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3,706,665

PREPARATION OF MAGNESIUM-CONTAINING LUBRICATING OIL DETERGENTS

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No Drawing, Filed Nov. 23, 1970, Ser. No. 92,136
Claims priority, application Great Britain, Nov. 23, 1969, 57,391/69

Int. Cl. C10m 1/44, 11/48
U.S. Cl. 252—32.7 HC

15 Claims

ABSTRACT OF THE DISCLOSURE

Detergents for lubricating oils are prepared by reacting a mixture of a phosphosulfurized polyolefin and an alkyl phenol sulfide or an alkylphenol with an alkanol solution of an alkoxide of magnesium or a carbonated alkoxide of magnesium.

This invention relates to the production of lubricating oil additives, and particularly to a process for the production of magnesium-containing lubricating oil additives.

Detergent and dispersant additives are added to what are called "premium" lubricating oils for the purpose of improving their dispersion power, and hence, when they are used in an internal combustion engine, of delaying the onset of piston seizure, the corrosion and wear of the cylinder, and the formation of sludge and carbon deposits.

One effective type of detergent additive is a blend of an alkaline earth metal salt of a phosphosulfurized polyolefin and an alkaline earth metal salt of an alkylphenol or alkylphenol sulfide, which blend may typically be made by the neutralization of a mixture of the phosphosulfurized polyolefin and alkylphenol or alkylphenol sulfide. Heretofore, the barium salts have been considered to be the most effective of the alkaline earth metal salts in this type of detergent additive, and these, as well as the calcium salts, can be made efficiently using the oxide or hydroxide of the metal.

It has now been found that for the production of magnesium-containing additives, certain other basic magnesium compounds are preferable as sources of the metal, and that the products so made are at least as effective as the barium salts as detergents. Moreover, they have the advantage that they give rise to less ash formation.

This invention comprises a process for the production of a detergent additive for lubricating oils, in which a mixture comprising a phosphosulfurized polyolefin and an alkylphenol sulfide or an alkylphenol is reacted with a solution of an alkoxide of magnesium or a carbonated alkoxide of magnesium in an alkanol.

The invention further comprises compositions that have been prepared by the process of the invention.

The alkylphenol sulfide, that is, a compound containing two or more alkylphenol residues linked by one or more sulfur atoms, or the alkylphenol is preferably one which has an aromatic nucleus that is substituted by an alkyl group having from 5 to 20 carbon atoms, especially from 7 to 12 carbon atoms. An alkyl group having 9 carbon atoms is often particularly satisfactory.

It is often preferable to use an alkylphenol sulfide rather than the alkylphenol itself. The sulfide can be a mono-sulfide, but disulfides, trisulfides, tetrasulfides, pentasulfides and other polysulfides are also very useful. A suitable alkylphenol sulfide can in fact be made from an appropriate alkylphenol by reaction with sulfur dichloride, the composition of the product depending on the molar ratio of alkylphenol to sulfur dichloride used and the alkylphenol residues being linked in general by monosulfide links.

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Examples of suitable alkylphenol sulfide and alkylphenol starting materials are nonylphenol and dodecylphenol and the product of reacting from three to five moles of an alkylphenol in which the alkyl group has from 7 to 11 carbon atoms with from two to four moles of sulfur dichloride. A particularly preferred example is the reaction product of four moles of nonylphenol and three moles of sulfur dichloride.

The polyolefin that is used in phosphosulfurized form is preferably one of relatively low molecular weight; it can be, for example, a polypropylene, polybutene or polyisobutylene, for instance one that has an average molecular weight between 500 and 2500, for example 1100. It can for instance have been phosphosulfurized by reacting it with a phosphorus sulfide such as, for example, P_4S_3 , P_4S_7 , or more preferably P_2S_5 . The phosphosulfurized polyolefin can be used as such, that is, in the form in which it is produced by phosphosulfurization.

