United States Patent Office 3,549,534 Patented Dec. 22, 1970

3,549,534

SULFURIZED CALCIUM ALKYLPHENOLATE LUBRICANT COMPOSITIONS AND METHOD OF MANUFACTURE

Richard A. Holstedt, Poughquag, James G. Dadura, Fishkill, Robert H. Krug, Cornwall, and Doris Love, Fishkill, N.Y., assignors to Texaco Development Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Sept. 5, 1969, Ser. No. 855,758
Int. Cl. C10m 1/38, 1/48
U.S. Cl. 252—42.7 18 Claims

ABSTRACT OF THE DISCLOSURE

A lubricating oil composition containing sulfurized normal calcium alkylphenolate detergent-dispersant of improved resistance to oxidation, said dispersant prepared by the sequential reaction of alkylphenol with calcium alkoxyalkoxide followed by sulfurization of the formed calcium alkylphenolate at a temperature between 400 and 425° F. in the presence of a hydrocarbon lubricating oil, said reaction preferably followed by a deodorizing treatment of the resultant product via venting with inert gas at less than about 225° F., said composition preferably containing a supplementary detergent-dispersant comprising the ethylene oxide derivative of an inorganic phosphorus acid free, steam hydrolyzed polybutene-P_2S_5 reaction product.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is related to coassigned application, Ser. No. 640,362, filed May 22, 1967.

BACKGROUND OF DISCLOSURE

This invention is in the field of art relating to fluid compositions specialized and designed for use between two relatively moving surfaces in contact therein for reducing the friction therebetween and preserving the surface. The lubricant compositions of the invention contain a compound which has a calcium component linked to a carbon through oxygen and preferably containing in addition a detergent-dispersant for lube oil composed of carbon, hydrogen, oxygen, phosphorus and sulfur.

It is well known that lubricating oils tend to deteriorate under the conditions of use in present day diesel and automotive engines with attendant formations of sludge, lacquer, resinous materials which adhere to the engine parts particularly the piston ring groove and thereby lowering the operating efficiency of the engine. To counteract the formation of these deposits certain chemical additives have been found which added to lubricating oils have the ability to keep the deposit forming materials suspended in oil so that the engine is kept clean and in efficient operation condition for extended periods of time. These agents are known in the art as detergents and/or dispersants. Metal organic compounds are particularly useful in this respect. One class of metal organic compounds which have been found so useful are the calcium sulfurized normal alkylphenolates. It is to be noted the term "normal" employed hereinbefore and hereinafter denotes the ratio of the number of equivalents of calcium moiety to the number of equivalents of alkylphenol moiety is about 1, that is, the "calcium metal ratio" is about 1.

Although the sulfurized normal calcium alkylphenolates of the past were effective dispersant-detergents they had the drawback of deteriorating to various extents under engine operating conditions to form undesirable oxidation products which undesirably promoted an increase in lubricant viscosity and corrosion which in turn resulted in excessive bearing wear. Sulfurized calcium alkylphenolates of substantially improved oxidation resistance are described in coassigned, copending application, Ser. No. 640,362, wherein the sulfurized calcium alkylphenolate is prepared by the sequential or simultaneous contact of alkylphenolate with calcium alkoxyalkoxide and sulfur at a temperature ranging between about 0 and 480° F. followed by deodorizing. Although the development outlined in the copending application produced compositions of substantially increased oxidation resistance, there was a continuing need for still further improvement.

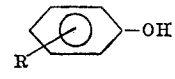
SUMMARY OF INVENTION

We have discovered, and this constitutes our invention, improved sulfurized normal calcium alkylphenolate lubricant compositions which are substantially less susceptible to undesirable oxidation during engine operation than sulfurized normal calcium alkylphenolates heretofore known. More particularly, we have discovered a particular combination of reaction conditions which produces a sulfurized normal calcium alkylphenolate composition which has about twice the ability to resist oxidative decomposition than the best of previous sulfurized normal calcium alkylphenolates. Most specifically, we have discovered in the preparation of the lubricant compositions of the invention subsequently described that it is critical to maintain the sulfurization temperature between 400 and 425° F. in order to obtain the outstanding oxidation resistant properties. In addition, the subject invention relates to a lubricating oil composition comprising a hydrocarbon oil of lubricating viscosity containing between about 0.1 and 90 wt. percent of a novel sulfurized normal calcium alkylphenolate dispersant which is significantly less susceptible to undesired oxidation during engine operation, said composition most advantageously containing between about 0.3 and 6 wt. percent of an ethoxylated inorganic phosphorus acid free, steam hydroylzed polybutene-P_2S_5 reaction product in addition to between about 0.1 and 7.5 wt. percent sulfurized calcium alkylphenolate.

