiophosphate, ditolyldithiophosphate, etc. and alkylaryldithiophosphates, such as butylphenyldithiophosphate, amyltolyldithiophosphate, etc.

A particularly preferred zinc dithiophosphate is prepared by reacting zinc oxide with the reaction product of isopropyl or butyl alcohol, phosphorus pentasulfide (P_2S_5) and methylisobutyl carbinol. Another preferred zinc dithiophosphate is prepared by reacting zinc oxide with the reaction product of tetrapropenylphenol and phosphorus pentasulfide (P_2S_5).

The lubricant composition is prepared by simply mixing the zinc dithiophosphate ester and the carbonated or uncarbonated magnesium phenoxide within a suitable lubricating oil. The amount of magnesium phenoxide which may be present within the lubricating oil to impart the desired thermal stability varies depending upon the particular magnesium phenoxide employed, the type of lubricating oil used, the presence of other additives, the type and amount of zinc dithiophosphate ester, etc. Generally, however, the amount of magnesium phenoxide employed within the lubricating oil will vary from 0.5 to 5 weight parts and preferably from 1 to 2 weight parts per part of zinc dithiophosphate. Generally this ranges from 1 to 5 weight percent and usually from 1 to 4 weight percent of the final lubricant composition. Normally, the amount of zinc dithiophosphate within the lubricant ranges from 0.3 to 2 weight percent of the final composition.

The lubricating oils which may be employed in the practice of this invention include a wide variety of oils such as naphthenic base, paraffin base and mixed base lubricating stocks. Other hydrocarbon oils which may be employed include lubricating oils derived from coal products and synthetic oils, e.g. (alkylene polymers, such as polypropylene, butylene, etc. and mixtures thereof), alkylene oxide type polymers (e.g. alkylene oxide polymers prepared by polymerizing alkylene oxide such as propylene oxide, etc., in the presence of water or alkanols, e.g. ethyl alcohol), carboxylic acid esters (e.g. those which were prepared by esterifying carboxylic acids such as adipic acid, azelaic acid, subaric acid, sebacic acid, alkenylsuccinic acid, fumaric acid, maleic acid, etc., with the alcohol such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, pentaerythritol, etc.), liquid esters of phosphorus such as trialkyl phosphate (tributyl phosphate) dialkylarylphosphate, triaryl phosphate (tricresyl phosphate), etc. alkyl benzenes, polyphenols (e.g. bis phenols and terphenols), alkyl biphenyl ethers, polymers of silicone e.g. tetraethyl silicate, tetraisopropyl silicate, hexyl (4-methyl-2-pentoxy)disilicane, poly(methyl)siloxane an poly-(methylphenyl)siloxane, etc. The lubricating oils generally have a viscosity which ranges from 50 to 1000 SUS second Universal Saybolt and usually from 100 to 800 SUS at 100° F.

In addition to the zinc dithiophosphate and magnesium phenoxide, other additives may be successfully employed within the lubricating composition of this invention without adversely effecting its high stability and performance over a wide temperature scale. One type of additive is an anti-oxidant or oxidation inhibitor. This type of additive is employed to prevent varnish and sludge formation on metal parts in gasoline and diesel engines and to inhibit corrosion of alloyed bearings. Typical antioxidants are organic compounds containing sulfur, phosphorus or nitrogen, such as organic amines, sulfides, hydroxysulfides, methanols, etc., alone or in combination with metals such as zinc, tin or barium. Particularly useful antioxidants include phenyl-α-naphthylamine, bis(alkylphenyl)amine, N,N-diphenyl-p-phenylene-diamine, 2,2,4-trimethyldihydroquinoline oligomer, bis(4-isopropylaminophenyl)ether, N-acyl-aminophenol, N-acylphenothiazine, N-hydrocarbylamides or ethylenediaminetetraacetic acid, alkylphenol-formaldehyde-amine polycondensates, etc.

Other types of lubricating oil additives which may be employed in the practice of this invention include tacki-

ness agents, dropping point improvers, lubricating agents, color correctors, odor control agents, etc. as well as other anti-wear agents such as tricresyl phosphate, sulfurized sperm oil, etc.

The stabilizers of this invention may also be employed in grease compositions to increase the bearing life and other endurance properties of the grease. These agents may successfully be employed with such thickening agents as polyurea as disclosed in U.S. Pat. Nos. 3,323,210; 3,281,361; 3,346,497 and 3,402,027; calcium stearate, lithium stearate, aluminum complexes such as disclosed in U.S. Pat. Nos. 2,599,553; 3,345,291 and 3,514,400, etc. Generally when employed in grease formulations, the amount of magnesium phenoxide present will range from 0.5 to 5 weight percent and preferably from 1 to 2 weight percent of the final grease composition.