The alkylphenol sulfide or alkylphenol and the phosphosulfurized polyolefin can be used in any desired relative proportion, but usually it is preferred to employ these in a weight ratio between 1:12 and 6:1, especially between 1:9 and 4:1, and more preferably between 3:7 and 1:1.

The magnesium alkoxide can be, for example, magnesium methoxide, ethoxide, propoxide or isopropoxide. These compounds are produced by reacting clean magnesium metal with excess alkanol and the solution thus formed can be used to neutralize the mixture of a phosphosulfurized polyolefin and an alkylphenol sulfide or an alkylphenol. Iodine or mercury can be used to initiate the reaction between magnesium and the alkanol if desired but only a catalytic amount should be used. The magnesium alkoxides or solutions containing them should be protected from atmospheric moisture. The solution of magnesium alkoxide in alkanol can conveniently also contain a liquid hydrocarbon, for example aromatic hydrocarbons such as benzene, toluene and xylene, and various petroleum fractions such as the naphthenic hydrocarbons, light oils and other oils of various kinds because liquid hydrocarbons reduce the tendency for the magnesium alkoxide to separate as a solid phase from the mixture and allow the use of less alcohol. The liquid hydrocarbon can either be present before the reaction between magnesium and the alkanol commences or can be added during or after the reaction. The reaction between magnesium and the alcohol can conveniently take place at any temperature from 10° to 120° C., preferably at from 40 to 80° C., more preferably at from 50 to 60° C. and can be started at, for example, room temperature or at from 50 to 60° C. and the mixture can either reflux during the exothermic reaction or can be cooled to moderate the reaction.

When carbonated magnesium alkoxide is used to neutralize the mixture of a phosphosulfurized polyolefin and an alkylphenol sulfide or an alkylphenol it is made by passing or dissolving carbon dioxide in a solution of magnesium alkoxide in an alkanol or an alkanol-liquid hydrocarbon solvent. This reaction is suitably carried out at from 20° to 120° C., preferably at from 30° to 80° C. and more preferably at from 45° to 65° C. A suitable technique is to introduce carbon dioxide gas under the surface of the magnesium alkoxide solution. It is believed that a complex is produced when carbon dioxide reacts with a magnesium alkoxide in an alkanol and that magnesium alkoxide is completely converted into carbonated magnesium alkoxide when two moles of carbon dioxide have reacted with each mole of magnesium alkoxide. A product in which at least 1.2 moles of carbon dioxide have reacted with each mole of the magnesium alkoxide, that is, a product in which at least 50%, preferably at least 60% of the magnesium alkoxide has been converted into carbonated magnesium alkoxide, has been found to be espe-

cially satisfactory for the neutralization. A product in which about 2 moles, e.g., 1.8 to 2.2 moles, of carbon dioxide have reacted with each mole of magnesium alkoxide, that is, a product in which about 100% of the magnesium alkoxide has been converted into carbonated magnesium alkoxide, is especially preferred.

The product of neutralizing the mixture of a phosphosulfurized polyolefin, an alkylphenol sulfide or an alkylphenol with a magnesium alkoxide or a carbonated magnesium alkoxide can either be neutral or overbased. To obtain a neutral product equivalent weights of the reactants are used. To obtain an overbased product an excess of the magnesium alkoxide or the carbonated magnesium alkoxide is added. The magnesium alkoxide or the carbonated magnesium alkoxide in the alkanol can be added to the mixture comprising a phosphosulfurized polyolefin, an alkylphenol sulfide or an alkylphenol, or vice versa.

It is usual to reflux the reaction mixture to complete the neutralization. An overbased product obtained from an excess of magnesium alkoxide or from an excess of magnesium alkoxide which has been incompletely carbonated will contain magnesium alkoxide and such an overbased product is usually carbonated at from 20 to 150° C., preferably at from 120 to 150° C. after distillation to this temperature. If carbonation is carried out at from 20° to 70° C. any excess alcohol is preferably removed after the treatment is complete; this can conveniently be done by distillation, by-product water being removed at the same time, often in the form of an azeotrope. If the overbased product is not carbonated, it is preferable to add a small quantity of water to hydrolyze the remaining alkoxide so that the product is then overbased with magnesium oxide or hydroxide.