DETAILED DESCRIPTION OF THE INVENTION

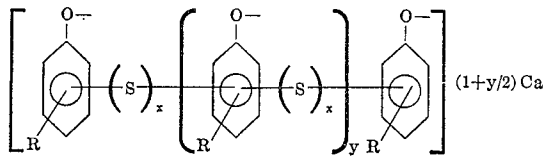
Specifically, the lubricating composition of the invention is prepared by a two stage procedure:

In the first stage in the presence of a lubricating oil there is contacted (1) an alkylphenol of the formula:



where R represents one or two monovalent saturated aliphatic radicals of from 5 to 50 carbons, preferably 10 to 15 carbons, and where at least one ortho or para position remains unsubstituted and (2) a calcium alkoxyalkoxide of the formula $Ca(O—A—OR')_2$ where A is a divalent saturated aliphatic hydrocarbon radical (alkanediyl) of from 1 to 6 carbons and R' is alkyl of from 1 to 25 carbons at a temperature between about 32 and 400° F., utilizing a mole ratio of alkylphenol to calcium alkoxyalkoxide of between about 1.8:1 and 2.2:1, prefer-

ably 2:1, to form the normal calcium alkylphenolate intermediate, then as a second stage contacting said intermediate with sulfur at a temperature between 400 and 425° F. utilizing a mole ratio of alkylphenol to sulfur of between about 1:0.15 and 1:8, preferably between about 1:0.5 and 1:3. The sulfurized normal alkylphenolate may be characterized by the following theoretical formula:



where R is as heretofore defined, x is an average integer of from 1 to 4 and y is an integer of 0 to about 10. It is to be noted that x and y are defined as average integers and the foregoing formula is only set forth as a hypothetical representation since sulfurized normal calcium alkylphenolate is in essence a complex mixture of substances including mono and polysulfides which can be accurately defined only in terms of process. In any case, the R group is believed to be primarily in the para position with the sulfur links mainly in the ortho position. Further, there is probably also a significant amount of covalent character to the calcium-oxygen bond. It is to be noted that the calcium and sulfur contents of the sulfurized calcium phenolate component are respectively between about 1 and 8 wt. percent and 0.5 and 12 wt. percent.

Under advantageous conditions, the alkylphenol in the first stage is contacted with the calcium alkoxyalkoxide in a nitrogen (inert gas) atmosphere at a temperature between about 50 and 350° F. for a period of time of between about 0.1 to 5 hours. The formed calcium alkylphenolate intermediate may be stripped with an inert gas while increasing the temperature to between 400 and 425° F. to remove volatile materials. The hydrocarbon lubricating medium is carried along through the entire procedure and forms a part of the final lubricating oil composition.

As a next step to the stripped or unstripped reaction mixture of the first stage there is charged sulfur, sulfur being preferably introduced into the reaction system as slurry in hydrocarbon lubricating oils such slurry most preferably having a sulfur concentration of between about 10 and 25 wt. percent. The lubricating oil as in the case in the first stage continues on and is found in the final concentrate product. The reaction temperature is adjusted to between 400 and 425° F., preferably between 405 and 415° F., and the second stage sulfurization reaction normally continues between about 3 and 12 hours.

Also, under advantageous conditions, the calcium alkoxyalkoxide reactant in the first stage is introduced into the reaction system as a solution if not already in liquid form to facilitate reactant contact. The solvent medium usually is the corresponding alkoxyalkanol (if liquid) of the alkoxyalkoxide component. The concentration of the calcium alkoxyalkoxide in the solvent medium is advantageously between about 20 and 60 wt. percent.

The entire reaction in both first and second stages is advantageously conducted in an inert gas atmosphere with continuous inert gas purging in order to insure the ready removal of volatile by-products and decrease the formation of undesired oxidation products. The inert gas rates normally employed ranges between about 0.005 and 1 s.c.f.h./gallon. Further, agitation is normally employed in all phases of the reaction in order to facilitate ingredient contact. Still further, if carbonate values are desired in the final product the second stage reaction mixture is carbon dioxide blown at the end of the second stage reaction, e.g. at a rate of 0.1 to 2 s.c.f.h./gallon for 0.2 to 2 hours between 410 and 425° F.

As desirable further steps, the formed sulfurized normal calcium alkylphenolate lubricating composition is

subjected to a deodorization treatment and/or filtration. In the deodorization it was unexpectedly found that this could only be accomplished satisfactorily by cooling the second stage reaction mixture from between about 400 and 425° F. to below about 225° F., e.g. room temperature to 225° F. over a period of at least 2 hours, preferably between about 2 and 8 hours while passing nitrogen through said mixture at a rate of between about 0.1 and 2 s.c.f.h./gallon. Deodorization is normally continued until no detectable H_2S odor is found which is normally measured as less than 3 p.p.m. H_2S and a Copper Strip Corrosion Test (ASTM D–130) of 2A maximum at 3 hours and 212° F.

Fltration of the deodorized product may be accomplished by standard means. A preferred filtration is accomplished by adding between about 0.01 and 1 wt. percent diatomaceous earth and passing the material to be filtered through a pressure leaf filter precoated with diatomaceous earth at a temperature between about 200 and 300° F. and a pressure between about 5 and 100 p.s.i.g.

As heretofore stated, the sulfurized normal calcium alkylphenolate contents in the lubricating oil compositions contemplated herein may range anywhere from 0.1 to 90 wt. percent. The higher concentrations, e.g., between about 10 and 90 wt. percent sometimes referred to in the art as concentrates are normally found in lubricant compositions resulting directly from the manufacture of the sulfurized normal calcium alkylphenolate, whereas the preferred sulfurized phenolate in finished lubricating oil composition employed for engine use is between about 0.1 and 7.5 wt. percent with a calcium concentration in the finished (dilute) lubricant of between about 0.06 and 0.5 wt. percent, preferably between 0.1 and 0.4 wt. percent. In any case, in the entire percent range the additive in the lubricating composition invention will function as the detergent-dispersant and the resultant compositions will at least have some lubricating function.