In many instances it may be advantageous to form concentrates of the magnesium phenoxide within an organic, preferably hydrocarbon, carrier liquid. The employment of concentrates provides a convenient method for handling and transporting the magnesium phenoxide for their subsequent dilution and use. Concentration of the magnesium phenoxide within these concentrates may vary from 20 to 30 weight percent of the final concentrate.

It should be well recognized that the instant magnesium phenoxide may be successfully employed in lubricant applications wherein zinc dithiophosphate is employed as an anti-wear agent. Thus, the magnesium phenoxides may be employed in lubricating oils such as motor oils, gear oils, transmission fluids, hydraulic fluids, cutting oils and lubricating oils for pneumatic devices such as jackhammers, sinkers, stoppers, drifters and downhole drills. The magnesium phenoxides of this invention are particularly useful in motor oils and transmission fluids.

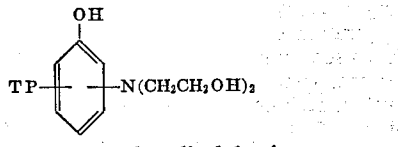
The magnesium phenoxide may also be employed in mist lubricants. In a mist lubricating system, the lubricant is atomized in a mist generator and carried through conduits by an air stream. The lubricant droplets are coalesced and collected at the lubricating site. Such systems permit simultaneous lubrication at several remote lubricating points from a central lubricant reservoir.

The following examples are presented to illustrate the practice of specific embodiments of this invention and should not be interpreted as limitations upon the scope of the invention.

Example 1

This example is presented to demonstrate the preparation of a representative Mannich base intermediate as employed in the practice of this invention. A 2000 ml. reaction vessel is charged with 350 g. of polypropenylphenol, having an average molecular weight of approximately 262, 260 g. of diethanol amine, 300 ml. of isopropanol and 212 g. of an aqueous formaldehyde solution (37%). The contents of the reaction vessel are agitated and refluxed at a temperature of 180°–190° F. for a period of 18 hours. At the end of the 18 hour period, the mixture is washed four times with distilled water, each time allowing the mixture to form separate liquid phases and decanting the aqueous phase. The solution is dehydrated by azeotropic distillation with benzene. Finally, the crude Mannich base is stripped at 250° F. for 10 minutes to recover 505 grams of product base.

The Mannich base is analyzed and found to contain 4.06 percent nitrogen and have an alkalinity value of 448. The calculated structure of the Mannich base is as follows:



wherein TP is tetrapropenyl radical having an average of 9 to 12 carbons.

Example 2

A one-liter resin-lined flask, equipped with a stirrer, thermometer, and a nitrogen gas inlet and an outlet connected to a turned down condenser is charged with 187 g. of the Mannich base produced by the method of Example 1, 187 g. of 126 neutral oil and approximately 500 g. of a methanol solution containing 8 wt. percent of magnesium methoxide. The contents are vigorously stirred under a nitrogen gas stream and heated slowly to a temperature between 64 and 75° C. with methanol being distilled from the solution and collected within the turned down condenser. An additional 763 g. of methanol containing 8 weight percent magnesium hydroxide are slowly charged to the reaction vessel over a 4½ hour period.

After all of the magnesium methoxide has been charged to the reactor, 84 g. of additional 126 neutral oil is added and the temperature increased to 100° C. and maintained for an additional 30 minutes. At the end of this period, all of the methanol is removed from the reaction mixture. The remaining reaction mixture weighed 493 g. and is calculated to contain 45 weight percent of magnesium phenoxide.

Thereafter, 482 g. of the magnesium phenoxide solution is transferred to a two liter resin flask and 800 ml. of toluene added to the solution and heated to reflux at a temperature of about 110° C. and maintained at those conditions for 1¾ hours. The contents of the reactor are then cooled to 80° C. and the reaction mixture carbonated for 1 hour by bubbling carbon dioxide through the mixture at the rate of 0.5 liter per minute.