The final product is preferably added to a lubricating oil in an amount corresponding to a magnesium content between 0.005% and 1% by weight of the final composition, for instance between 0.005% and 0.05%, especially about 0.03% by weight. Oil compositions containing higher proportions of the product, for instance corresponding to a magnesium content of up to 10% by weight, especially from 0.5% to 5% by weight, are also useful as concentrates to be diluted with more oil before use.

It is often advantageous to include an organic sulfonic acid in the mixture of the phosphosulfurized polyolefin and the alkylphenol sulfide or the alkylphenol to be neutralized because the product has very satisfactory properties. The method of neutralizing the phosphosulfurized polyolefin and the alkylphenol sulfide or the alkylphenol is exactly the same when it contains an organic sulfonic acid. Suitable organic sulfonic acids are alkylarylsulfonic acids especially alkylbenzenesulfonic acids. The alkyl groups preferably have from 8 to 30 carbon atoms, e.g., nonyl, dodecyl, tridecyl, tetradecyl or pentadecyl groups. Sulfonated wax/benzene condensate is also suitable.

The proportions of the phosphosulfurized polyolefin, the organic sulfonic acid and the alkylphenol sulfide or the alkylphenol are such that the organic sulfonic acid preferably does not exceed 75% by weight of the mixture. The weight of the amount of the organic sulfonic acid which can be present in the mixture is suitably from 10% to 50% by weight and preferably from 15% to 30% by weight.

However, if desired the product of neutralizing the mixture of the phosphosulfurized polyolefin and the alkylphenol sulfide or the alkylphenol can be used alone as a lubricating oil additive or it may be mixed with a sulfonated detergent additive. Suitable sulfonated additives include the neutral or overbased magnesium, calcium or barium salts of sulfonated aromatic hydrocarbons especially alkylbenzenesulfonic acids in which the alkyl groups have from 8 to 30 carbon atoms, e.g., the salts of nonyl-, dodecyl-, tridecyl-, tetradecyl- or pentadecyl-benzenesulfonic acid. The weight of sulfonated additive is preferably not more than 50% by weight of the combined weight of itself and the product of the invention, for example,

between 10% and 45%, especially between 15% and 30%. About 25% by weight is often a good proportion to use.

The lubricating oil composition may contain other conventional additives such as corrosion inhibiting agents, oxidation inhibiting agents such as phenols, arylamines and zinc dialkyl dithiophosphates, viscosity index improvers such as the polymethacrylates, antiwear agents such as tricresyl phosphate and copper inhibiting agents such as oxamide derivatives.

The process of the invention is illustrated by the following examples.

EXAMPLE 1

This example describes the production of a neutral detergent oil additive according to the invention.

(i) Methylate carbonate complex

Methanol (61 ml.) is added slowly to a stirred mixture of magnesium turnings (4 g., 0.1645 g. atom) and oil (25.8 g.) at 55° C. The resulting reaction is regulated by cooling and by the controlled addition of methanol. Complete conversion of the metal to methylate is achieved by a final refluxing period of about ½ hour.

The stirred mixture is then cooled to 60° C. and carbonated at this temperature by introducing carbon dioxide gas under the surface of the mixture. Carbon dioxide is stopped after about 100% conversion of methylate to carbonated magnesium methoxide.

(ii) Neutralization

The above carbonated solution is added over 5 minutes to the following stirred mixture at 50° C.

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Phosphosulfurized polyolefins in which the olefin is polybutene of molecular weight 900 (0.9 meq./g.; ca. 30% oil) -----	153.8
Dilute nonylphenol sulfide (1.06 meq./g.; ca. 49% oil) -----	83.2
Alkylbenzenesulfonic acid (mol. wt. 480, 1.51 meq./g.; ca. 39% oil) -----	57.5
Process oil (a light spindle oil) -----	104.9
1 0.1384 equivalent.	
2 0.088 equivalent.	
3 0.0868 equivalent.	