In the finished lubricating oil composition other additives may be included such as pour depressors, antioxidants, silver corrosion inhibitors, viscosity index improvers, oleanous agents and mixtures thereof. Exactly what other additives are included in the finished oil and the particular amounts therein will, of course, depend on the particular use the finished oil product is to be put to. One of the most suitable uses found for the sulfurized normal calcium alkylphenolate produced herein are as lubricants for railway diesel engines. When this is the case there is desirably included in the oil in addition to the aforedescribed sulfurized calcium alkylphenolate, ethoxylated inorganic phosphorus acid free, steam hydrolyzed polybutene-P_2S_5 reaction product further described in U.S. Pat. Nos. 3,272,744 and 3,087,956. This supplementary detergent appears to cooperate to an unexpected degree with the subject sulfurized normal calcium alkylphenolate to give finished oil compositions particularly suitable for lubricating diesel engines, i.e., of high detergency while remaining thermally stable and resistant to undesirable oxidative decomposition. The ethoxylated reaction product is present in the finished compositions of the invention in amounts of between about 0.3 and 6 wt. percent (oil free basis), preferably between about 0.8 and 4 wt. percent and, in any case, in sufficient amount to give a phosphorus content in the finished (dilute) composition of between about 0.006 and 0.15 wt. percent, preferably between 0.01 and 0.08 wt. percent. The sulfurized calcium alkylphenolate ethoxylated polybutene-P_2S_5 containing finished formulations are normally preperad by blending a lubricating oil concentrate of the sulfurized alkylphenolate and a lubricating oil concentrate of ethoxylated polybutene-P_2S_5 reaction product and then diluting the resultant mixture with additional hydrocarbon lubricating oil until the desired concentration of the additive is obtained. A most preferred finished composition contains both additives wherein the calcium content is between about 0.10

and 0.40 wt. percent and a phosphorus content is between about 0.015 and 0.06 wt. percent.

Suitable base oils useful in the compositions of the invention as well as diluent in the manufacture of the sulfurized calcium alkylphenolate concentrate and the finished compositions include a wide variety of hydrocarbon lubricating oils such as naphthenic base, paraffinic base and mixed base mineral oils or other hydrocarbon lubricants, e.g., lubricating oils derived from coal products and synthetic hydrocarbon oils, e.g., polyalkylene such as polypropylene, polyisobutylene of a molecular weight of between about 250 and 2500. Advantageously, the base oils have an SUS viscosity at 100° F. between about 50 and 2000. In formulating the diesel oil composition embodiment of the invention, the finished composition desirably has an SUS viscosity between about 900 and 1100 at 100° F.

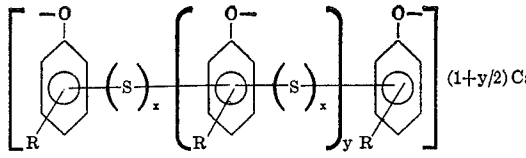
Specific examples of the alkylphenol reactants contemplated herein are 4-octylphenol, 4-tertiary octylphenol, 2-decylphenol, 2 - dodecylphenol, 4 - hexadecylphenol, 3,4 - didodecylphenol, 2-nonylphenol, 4-tricontylphenol, 4-eicosylphenol, a mixture of decylphenol and dodecylphenol ($C_{10}+C_{12}$ alkylphenol), and mixtures of 2 and 4 positioned monoalkyl and dialkylphenols. It is to be noted that the alkylphenols employed will normally be para-alkylphenols, however, 2,4-substituted alkylphenols may also be employed. The only restriction is at least one ortho or parapositioned of the alkylphenol reactant is desirably available for sulfurization.

Examples of the calcium alkoxyalkoxide reactants contemplated herein are calcium 2-methoxyethoxide, calcium 1-methoxypropoxide, calcium 3-methoxybutoxide, calcium 2-ethoxyethoxide and calcium 4-dodecoxyhexoxide.

Examples of the alkoxyalkanol diluents associated with the alkoxyalkoxide reactant are 2-methoxyethanol, 1-methoxypropanol, 3-methoxybutanol, 2-ethoxyethanol and dodecoxyhexanol.

The inert gas normally employed is nitrogen and most preferably nitrogen with a purity at least about 99 wt. percent.

Specific examples of the sulfurized normal calcium alkylphenolates expressed in the terms of the hypothetically descriptive formula are:



where R is 4-octyl, x is 1 and y is 0; R is 4-dodecyl, x is 1 and y is 1; R is 4-eicosyl, x is 3 and y is 5; R is 2,4-didecyl, x is 2 and y is 3 and mixtures thereof. It is to be noted that x and y are set forth as average integers and the formula is merely set forth for the purpose of representation since sulfurized normal calcium alkylphenolate is in essence a complex mixture and truly definable in terms of process only.

The ethoxylated derivative of inorganic phosphorus acid free, steam hydrolyzed polybutene-P_2S_5 reaction product is prepared by first reacting a polybutene of a molecular weight of between about 800 and 250 wherein the reaction constituting between about 5 and 40 wt. percent P_2S_5 at an elevated temperature between about 212 and 600° F. in a non-oxidizing atmosphere, e.g., nitrogen, followed by hydrolyzing the resultant product by contacting with steam at a temperature between about 212 and 500° F., the steam treatment of the P_2S_5-polybutene reaction product results in its hydrolysis to form inorganic phosphorus acids in addition to the hydrolyzed organic product. Hereinafter and hereinbefore the term "polybutene" denotes derivatives of isobutene as well as butene.