The reactor contents weighed 1074 g. of which 537 g. are decanted into a two-liter beaker. To the remaining one-half of the contents, an additional 500 ml. of toluene are added and the combined mixture heated under stirring with a nitrogen purge to 80° C. The reactor contents are then filtered through a diatomaceous filter and the filtrate collected. The filtrate is then stripped of toluene by heating the same to a temperature of 120° C. under a vacuum of 200 mm. of mercury absolute. When most of the toluene has been stripped from the solution, 60 g. of 126 neutral oil are added. This mixture weighed 538 g. and is calculated to be 39.8 weight percent of magnesium phenoxide in 126 neutral oil. The product is analyzed by emission spectroscopy and found to contain 3.23 weight percent of magnesium. The solution has a total alkalinity value of 217.6 mg. of KOH/g. and a basic N alkalinity value of 49.7 mg. of KOH/gram and a magnesium alkalinity value of 167.4 mg. of KOH/g. The calculated nitrogen content is 1.24 weight percent nitrogen and the calculated magnesium is 3.36 percent magnesium.

Example 3

A one liter resin flask equipped with a stirrer, thermometer, nitrogen gas inlet and outlet connected to a turned down condenser is charged with 154.8 g. of 2-bis(hydroxyethyl)methyl-4-alkylphenol [1] and 155 g. of 126 neutral oil. Contents of the reactor are stirred and 647 g. of a methanol solution containing 8 wt. percent of magnesium methoxide is slowly charged to the reactor. The mixture is heated to 64° C. over a period of approximately 30 minutes and maintained at that temperature over a 45 minute period with methanol being distilled from the mixture and removed from the system. The mixture is then heated to 115° C. over a period of one hour with a total of 585 g. of methanol being removed from the system by distillation. The remaining reaction products within the vessel weighed 359 g. and an infrared spectrum revealed that no detectable hydroxyl units remained in the compound.

The reaction product is then subjected to carbonation by passing carbon dioxide through the solution over a 30 minute period at a temperature of 115–125° C. The red-

[1] The alkylphenol is a cracked wax alkylated phenol.

dish-brown reaction product weight 343 g. and is calculated to be 54.8 weight percent of magnesium phenoxide in 126 neutral oil. A sample of the reaction product is tested for its alkalinity value and analyzed for magnesium content by emission spectroscopy.

The total alkalinity value (AV), is measured to be 250.8 mg. KOH/g. with a basic nitrogen AV of 48 mg. of KOH/g. and a basic magnesium AV being 202.8 mg. of KOH/g. Based on the measured AV values, the calculated nitrogen content is 1.19% and the calculated magnesium content is 4.39%. The magnesium content as determined by emission spectroscopy is 3.9%.

Example 4

This example is presented to demonstrate the effectiveness of the magnesium phenoxide compounds in stabilizing the thiophosphate anti-wear agents. In this test a lubricant of 480 neutral oil and 2 weight percent zinc bis(tetrapropenylphenyl) dithiophosphate is mixed together with 2 weight percent of various stabilizing compositions. For comparison purposes, lubricant A contains no stabilizer. In lubricant B, a stabilizing agent consisting of an overbased calcium sulfonate containing 11.4 weight percent calcium is added to the mixture. In lubricant C, commercial sulfurized calcium phenate containing 9.25% calcium is employed as the stabilizing agent. In lubricants D and E magnesium phenoxides prepared by the methods in Examples 2 and 3 are employed in the respective solutions. The five solutions are then subjected to a copper strip corrosion test under the procedure presented in ASTM D130–68. The ASTM rating after 3 hours and a 300° F. of the copper strip in the oil phase is set forth in the following Table 2.

TABLE 2

Copper strip corrosion test

Lubricant	Additive	Rating	Description of Test Strip
A	None	4	Transparent black with peacock green barely showing.
B	Calcium sulfonate	3	Magenta overcast on brassy strip.
C	Calcium phenate	2	Multicolored with lavender blue overlaid on claret red.
D	Magnesium phenoxide	1	Light orange.
E	do	1	Dark orange.

The above table clearly demonstrates the superior rust inhibition of lubricants D and E over lubricants A, B and C.

Example 5

This example is presented to demonstrate the oxidative stabilizing properties of the magnesium phenoxides. In the test, five different lubricants are studied. The various lubricants are prepared by admixing various stabilizers with a multiservice motor oil containing 7 mmoles/kg. of zinc diaryl dithiophosphate and 11 mmols/kg. of zinc dialkyl dithiophosphate. The stabilizers employed herein are a carbonated magnesium phenoxide as prepared by the method of Example 2 (referred to herein as magnesium phenoxide-2), a carbonated magnesium phenoxide as prepared by the method of Example 3 (referred to herein as magnesium phenoxide-3), a conventional calcium phenate prepared by neutralizing a Mannich base (condensation of polypropenylphenol, formaldehyde and methylamine) with calcium hydroxide, and a conventional magnesium phenate prepared by neutralizing a Mannich base (condensation of polypropenyl phenol, formaldehyde and methylamine) with magnesium methoxide.