After refluxing for ¾ hour, water (10 ml.) is added and refluxing continued for a further ¼ hour. Methanol and water are then removed by distillation to a batch temperature of 150° C. and vacuum treatment at 150° C. Filtration at the rate of 380 g. in 34 minutes through 4% Hy-flow (which is a diatomaceous earth) gave a product having the following analytical data:

Percent mg. -----	0.89
TBN (mg. KOH/g.) -----	16.0
Percent organics -----	44.5

EXAMPLE 2

This example describes the production of an overbased detergent oil additive according to the invention.

(i) Methylate carbonate complex

Methanol (200 ml.) is added slowly to stirred previously warmed magnesium turnings (15.6 g., 0.641 g. atom). The ensuing vigorous reaction is controlled by cooling and by the gradual addition of xylene (100 ml.) which additionally helps to solubilize the magnesium methylate formed. Complete conversion of the metal to methylate is achieved by a final reflux period of about ½ hour.

The stirred mixture is then cooled to 50° C. and carbonated at this temperature by introducing carbon dioxide gas under the surface of the mixture. Carbon dioxide is stopped after about 60% conversion of the methylate to carbonated magnesium methoxide.

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(ii) Neutralization

The above carbonated solution is added over ½ hour to the following stirred mixture at 55° C.

Phosphosulfurized polybutene of molecular weight 900 (0.9 meq./g.; ca. 30% oil) -----	¹ 250.0
Dilute nonylphenol sulfide (1.06 meq./g.; ca. 49% oil) -----	² 135.3
Alkylbenzenesulfonic acid (mol. wt. 480; 1.51 meq./g.; ca. 30% oil) -----	³ 93.4
Process oil (a light spindle oil) -----	212.5

¹ 0.225 equivalent.

² 0.1434 equivalent.

³ 0.141 equivalent.

After refluxing at ca. 65° C. for 1 hour, water (20 ml.) is added and refluxing continued for a further ¼ hour. Removal of solvents to a batch temperature of 150° C. is then followed by a 10 minute carbon dioxide purge at 150° C. and vacuum treatment at 150° C. Filtration at the rate of 381 g. in 22 minutes through 4% Hyflow gave a product having the following analytical data:

Percnt Mg -----	2.11
Percent P -----	0.88
Percent S -----	3.62
TBN (mg. KOH/g.) -----	50
Percent organics -----	42.7

Supercharged Petter AVI engine tests on the products of Examples 1 and 2 showed them to be directly comparable in performance to the barium analogs.

EXAMPLE 3

This example describes the production of an overbased detergent oil additive according to the invention.

(i) Methylate carbonate complex

This complex was prepared as described in Example 1.

(ii) Neutralization

The above carbonated solution is added over 5 minutes to the following stirred mixture at 50° C.

Phosphosulfurized polyolefins in which the olefin is polybutene of molecular weight 900 (0.9 meq./g.; ca. 30% oil) -----	¹ 125.0
Dilute nonylphenol sulfide (1.06 meq./g.; ca. 49% oil) -----	² 67.6
Alkylbenzenesulfonic acid (mol. wt. 480, 1.51 meq./g.; ca. 39% oil) -----	³ 46.7
Process oil (a light spindle oil) -----	80.4

¹ 0.1125 equivalent.

² 0.0715 equivalent.

³ 0.0705 equivalent.

After refluxing for ¾ hour, water (10 ml.) is added and refluxing is continued for a further ¼ hour. Methanol and water are then removed by distillation to a batch temperature of 150° C. and vacuum treatment at 150° C. Filtration at the rate of 325.9 g. in 10 minutes through 4% Hyflow gave a product having the following analytical data:

Percent Mg -----	1.14
TBN (mg. KOH/g.) -----	16.0
Percent organics -----	44.3

EXAMPLE 4

(i) Methylate carbonate complex

Methanol (72 ml.) is added slowly to a stirred mixture of magnesium turnings (4.7 g.) and oil (30.3 g.) at 55° C. The resulting reaction was regulated by cooling and by the controlled addition of methanol. Complete conversion of the metal to methylate is achieved by a final refluxing period of 30 minutes.