The inorganic phosphorus acids are removed from the hydrolyzed product prior to reaction with alkylene oxide via standard procedure such as those disclosed in U.S. 2,951,835 and 2,987,512 wherein removal is effected by contact with synthetic hydrous alkaline earth metal silicates and syntheitc hydrous alkali metal silicates respectively. Inorganic phosphorus acids can also be removed by extraction with anhydrous methanol as disclosed in U.S. 3,135,729. The steam hydrolyzed inorganic phosphorus acid product is then contacted with ethylene oxide at a temperature between about 140 and 300° F., under a pressure ranging from 0 to 50 p.s.i.g., utilizing a mole ratio of ethylene oxide to hydrolyzed hydrocarbon-P_2S_5 reaction product of between 1:1 and 4:1, preferably between about 1.1:1 and 1.5:1. Execess ethylene oxide is removed after completion of the reaction by blowing the reaction mixture at elevated temperatures, generally with inert gas such as nitrogen. The foregoing reactions are conducted in the presence of a hydrocarbon lubricating oil of the type described in connection with the sulfurized normal calcium alkylphenolate. The lubricating oil normally constitutes between about 20 and 80 wt. percent of the reaction mixture. The introduction of the hydrocarbon lubricating oil normally takes place subsequent to steam hydrolysis. The ethoxylated derivative on an oil free basis normally has a sulfur content of between about 2 to 5 wt. percent and a phosphorus content of between about 4 and 6 wt. percent.

Specific examples of the ethoxylated derivative of inorganic phosphorus acid free, steam hydrolyzed polybutene-P_2S_5 reaction products are ethoxylated steam hydrolyzed polyisobutene (1100 M.W.)-P_2S_5 reaction product, ethoxylated steam hydrolyzed polybutene (1500 M.W.)-P_2S_5 reaction product, ethoxylated steam hydrolyzed polybutene (800 M.W.)-P_2S_5 reaction product, ethoxylated steam hydrolyzed polyisobutene (2000 M.W.)-P_2S_5 reaction product where the ethylene oxide component and reaction product component are present in a mole ratio of about 1:1.

The following examples further illustrate the compositions and method of the invention but are not to be construed as limitations thereof.

EXAMPLE I

This example illustrates the preparation of a lubricating oil concentrate of the sulfurized normal calcium alkylphenolate complex product.

To a 30 gallon stainless stell reactor heated by hot oil jacket there was charged 84 lbs. of 4–$C_{10}+C_{12}$ alkylphenol of a molecular weight of 295 (basis Hydroxyl No.) and 64 lbs. of a paraffinic base lubricating oil having an SUS viscosity at 100° F. of about 100. The resultant mixture was heated from ambient to 150° F. over an hour period with stirring which was continued 2½ hour period from 150 to 330° F. while purging the reaction mixture with nitrogen at a rate of 5 s.c.f.h. At the end of the 2½ hour purge period there was charged over a period of 1.5 hours while maintaining the temperature between 300 and 330° F. together with a nitrogen purge at a rate of 10 s.c.f.h. 73 lbs. of 38 wt. percent calcimum-2-methoxyethoxide in ethoxyethanol solution (7.4 wt. percent Ca content) and the resultant mixture was then stripped for a 3 hour period utilizing 10 s.c.f.h. nitrogen while raising the temperature to 410° F. To the stripped mixture there was charged over an hour period to the reaction mixture maintained at 410° F. 31.5 lbs. of 33⅓ wt. percent powdered sulfur-lubricating oil slurry said lubricating oil having an SUS viscosity of about 100 at 100° F. and the temperature was maintained at 410° F. for an additional 6 hours coupled with blowing with nitrogen at a rate of 10 s.c.f.h. At the end of the 6 hour period the reaction mixture was blown with carbon dioxide for a 3 hour period at 410° F. using a CO_2 rate of 25 s.c.f.h. whereupon the mixture was cooled to 200° F. and blown for an 8 hour period with nitrogen at a nitrogen rate of 10 s.c.f.h. The reaction mixture was then transferred to a filter tank whereupon 1 lb. of diatomaceous earth was added and it was passed through a 2 sq. ft. pressure leaf filter

precoated with diatomaceous earth at a temperature of 200° F., under a pressure of 10 p.s.i.g. The filted product was analyzed and found to be a 50 wt. percent sulfurized normal calcium 4-C_{10}+C_{12} alkylphenolate in lube oil. Further analysis is set forth in Table I below:

TABLE I

Tests:	Results
Specific gravity 60/60° F.	0.9779
Flash COC, ° F.	355
Viscosity, SUS 210° F.	198
Total base No.	86
Sulfur, wt. percent	3.2
Calcium, wt. percent	3.11
Sulfated ash, wt. percent	9.5
CO_2, wt. percent	0.57
H_2S, p.p.m.	2
Copper strip corrosion, 3 hrs. at 212° F.	1A
MacCoull corrosion test (bearing wt. loss), mg.[1]	4.9

[1] Conducted on a composition containing 6.9 wt. percent of said product plus 2.8 wt. percent of a 44:66 weight ratio of ethoxylated derivative of an inorganic phosphorus acid free, steam hydrolyzed polybutene (1100 M.W.)-P_2S_5 reaction product in paraffinic lube oil (100 SUS at 100° F.) and 90.3 wt. percent, to a paraffinic lube oil composite (10.3 wt. percent of 33.5 SUS at 100° F., 27.2 wt. percent 610 SUS at 130° F., 53.2 wt. percent at 845 SUS at 100° F.), wherein the final composition had a phosphorus content of 0.03 wt. percent, a calcium content of 0.20 wt. percent, a sulfated ash of 0.71 wt. percent and a viscosity of 973 SUS at 100° F.