The oxidation test comprises bubbling oxygen through the test composition at a temperature of 340° F. and measuring the time required for the solution to remove 1 liter of oxygen per 100.00 grams of solution. The results of this test are presented in the following Table 3.

TABLE 3

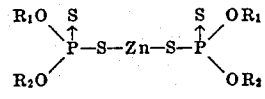
Oxidation test

	Auxiliary stabilizer	Concentration (mmols/kg.)	Oxygen takeup (hrs.)
1	None		5.2
2	Magnesium phenoxide-2	25	8.2
3	Magnesium phenoxide-3	50	6.9
4	Calcium phenate	25	5.8
5	Magnesium phenate	25	6.0

The above table clearly illustrates the effectiveness of the stabilizers of this invention in retarding the oxidation of the zinc dithiophosphates.

I claim:

1. A lubricant composition comprising (1) a major portion of a base oil, (2) 0.3 to 2 weight percent of a zinc dihydrocarbyl dithiophosphate having the structure:



wherein R_1 and R_2 are the same or different hydrocarbyl having from 3 to 30 carbons; and (3) from 0.5 to 5 weight parts per part of said zinc dihydrocarbyl dithiophosphate of a magnesium phenoxide prepared by reacting an alkylated phenol having from 14 to 42 carbon atoms, formaldehyde, and dialkanol amine having from 2 to 6 carbons to form a Mannich base and neutralizing the Mannich base with magnesium methoxide.

2. The composition defined in claim 1 wherein said magnesium phenoxide is subjected to carbonation at a temperature of from 50 to 100° C. and a carbon dioxide pressure of 1 to 50 atmospheres for a period of 30 minutes to 10 hours.

3. The composition defined in claim 2 wherein said R' is ethylene, and R_1 is butyl and said R_2 is phenyl.

4. A lubricant composition comprising (1) a major portion of a base oil having a viscosity between about 50 and 100 SUS at 100° F., (2) from 0.3 to 2 weight percent of a zinc dialkyl, diaryl or alkylaryl dithiophosphate and (3) from 0.5 to 5 weight parts per part of said zinc dithiophosphate of a carbonated magnesium phenoxide prepared by neutralizing a Mannich base prepared by condensing a C_{10} to C_{41} alkylated phenol, formaldehyde and a C_4 to C_{12} dialkanol amine, with magnesium methoxide and thereafter carbonating the neutralized reaction product with carbon dioxide at a temperature of about 50 to 100° C. and a carbon dioxide pressure of 1 to 50 atmospheres.

5. The composition defined in claim 4, wherein said alkylated phenol is tetrapropenyl phenol and said dialkanol amine is diethanol amine.

6. A lubricating composition comprising a base oil of lubricating viscosity and from 1 to 5 weight percent of a magnesium phenoxide prepared by reacting an alkylated phenol having from 14 to 42 carbon atoms, formaldehyde, and dialkanolamine having from 2 to 6 carbons to form a Mannich base and neutralizing the Mannich base with magnesium methoxide to form said magnesium phenoxide.

7. The composition defined in claim 6 wherein said magnesium phenoxide is additionally subjected to carbonation at a temperature of 50 to 100° C. and a carbon dioxide pressure of 1 to 50 atmospheres for a period from 0.5 to 10 hours.

8. The composition defined in claim 7 wherein said lubricating composition also contains from 0.3 to 2 weight percent of a zinc di(C_3–C_{30} hydrocarbyl) dithiophosphate.

9. The composition defined in claim 8 wherein said zinc dihydrocarbyl dithiophosphate is zinc di(tetrapropenylphenyl) dithiophosphate.

10. The composition defined in claim 7 wherein said alkylated phenol is a polypropenyl phenol having from

9 to 20 carbons in the polypropenyl group, and said dialkanol amine is diethanolamine.

References Cited

UNITED STATES PATENTS

2,725,357	11/1955	Kluge et al.	252—42.7
3,000,822	9/1961	Higgins et al.	252—32.7 E
3,057,800	10/1962	Verdol	252—42.7
3,454,496	7/1969	Schlobohm et al.	252—42.7 X
3,429,812	2/1969	Kivelevich et al.	252—42.7
3,501,527	3/1970	Little et al.	252—42.7 X
3,586,629	6/1971	Otto et al.	252—42.7

PATRICK P. GARVIN, Primary Examiner

A. H. METZ, Assistant Examiner

U.S. Cl. X.R.

252—42.7