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The stirred mixture is then cooled to 60° C. and carbonated at this temperature by introducing carbon dioxide gas under the surface of the mixture. The passage of carbon dioxide gas is stopped after about 100% conversion of methylate to carbonated magnesium methoxide.

(ii) Neutralization

The above carbonated solution is cooled to 50° C. when the following homogeneous mixture is added over 15 minutes.

Phosphosulfurized polybutene of molecular weight 900 (0.9 meq./g.; ca. 30% oil) -----	55.8
Dilute nonylphenol sulfide (1.06 meq./g.; ca. 49% oil) -----	300.0
Process oil (a light spindle oil) -----	36.0

After refluxing for 45 minutes, water (10 ml.) is added and refluxing continued for 15 minutes. Methanol and water are then removed by distillation to a bath temperature of 150° C. and vacuum treatment at 150° C. Filtration at the rate of 387 g. in 10 minutes through 4% diatomaceous earth gave a product having the following analytical data:

Percent Mg -----	1.08
TBN (mg. KOH/g.) -----	45
Percent organic -----	43.7
Percent phosphorus -----	0.35
Percent sulfur -----	4.98

While this invention has been described with respect to various specific examples and embodiments, it is understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the production of a detergent additive for lubricating oils which comprises reacting a mixture of a phosphosulfurized polyolefin and a compound selected from the group consisting of an alkylphenol sulfide and an alkylphenol with an alkanol solution of a compound selected from the group consisting of an alkoxide of magnesium and a carbonated alkoxide of magnesium.

2. A process of claim 1 wherein the aromatic nucleus of the alkylphenol sulfide is substituted with an alkyl group containing from about 5 to about 20 carbon atoms.

3. A process of claim 2 wherein the mixture comprises a phosphosulfurized polyolefin and an alkylphenol sulfide obtained by reacting from about 3 to about 5 moles of an alkylphenol in which the alkyl group contains from about 7 to about 11 carbon atoms with from about 2 to about 4 moles of sulfur dichloride.

4. A process of claim 3 wherein the phosphosulfurized polyolefin has an average molecular weight from about 500 to about 2500.

5. A process of claim 4 wherein the weight ratio of alkylphenol sulfide and alkylphenol to the phosphosulfurized polyolefin is from about 1:9 to about 4:1.

6. A process of claim 5 wherein the alkoxide is selected from the group consisting of methoxide, ethoxide, propoxide and isopropoxide.

7. A process of claim 6 wherein the alkanol solution further contains a liquid hydrocarbon.

8. A process of claim 1 wherein the carbonated alkoxide of magnesium is the reaction product of at least about 1.2 moles of carbon dioxide per mole of alkoxide.

9. A process of claim 1 wherein the reaction mixture is heated to reflux to complete the reaction.

10. A process of claim 1 wherein an excess of the alkoxide or carbonated alkoxide is employed in the reaction to produce an overbased product which is then

reacted with carbon dioxide at a temperature of from about 20° C. to about 150° C.

11. A process of claim 1 wherein the mixture further contains an organic sulfonic acid in from about 10% to about 50% by weight of the mixture.

12. A process of claim 11 wherein the organic sulfonic acid is an alkylbenzenesulfonic acid in which the alkyl group contains from about 8 to about 30 carbon atoms.

13. A product produced by the process of claim 1.

14. A composition comprising a major amount of a lubricating oil and a minor amount of a product of claim 13.

15. A composition of claim 14 wherein the magnesium content is from about 0.005% to about 1% by weight.

References Cited

UNITED STATES PATENTS

3,377,282 4/1968 Bell ----- 252—32.7 HC

FOREIGN PATENTS

570,814 2/1959 Canada.

DANIEL E. WYMAN, Primary Examiner

W. H. CANNON, Assistant Examiner

U.S. Cl. X.R.

252—18, 42.7; 260—137