EXAMPLE II

This example further illustrates the preparation of a lube oil concentrate of the sulfurized normal calcium alkylphenolate product and also demonstrates the advantage of deodorization.

To a 12 liter reactor there was charged 2295 grams of 4-C_{10}+C_{12} alkylphenol and 2445 grams of paraffinic lubricating oil having an SUS viscosity of 100 at 100° F. The resultant mixture was heated to 158° F. with nitrogen blowing at a rate of 0.5 liters/minute. To the heated stirred mixture there was charged 2145 grams (3.75 mole) of calcium 2-methoxyethoxide in 2-methoxyethanol and the resultant mixture was heated to 410° F. over a period of 3 hours with continued nitrogen flowing and continued removal of volatile materials. Three hundred grams of powdered sulfur (9.4 mole) was then charged and nitrogen blowing was continued at 410° F. for 4 hours. At the end of the 4 hour period the reaction mixture was filtered through diatomaceous earth and 4500 grams of the filtrate was set aside (Sample B). The remainder of the filtered product (Sample A) had deodorized by passing nitrogen over the surface at room temperature for a 24 hour period. Samples A and B were analyzed and determined to be 50 wt. percent lube oil solutions of sulfurized normal calcium 4-C_{10}+C_{12} alkylphenolate. Further analysis is set forth below in Table II:

TABLE II

	Found	Theory
Test A:		
Weight percent calcium	3.4	3
Weight percent sulfur	3.2	3
Kinematic viscosity at 210° F., cs	47	
TBN ($HClO_4$)	93	85
Odor	Good	
Test B:		
Weight percent calcium	3.3	3
Weight percent sulfur	3.2	3
Kinematic viscosity at 210° F	47	
TBN ($HClO_4$)	90	85
Odor	(1)	

[1] Poor (H_2S odor).

EXAMPLE III

This example illustrates a preferred procedure for deodorizing the formed sulfurized normal calcium alkylphenolate concentrates contemplated herein and the criticalities involved.

A synopsis of the procedure and materials employed together with the test data are set forth below:

In the procedure the materials and quantities employed were as follows:

TABLE III

Materials:	Wt. grams (mole)
4-C_{10}+C_{12} alkylphenol	1039 (3.75)
Paraffinic lube oil (100 SUS at 100° F.)	1332
Calium-2-methoxyethoxide in methoxyethanol	1069 (1.87)
Sulfur (powdered)	150 (4.7)

The procedure was as follows:

(1) All the agents except sulfur were combined at 158° F. and the reaction mixture was solvent stripped to 410° F. for a period of 2 hours while passing nitrogen therethrough at a rate of 400 mls./minute.

(2) Sulfur was then added with continued nitrogen blowing.

(3) The resultant mixture was nitrogen blown at a rate of 400 mls./minute at 410° F. for a period of about 4 hours and then was CO_2 blown (400 mls./minute) at 410° F. for 1 hour.

(4) The mixture was then cooled at 200° F. under nitrogen blowing (100 mls./minute) and a sample was removed and labeled C.

(5) The remaining reaction mixture was stirred and nitrogen blown at 200° F. for a further 7 hours with removal of samples every hour each removed sample being consecutively labeled D to J. The removed samples were subjected to the Copper Strip Corrosion Test for 3 hours at 212° F. (neat). A hydrogen sulfide analysis and an odor test was given and the results are reported below in Table III-A.

TABLE III-A

	N_2 blowing hours	Cu strip rating	H_2S (p.p.m.)	Odor
Run:				
C	0	2B	42	Strong H_2S, mild phenolic.
D	1	1A		No H_2S.
E	2	1B	3	No H_2S.
F	3	1A	1	No H_2S.
G	4	2A	1	No H_2S.
H	5	1A	0	No H_2S.
I	6	1A	1	No H_2S.
J	7	1A	1	No H_2S.

In addition, example utilizing sulfurized phenolate products of the type described herein were subjected to additional comparative deodorization techniques without satisfactory removal of hydrogen sulfide and the resultant odor. Specifically, for one deodorization run the phenolate product was vented for 6 hours with air while cooling from 300 to 120° F. The vented product had an unsatisfactory hydrogen sulfide content of 22, an unsatisfactory Copper Strip Corrosion rating of 2B. Another sample for a step 5 in the aforedescribed test was deodorized by stirring open to the atmosphere for 3 hours at 200° F. At the end of the stirring the sample had an unsatisfactory hydrogen sulfide content of 5, and an unsatisfactory Copper Strip Corrosion rating of 2C and a mold odor of H_2S.

EXAMPLE IV

The example illustrates the criticality of preparing the sulfurized normal calcium alkylphenolate using sulfurization temperatures between 400 and 425° F., the uniqueness of said sulfurized alkylphenolates and the uniqueness of the compositions containing said sulfurized alkylphenolates

The overall procedure of Example I was essentially repeated with the material exception that in addition to sulfurization runs conducted at 410° F. comparative sulfurization runs were conducted at 350, 375, 400 and 425° F. Lubricating oil compositions containing the resultant sulfurized normal calcium alkylphenolates formed at the

various sulfurization temperatures were tested in the MacCoull Corrosion Test. The compositions tested were of the following average make-up.

TABLE IV

Components:	Wt. percent
Mineral lube oil	90.35
Sulfurized normal Ca alkylphenolate concentrate [1]	6.90
Ethoxylated derivative concentrate [2]	2.75

[1] Product of Example I type.

[2] A 44:66 weight ratio of ethoxylate derivative of an inorganic phosphorus acid free, steam hydrolyzed polybutene (1100 M.W.)—P_2S_5 reaction product wherein the derivative was formed using a 1:1 mole ratio of ethylene oxide to reaction product.

Typical analysis of the compositions tested found the following:

TABLE IV-A

Properties:	Results
Gravity, ° API	23.8
SUS viscosity, 100° F.	211
SUS viscosity, 210° F.	14.9
VI	70
Ca, wt. percent	0.21
P. wt. percent	0.03

MacCoull Corrosion Test data on the aforedescribed test compositions is reported below in Table IV–B:

TABLE IV-B

	Sulfurization temp. of phenolate component, ° F.	10 hr. bearing wt. loss, mg. MacCoull corr.
Composition:		
K	305	59
L	375	90
M	400	10
N	410	4
O	410	6
P	410	2
Q	410	3
R	410	7
S	410	8
T	410	5
U	425	15

EXAMPLE V

This example illustrates preparation and testing of the finished lubricating compositions containing the sulfurized normal calcium alkylphenolate and ethoxylated inorganic phosphorus acid free, steam hydrolyzed polybutene-P_2S_5 reaction product.

To a 3 gallon container fitted with a stirring means there was charged 855 grams of a paraffinic lube oil of an SUS viscosity at 100° F. of about 335, 3388 grams of a paraffinic lube oil having an SUS viscosity of about 845 at 100° F., 1941 grams of paraffinic lube oil having an SUS viscosity of about 610 at 100° F., 470 grams of the lube oil concentrate product of sulfurized calcium alkylphenolate as prepared in Example III, 227 grams of a lube oil solution consisting of a 44:66 weight ratio of ethoxylated reaction product:100 SUS at 100° F. paraffinic lube oil and 22 grams of a paraffin lube oil having an SUS viscosity of 100 at 100° F., said ethoxy reaction product being the ethoxylated derivative of an inorganic phosphorus acid free, steam hydrolyzed polybutene (1100 M.W.)-P_2S_5 reaction product wherein the mole ratio of ethylene-oxide component to reaction product in said derivative is about 1:1 and the mole ratio of polybutene to P_2S_5 in said reaction product is about 1:1. Also included was 0.7 gram of a silicone antifoamant. The stirring means in the blender was actuated and the contents mixed at 150° F. for 15 minutes.

The resultant mixture gave the following analysis:

TABLE V

Test:	Results
Gravity	23.9
Flash, COC, ° F.	480
Vis. 100° F. SUS	977
210° F. SUS	77.5
Viscosity index	70
Pour pt., ° F.	10
Color, ASTM (dilute)	L55
Total base No. (perchlorate)	6.7
Sulfated ash percent	0.72
Calcium, wt. percent	0.22
Phosphorus, wt. percent	0.03

and the resultant mixture was stirred at 175° F. to accomplish blending. The resultant blend was subjected to the well known Caterpillar 1–H Engine Test (Caterpillar Tractor Co.) which is described in Caterpillar Information Letter No. 46. At the end of 480 hours of engine operation the engine's pistons had a Pass rating. In contrast, when comparative lube oil compositions which were essentially identical to said resultant blend with the exception that a commercially sold calcium 4–C_{10}+C_{12}-alkylphenol sulfide was substituted for the sulfurized normal calcium C_{10}+C_{12} alkylphenolate component the quantity of sulfide in the comparative composition being adjusted so that the calcium level is 0.20 wt. percent. At the end of 240 hours of engine operation utilizing the comparative compositions the pistons had a Fail rating.

EXAMPLE VI

This example further illustrates the superiority of the lubricant compositions of the invention and the criticality of the sulfurized normal calcium alkylphenolate-ethoxylated polybutene-P_2S_5 combination herein in respect to reducing bearing weight loss and in engine oxidation operation. Various compositions were subjected to the 10 hour MacCoull Corrosion Test wherein bearing weight loss and change in viscosity of the particular lube oil compositions tested are measured. In Run A a composition essentially identical to the resultant blend of Example IV, except the quantity of the ethoxylated derivative was increased to give .05 wt. percent phosphorus in the finished composition, was tested together with comparative compositions (Runs B, C and D) which was essentially identical to the test composition of Run A with the exception the sulfurized normal calcium alkylphenolate of Run A was substituted for by various analogous detergent dispersant phenolate materials, the weight of all the phenolate material being adjusted to give a final calcium content of 0.20 wt. percent and the weight of the inorganic phosphorus acid free, steam hydrolyzed ethoxylated polybutene-P_2S_5 reaction product being adjusted so that the final test composition has a phosphorus content of 0.05 wt. percent. The test data and results are reported below in Table VI:

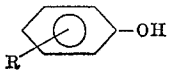
TABLE VI

Run	A	B	C	D	E
Ethoxylated derivative, wt. percent	5.0	4.6	4.6	5.0	5.0
Phenolate, wt. percent:					
Sulfurized normal calcium alkylphenolate.	6.8				
Ca salt of 4-C_{10}+C_{12} alkylphenol sulfide (3:2 mole ratio).		6.9			
Calcium 4-C_{10}+C_{12} alkylphenolate			6.5		
Sulfurized magnesium 4-C_{10}+C_{12} alkylphenolate.				6.9	
Ca carboxylated methylene bridged 4-C_{10}-C_{12} alkylphenol.					6.3
MacCoull corrosion:					
Bearing wt. loss, mg	42	89	112	77	63
Percent Viscosity increase	50	113	359	110	101

We claim:

1. A lubricating oil composition comprising a major amount of an hydrocarbon oil of lubricating viscosity containing between about 0.1 and 90 wt. percent of a sulfurized normal calcium alkylphenolate, said alkylphenolate

having a calcium metal ratio of about 1, a calcium content between about 1 and 8 wt. percent and a sulfur content between about 0.5 and 12 wt. percent and wherein said sulfurized calcium alkylphenolate is produced by contacting in a hydrocarbon lubricating oil medium an alkylphenol of the formula:



where R is alkyl of from 5 to 50 carbons, with calcium alkoxyalkoxide of the formula $(R'—O—A—O)_2Ca$ where A is alkanediyl of from 1 to 6 carbons and R' is alkyl of from 1 to 25 carbons at a temperature between about 200 and 400° F. utilizing a mole ratio of said alkylphenol to calcium alkoxyalkoxide of between about 1.8:1 and 2.2:1 thereby forming calcium alkylphenolate, contacting said calcium alkylphenolate with sulfur in the presence of a hydrocarbon lubricating oil at a temperature between 400 and 425° F. utilizing a mole ratio of said calcium alkylphenolate to sulfur of between about 1:0.15 and 1:8 to form said lubricating oil composition.

2. A lubricating oil composition in accordance with claim **1** wherein the reaction ingredients are continuously blown with inert gas.

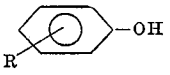
3. A lubricating oil composition in accordance with claim **2** wherein the formed lubricating oil composition is deodorized by reducing the temperature to below about 225° F. and blowing nitrogen gas therethrough at a rate of between about 0.005 and 1 s.c.f.h./gallon for at least 2 hours.

4. A lubricating oil composition in accordance with claim **1** where the formed lubricating oil composition is treated immediately following sulfurization with CO_2 at between 400 and 425° F. using a gas rate of about 0.1 and 2 s.c.f.h./gallon for between about 0.1 and 2 hours followed by reducing the temperature to less than about 225° F. and blowing a nitrogen gas therethrough at a rate of between about 0.005 and 1 s.c.f.h./gallon for at least 2 hours.

5. A lubricating oil composition in accordance with claim **1** wherein said alkyl in said alkylphenol is of from 10 to 15 carbons.

6. A lubricating oil composition in accordance with claim **1** wherein said alkylphenol is 4–C_{10}+C_{12} alkylphenol, said hydrocarbon lubricating oil is a paraffinic based lubricating oil having an SUS viscosity between about 50 and 2000 at 100° F., said calcium alkoxyalkoxide is calcium 2-methoxyethoxide, said calcium alkylphenolate is calcium 4–C_{10}+C_{12} alkylphenolate, said sulfurized calcium alkylphenolate is sulfurized normal calcium 4–C_{10}+C_{12} alkylphenolate, said calcium content in said lubricant composition is about 0.2%.

7. A method of producing a lubricating oil composition comprising a major amount of an hydrocarbon oil of lubricating viscosity containing between about 0.1 and 90 wt. percent of a sulfurized normal calcium alkylphenolate, said alkylphenolate having a calcium metal ratio of about 1, a calcium content of between about 1 and 8 wt. percent and a sulfur content between about 0.5 and 12 wt. percent comprising first contacting in a hydrocarbon lubricating oil medium with an alkylphenol of the formula:



where R is alkyl of from 4 to 100 carbons with calcium alkoxyalkoxide of the formula $(R'—O—A—O)_2Ca$ where A is alkanediyl of from 1 to 6 carbons and R' is alkyl of from 1 to 25 carbons at a temperature between about 50 and 3500 F. utilizing a mole ratio of alkylphenol to calcium alkoxide of between about 1.8:1 and 2.2:1 to form a normal calcium alkylphenolate then second contacting said formed calcium alkylphenolate with sulfur at a temperature between 400 and 425° F. in a mole ratio of said calcium alkylphenolate to said sulfur of between about 1:0.15 and 1:8 to form said lubricant composition, said contactings being conducted in the presence of a hydrocarbon oil of lubricating viscosity.

8. A method in accordance with claim **7** wherein the reaction mixtures are continuously blown with an inert gas during said contactings.

9. A method in accordance with claim **8** wherein the formed lubricating oil composition is deodorized by reducing the temperature below about 225° F. and blowing nitrogen therethrough at a rate of between about 0.005 and 1 s.c.f.h./gallon for at least 2 hours.

10. A method in accordance with claim **7** wherein the formed lubricating oil composition is further treated with CO_2 at between 400 and 425° F. using a gas rate of between about 0.1 and 2 s.c.f.h./gallon for between about 0.2 and 2 hours followed by reducing the temperature to below about 225° F. and blowing nitrogen therethrough at a rate of between about 0.005 and 1 s.c.f.h./gallon for at least 2 hours.

11. A method in accordance with claim **7** wherein said alkyl in said alkylphenol is of from 10 to 15 carbons.

12. A method in accordance with claim **7** wherein said lubricating oil is a paraffinic based lubricating oil having an SUS viscosity at 100° F. of between about 50 and 2000, said alkylphenol is 4–C_{10}+C_{12} alkylphenol, said calcium alkoxyalkoxide is calcium 2-methoxyethoxide, said calcium alkylphenolate is calcium 4–C_{10}+C_{12} alkylphenolate and said sulfurized calcium alkylphenolate is sulfurized calcium 4–C_{10}+C_{12} alkylphenolate.

13. A lubricating oil composition comprising a major amount of an hydrocarbon oil of a lubricating viscosity containing between about 0.3 and 6 wt. percent of an ethoxylated inorganic phosphorus acid free, steam hydrolyzed polybutene (800–25°° M.W.)-P_2S_5 reaction product, said ethylene oxide moiety being present in respect to said steam hydrolyzed polybutene-P_2S_5 reaction product in a mole ratio of about 1:1 and the polybutene and P_2S_5 components being present in a mole ratio of about 1:1 and between about 0.1 and 7:5 wt. percent of a sulfurized normal calcium alkylphenolate, said alkylphenolate having a calcium metal ratio of about 1, a calcium content of between about 1 and 8 wt. percent, and a sulfur content between about 0.5 and 12 wt. percent, wherein said sulfurized calcium alkylphenolate is produced by contacting in a hydrocarbon lubricating oil medium, alkylphenol of the formula:



where R is alkyl of from 5 to 50 carbons with calcium alkoxyalkoxide of the formula $(R'—O—A—O)_2Ca$ where A is alkanediyl of from 1 to 6 carbons and R' is alkyl of from 1 to 25 carbons at a temperature between about 50 and 350° F. utilizing a mole ratio of said alkylphenol to calcium alkoxyalkoxide of between about 1.8:1 and 2.2:1 to form a calcium alkylphenolate then contacting said formed alkylphenolate with sulfur at a temperature between 400 and 425° F. utilizing a mole ratio of said calcium alkylphenolate to said sulfur of between about 1:0.15 and 1:8, thereby forming a resultant mixture of said hydrocarbon oil and said sulfurized normal calcium alkylphenolate.

14. A lubricating oil composition in accordance with claim **3** wherein the reaction mixtures in said contacting are continuously blown with inert gas.

15. A composition in accordance with claim **14** wherein nitrogen gas is passed through said resultant mixture at a rate of between about 0.005 and 1 s.c.f.h./gallon at a temperature less than about 225° F. for at least 2 hours.

16. A lubricating oil composition in accordance with claim **13** where the formed lubricating oil composition is further treated with CO_2 at between 400 and 425° F. using a gas rate of between about 0.1 and 2 s.c.f.h./gal-

lon for between about 0.2 and 2 hours followed by reducing the temperature to less than about 225° F. and blowing with nitrogen therethrough at a rate of between about 0.1 and 2 s.c.f.h./gallon for at least 2 hours.

17. A lubricating oil composition in accordance with claim **13** wherein said alkyl in said alkylphenol is of from 10 to 15 carbons.

18. A lubricating oil composition in accordance with claim **13** wherein the calcium content in said lubricating oil composition is between about 0.06 and 0.5 wt. percent, the phosphorus content is between about 0.006 and 0.15 wt. percent, said lubricating oil being a paraffinic based lubricating oil of an SUS viscosity between about 50 and 2000 at 100° F., said polybutene is of a molecular weight of about 1100, said alkylphenol is 4–C_{10}+C_{12} alkylphenol, said calcium alkoxyalkoxide is calcium 2-methoxyethoxide, said calcium alkylphenolate is calcium 4–C_{10}+C_{12} alkylphenolate, and said sulfurized normal calcium alkylphenolate is sulfurized normal calcium 4–C_{10}+C_{12} alkylphenolate.

References Cited

UNITED STATES PATENTS

2,680,096	6/1954	Walker et al.	252—42.7
2,870,134	1/1959	Kluge et al.	252—42.7X
3,474,035	10/1969	Dadura	252—42.7

DANIEL E. WYMAN, Primary Examiner

W. H. CANNON, Assistant Examiner

U.S. Cl. X.R.

252—18

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. U. S. 3,549,534 **Dated** December 22, 1970

Inventor(s) Richard A. Holstedt, James G. Dadura, Robert H. Kru and Doris Love

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, lines 7-8, "Texaco Development Corporation" should read --Texaco Inc.--. Column 4, line 14, "Fltration" should read --Filtration--. Column 5, line 62, "250" should read --2500--. Column 6, line 12, "Execess" should read --Excess--. Column 6, line 45 "stell" should read --steel--. Column 11, line 71, "3500 F." should read --350°F.--. Column 12, line 35, "25°°" should read --2500--.

Signed and sealed this 4th day of May 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents