605526

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Patents Act

APPLICATION FOR A STANDARD PATENT

~~I~~/We Mobil Oil Corporation

of 150 East 42nd Street,
New York,
New York,
UNITED STATES OF AMERICA.

hereby apply for the grant of a standard patent for an invention entitled:

REACTION PRODUCTS OF DIALKYL AND TRIALKYL PHOSPHITES WITH ELEMENTAL SULFUR AND METHOD OF PREPARING SAME

which is described in the accompanying complete specification.

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 16-10-90

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8 DEC 1987
Melbourne

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PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
Mobil Oil Corporation

By: David B Fitzpatrick

Our Ref : 77817
POF Code: 1462/1462

PATENT OFFICE 100 ONE HUNDRED DOLLARS
PATENT OFFICE 50 FIFTY DOLLARS
PATENT OFFICE 5 FIVE DOLLARS

6012q/1

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F-4520(4034)

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DECLARATION FOR A PATENT APPLICATION

▼ INSTRUCTIONS

(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

In support of the (a) Non-Convention application made by
(b)

MOBIL OIL CORPORATION

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(hereinafter called "applicant(~~s~~) for a patent (c) for an invention entitled (d) REACTION PRODUCTS OF DIALKYL AND TRIALKYL PHOSPHITES WITH ELEMENTAL SULFUR AND METHOD OF PREPARING SAME

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

I/~~We~~ (e) EDWARD H. VALANCE of Mobil Oil Corporation of
150 East 42nd Street, New York, New York 10017,
UNITED STATES OF AMERICA

do solemnly and sincerely declare as follows:

1. [illegible]

*(**or**, in the case of an application by a body corporate)*

1. I am/~~We are~~ authorized to make this declaration on behalf of the applicant(~~s~~).

2. [illegible]

*(**or**, where the applicant(s) is/are not the actual inventor(s))*

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f) ANGELINE VAIRD CARDIS, 350 W. Front Street, Burlington County, Florence, New Jersey, USA

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

is/~~are~~ the actual inventor(~~s~~) of the invention and the facts upon which the applicant(~~s~~) is/~~are~~ entitled to make the application are as follows:
(g)

The Applicant is the assignee of the invention from the actual inventor.

(Note: *Paragraphs 3 and 4 apply **only** to Convention applications)*

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

~~3. The basic application(s) for patent or similar protection on which the application is based~~ is/are identified by **country, filing date, and basic applicant(s)** as follows:
(h)

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) ~~made in a Convention country in respect of the invention the subject of the application.~~

(k) Insert PLACE of signing
(l) Insert DATE of signing
(m) Signature(s) of declarant(s)

Note: No legalization or other witness required

Declared at (k) Fairfax, Virginia, U.S.A.

Dated (l) December 10, 1987

(m) MOBIL OIL CORPORATION

BY: Edward H. Valance
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To: The Commissioner of Patents

P18/7/78

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-82229/87
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REACTION PRODUCTS OF DIALKYL AND TRIALKYL PHOSPHITES WITH ELEMENTAL SULFUR AND METHOD OF PREPARING SAME

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(56) Prior Art Documents
GB 2123429
US 3197496
US 2862016

(57) Claim

1. A process for making a reaction product suitable for use as an additive in lubricating oils which process comprises reacting in the absence of catalyst a di- or tri-(substituted or unsubstituted hydrocarbyl) phosphite of the general formula $(R_1O)_2$ POR_2 where R_1 is a hydrocarbon radical of 4 to 18 carbon atoms and R_2 is hydrogen or a hydrocarbon radical of 4 to 18 carbon atoms with elemental sulfur in a mole ratio of sulfar to phosphite of between 0.8
and 1.2 at a temperature from 75^o to 110^{o}C.

This document contains the amendments made under Section 49 and is correct for printing

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COMPLETE SPECIFICATION
(ORIGINAL)

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Complete Specification for the invention entitled:

REACTION PRODUCTS OF DIALKYL AND TRIALKYL PHOSPHITES WITH ELEMENTAL SULFUR AND METHOD OF PREPARING SAME

Our Ref : 77817
POF Code: 1462/1462

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

REACTION PRODUCTS OF DIALKYL AND TRIALKYL PHOSPHITES WITH ELEMENTAL SULFUR AND METHOD OF PREPARING SAME

This invention relates to reaction products of dialkyl and trialkyl phosphites with elemental sulfur, reaction of the resulting product with epoxides, olefins, and amines, and use of any of these products in lubricating oil formulations.

U.S. Patent 3,984,448 discloses the use of metal oxides, such as those of copper, calcium, barium, magnesium, zinc, cadmium, titanium or lead in conjunction with elemental sulfur and O,O-dialkylphosphorus acid esters to produce dialkyl thiophosphates.

U.S. Patent 4,242,511 discloses the reaction of O,S-dialkylthiophosphoric acid esters by subjecting a thiophosphate to partial dealkylation in forming the salt of the dealkylated product by treatment with an amine.

Although dithiophosphate products are known lubricant additives, their preparation involves processes resulting in noxious, undesirable by-products such as hydrogen sulfide and chloride-containing waste streams.

This invention provides a process for making a first reaction product suitable for use as an additive in lubricating oils comprising reacting a dialkyl or trialkyl phosphite with elemental sulfur in a mole ratio of sulfur to phosphite of between 0.8 and 1.2 at a temperature between 75° and 110°C and in the absence of any catalytic material added to promote reaction of the two reactants.

This invention further provides a process for making a second reaction product also suitable for use as an additive in lubricating oils comprising reacting the first product with an amine, olefin or alkylene oxide in a mole ratio of amine, olefin or alkylene oxide to phosphite of 0.9 to 1.2 at a temperature between 10° and 90°C.

This invention further provides a process for making a third reaction product suitable for use as an additive in lubricating oils comprising reacting the second product with P_2O_5 at a P_2O_5: product mole ratio of 1:3.

This invention also provides a lubricant composition comprising a lubricant and from 0.1% to 10% by weight of the total composition of the obtained first, second and third products.

According to the present invention, a first reaction product is obtained by reacting dialkyl or trialkyl phosphites of the general formula

$$(R_1O)_2POR_2$$

where R_1 is a hydrocarbon radical of 4 to 18 carbon atoms and R_2 is hydrogen or a hydrocarbon radical of 4 to 18 carbon atoms with elemental sulfur in the absence of any added catalyst in the presence of pulverulent sulfur at elevated temperature. Useful dialkyl or trialkyl phosphites include oleyl, phenyl, nonyl phenyl, octylphenyl, 2-ethyl hexyl, 1,3-dimethylbutyl, tridecyl, isodecyl, octyl and butyl, and mixed phosphites of the above radicals. If desirable, an unreactive organic solvent can be utilized. Preferably the organic solvent is selected from benzene, toluene, xylene, and mixed alkyl and aromatic petroleum distillates. The pulverulent sulfur should conveniently have a mean particle size of less than one millimeter, preferably less than 0.01 millimeters, as this enables the reaction to be shortened. Reaction temperatures between 75 and 110°C are preferred and a mole ratio of sulfur to phosphite of 0.8 to 1.2 is preferred. The reaction is carried out, preferably under a blanket of material such as nitrogen or other non-reactive gas. At the end of the reaction period the reaction mixture is allowed to cool to room temperature. The desired product is then stripped under vacuum to remove solvent and volatile byproducts and can be subsequently filtered or decanted from the reaction vessel.

This first reaction product thus obtained may then be further reacted with an amine, olefin, or alkaline oxide. The mole ratio of one of these reactants reacted with one mole of phosphite in the reaction product is 0.9 to 1.2. This second reaction is effected by mixing the reactants and allowing them to react (with added heat, if desirable) at a temperature between about 10°C and about 90°C. The second product obtained can then be separated and purified by filtration and decantation. This second product is then suitable for use in lube oil and grease formulations.

The amine compound to be reacted with the first product formed by the alkyl phosphite and sulfur can be primary, secondary or tertiary. Preferred amines include Primene 81R, benzotriazole, tolutriazole, amine-containing polymeric succinimides, and aromatic amines such as dialkyl diphenylamine and (alkylated) phenyl naphthylamines.

If olefins are to be utilized they can be selected from vinyl ethers, esters and amides and other such activated olefins.

Useful alkylene oxides include ethylene oxide and propylene oxide.

The first and second products obtained which are useful as a lube oil additive may be further reacted with phosphorus pentoxide, P_2O_5 in a mole ratio of about 1 mole of P_2O_5 to about 3 moles of thiophosphate product to form a third product having improved performance..

The resulting reaction products of this invention are used with lubricating oils or greases to the extent of from about 0.1% to about 10% by weight of the total composition. Furthermore, other additives, such as detergents, antioxidants, antiwear agents and the like may be present. These can include phenates, sulfonates, succinimides, zinc dialkyl dithiophosphates, polymers, calcium and magnesium salts of phenates and sulfonates, including overbased salts of the same, and the like.

The lubricants contemplated for use with the esters herein disclosed include mineral and synthetic hydrocarbon oils of lubricating viscosity, mixtures of mineral oils and synthetic oils and greases from any of these, including the mixtures. The synthetic hydrocarbon oils include long-chain alkanes such as cetanes and olefin polymers such as oligomers of hexene, octene, decene, and dodecene, etc. These vicinal diols are especially effective in synthetic oils formulated using mixtures of synthetic hydrocarbon olefin oligomers and lesser amounts of hydrocarbyl carboxylate ester fluids. The other synthetic oils, which can be used alone with the compounds of this invention, or which can be mixed with a mineral or synthetic hydrocarbon oil, include (1) fully esterified ester oils, with no free hydroxyls, such as pentaerythritol esters of monocarboxylic acids having 2 to 20 carbon atoms, trimethylolpropane esters of monocarboxylic acids having 2 to 20 carbon atoms, (2) polyacetals and (3) siloxane fluids. Especially useful among the synthetic esters are those made from polycarboxylic acids and monohydric alcohols. More preferred are the ester fluids made by fully esterifying pentaerythritol, or mixtures thereof with di- and tripentaerythritol, with an aliphatic monocarboxylic acid containing from 1 to 20 carbon atoms, or mixtures of such acids.

A wide variety of thickening agents can be used in the greases of this invention. Included among the thickening agents are alkali and alkaline earth metal soaps of fatty acids and fatty materials having from 12 to 30 carbon atoms per molecule. The metals are typified by sodium, lithium, calcium and barium. Fatty materials are illustrated by stearic acid, hydroxystearic acid, stearin, cottonseed oil acids, oleic acid, palmitic acid, myristic acid and hydrogenated fish oils.

Other thickening agents include salt and salt-soap complexes as calcium stearate-acetate (U.S. Patent No. 2,197,263), barium stearate acetate (U.S. Patent No. 2,564,561), calcium stearate-caprylate-acetate complexes (U.S. Patent No. 2,999,065), calcium caprylate-acetate (U.S. Patent No. 2,999,066), and calcium salts and soaps of low-, intermediate- and high-molecular weight acids and of nut oil acids.

Another group of thickening agents comprises substituted ureas, phthalocyanines, indanthrene, pigments such as perylimides, pyromellitdiimides, and ammeline.

The preferred thickening gelling agents employed in the grease compositions are essentially hydrophobic clays. Such thickening agents can be prepared from clays which are initially hydrophilic in character, but which have been converted into a hydrophobic condition by the introduction of long chain hydrocarbon radicals onto the surface of the clay particles prior to their use as a component of a grease composition, as, for example, by being subjected to a preliminary treatment with an organic cationic surface active agent, such as an onium compound. Typical onium compounds are tetraalkylammonium chlorides, such as dimethyl dioctadecyl ammonium chloride, dimethyl dibenzyl ammonium chloride and mixtures thereof. This method of conversion, being well known to those skilled in the art, is believed to require no further discussion, and does not form a part of the present invention. More specifically, the clays which are useful as starting materials in forming the thickening agents to be employed in the grease compositions, can comprise the naturally occurring chemically unmodified clays. These clays are crystalline complex silicates, the exact composition of which is not subject to precise description, since they vary widely from one natural source to another. These clays can be described as complex inorganic silicates such as aluminum silicates, magnesium silicates, barium silicates, and the like, containing, in addition to the silicate lattice, varying amounts of cation-exchangeable groups such as sodium. Hydrophilic clays which are particularly useful for conversion to desired thickening agents include montmorillonite clays, such as bentonite, attapulgite, hectorite, illite, saponite, sepiolite, biotite, vermiculite, zeolite clays, and the like. The thickening agent is employed in an amount from about 0.5 to about 30, and preferably from 3 percent to 15 percent by weight of the total grease composition.

Having described the invention in general aspects, the following examples are offered as specific illustrations. Parts are by weight.

EXAMPLE 1

A one-liter flask was charged with 209.3 grams of tris-2-ethylhexylphosphite and 16 grams of sulfur under a nitrogen atmosphere. The initial reaction elevated the temperature to 109°C. When the temperature started to decline, heat was applied to maintain 100°C for eight hours. The product when analyzed was determined to contain 6.7 percent of phosphorus and 7.5 percent of sulfur.

EXAMPLE 2

In accordance with the procedure of Example 1 a product was made from 208 grams of tri-isopropyl phosphite and 32 grams of sulfur. Analysis of the product showed 6.57 percent of phosphorus and 11.6 percent of sulfur.

EXAMPLE 3

To 388g (2.0 moles) dibutylhydrogen phosphite was added 64g (2.0 moles) sulfur. The temperature was raised to 100°C under a nitrogen atmosphere with stirring and held for eight hours. The resulting reaction mixture was cooled to ambient temperature and the desired reaction product was recovered.

EXAMPLE 4

Sulfur (32g, 1.0 mole) and bis-(2-ethylhexyl) hydrogen phosphite (306g, 1.0 mole) were stirred under nitrogen as the temperature was increased from ambient to 100°C. Products were also made following the procedure of Example 4, from di-oleylhydrogen phosphite, and dilaurylhydrogen phosphite.

Example 5

To 388g (2.0 moles) dibutylhydrogen phosphite was added 64g (2.0 moles) sulfur. The temperature was raised to 100°C under a nitrogen atmosphere with stirring and held for eight hours.

The reaction mixture was cooled to ambient temperature and then held in an ice bath as propylene oxide (204g, 3.5 moles) was added over one and one-half hours. The temperature was increased to reflux the excess propylene oxide (pot temperature = 90°C). After two hours, the excess propylene oxide had distilled up the condenser. Heptane (100cc) was added, and refluxing was continued an additional three hours. The solvent was distilled off and the product was vacuum topped at 20mm Hg, 100°C.

The product was cooled to 50°C and filtered through diatomaceous earth.

Example 6

The product of Example 5 (113.6g, 0.2 moles) was stirred at 50°C under nitrogen as phosphorus pentoxide (9.5g, .066 moles) was added in portions over forty-five minutes. The temperature was raised to 75°C and held two and one-half hours. The product was then filtered.

The recovered filtrate, the product, was stirred at 50°C as Primene 81R (21.7g) was added dropwise over twenty minutes. Primene 81R is a mixed C_{12} to C_{14} tertiary alkyl primary amine produced and sold commercially by Rohm and Haas Co. This final product was stirred an additional hour at 50°C.

Following the procedures of Examples 1 and 2, products were prepared from dilaurylhydrogen phosphite, bis-2-ethylhexylhydrogen phosphite, and dioleylhydrogen phosphite.

Example 7

Sulfur (32g, 1.0 mole) and bis-(2-ethylhexyl) hydrogen phosphite (306g, 1.0 mole) were stirred under nitrogen as the temperature was increased from ambient to 100°C. At 100°C, Primene 81R (191 grams) was added dropwise over twenty minutes. After the addition, stirring was continued an additional hour at 100°C. The temperature was reduced to 50°C and the product was filtered through diatomaceous earth.

Following the procedure of Example 7, products were also made from dibutylhydrogen phosphite, di-oleylhydrogen phosphite, and dilaurylhydrogen phosphite.

Evaluation of Products

The products described in Examples 1 and 2 were blended in mineral oil and tested in the Shell Four-Ball Wear Test. The results in Table 1 demonstrate the antiwear protection afforded by these products.

TABLE 1

FOUR BALL WEAR TEST SCAR DIAMETER (mm)

1/2 Inch Balls, 52100 Steel, 60 Kg., 30 Minutes, 1.5% Additive

	1000 RPM		2000 RPM	
Temperature, °F	200°F	300°F	200°F	300° F
Base Stock	1.02	1.92	4.12	3.85
Example 1	0.57	0.75	0.82	0.87
Example 2	0.65	0.50	0.70	0.70

The product of Example 1 was combined at 0.6 weight percent into a fully formulated hydraulic oil and compared to the same formulation using 0.7 weight percent of commercial zinc dithiophosphate in the Vickers V104C pump Wear Test (ASTM D2882) The results were as follows and demonstrated the antiwear performance of the products herein disclosed.

TABLE 2

Formulation Containing	ASTM D28882 Wear, Milligrams
Zinc dithiophosphate	27
Example 1 Product	22

The products described in Examples 5, 6 and 7 were blended in mineral oil and tested in the Shell Four-Ball Wear Test. The results which are summarized in Table 3 demonstrate the antiwear protection afforded by these products. The mineral oil blends were further evaluated for EP properties in the Four-Ball Weld Test. The results are listed in Table 4.

TABLE 3
FOUR BALL WEAR TEST SCAR DIAMETER (MM)

1/2 Inch Balls, 52100 Steel, 60 Kg., 30 Minutes, 1.5%

Example	R	Temp., °C (°F)	1000 RPM	2000 RPM
Base Stock		93 (200)	1.5	2.0
		199 (390)	1.8	1.9
5	Butyl	93 (200)	0.53	0.8
		199 (390)	0.8	0.75
5	2-Ethylhexyl	93 (200)	0.55	0.5
		199 (390)	1.6	1.6
5	Lauryl	93 (200)	0.55	0.5
		199 (390)	1.4	1.9
5	Oleyl	93 (200)	0.6	1.6
		199 (390)	1.4	1.7
6	Butyl	93 (200)	0.5	0.7
		199 (390)	1.2	1.7
6	2-Ethylhexyl	93 (200)		
		199 (390)		
6	Lauryl	93 (200)		
		199 (390)		
6	Oleyl	93 (200)	0.5	0.8
		199 (390)	1.7	1.8
7	Butyl	93 (200)	0.5	0.5
		199 (390)	1.1	1.8
7	2-Ethylhexyl	93 (200)	0.55	0.75
		199 (390)	0.55	1.75
7	Lauryl	93 (200)	0.5	1.5
		199 (390)	0.8	1.7
7	Oleyl	93 (200)	0.4	0.6
		199 (390)	1.4	1.7

TABLE 4

FOUR-BALL WELD, 1.5% ADDITIVE CONCENTRATION

Example	R	Weld Load (Kg)	Mean Hertz Load
Base Stock		126	26.9
5	Butyl	200	46.6
5	2-Ethylhexyl	160	37.1
5	Lauryl	160	34.4
5	Oleyl	160	41.1
6	Butyl	200	40.9
6	2-Ethylhexyl		
6	Lauryl		
6	Oleyl	200	40.6
7	Butyl	200	46.3
7	2-Ethylhexyl	200	43.6
7	Lauryl	200	48.4
7	Oleyl	200	41.2

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for making a reaction product suitable for use as an additive in lubricating oils which process comprises reacting in the absence of catalyst a di- or tri-(substituted or unsubstituted hydrocarbyl) phosphite of the general formula $(R_1O)_2$ POR_2 where R_1 is a hydrocarbon radical of 4 to 18 carbon atoms and R_2 is hydrogen or a hydrocarbon radical of 4 to 18 carbon atoms with elemental sulfur in a mole ratio of sulfar to phosphite of between 0.8 and 1.2 at a temperature from 75° to 110°C.

2. A process according to claim 1 further comprising reacting the product with a further reactant which is an aliphatic or aromatic amine or a basic heterocyclic compound containing at least one ring nitrogen atom; an olefinic compound; or an alkylene oxide; in a mole ratio of further reactant to phosphite of 0.9 to 1.2 at a temperature from 10° to 90°C to provide a further product.

3. A process according to claim 2 which further comprises reacting the further product with P_2O_5.

4. A process according to claim 3 wherein the mole ration of P_2O_5 to reaction product is 1 mole of P_2O_5 to 3 moles of the further product.

5. A process according to any preceding claim wherein said phosphite has the formula $(R_1O)_2POR_2$ where R_1 represents a C_4 to C_{18} alkyl or a C_6 to C_{18} alkyl or a C_6 to C_{18} aryl group which may be the same as or different from R_1.

6. A process according to any preceding claim wherein the di- or tri-hydrocarbyl phosphite comprises one or more substituents, which may be the same or different selected

from oleyl, phenyl, nonylphenyl, octylphenyl, 2-ethyl hexyl, 1, 3-dimethyl butyl, tridecyl, isodecyl, octyl, butyl, or a mixture of such phosphites.

7. A process according to claim 2, 3, 4, 5 or 6 further reactant comprises a (C_{12} to C_{14} tert. alkyl) primary amine or a mixture thereof; benzotriazole; or tolutriazole.

8. A process according to claim 2, 3, 4, 5 or 6 wherein the further reactant comprises amine-containing polymeric succinimide, or an aromatic amine.

9. A process according to claim 2, 3, 4, 5 or 6 wherein the further reactant comprises a vinyl ether, a vinyl ester or a vinyl amide.

10. A process according to claim 2, 3, 4, 5 or 6 wherein the further reactant comprises ethylene oxide or propylene oxide.

11. A process according to any preceding claim including the additional step of separating the products obtained from each step.

12. A process substantially as hereinbefore described with reference to any one of Examples 1 to 7.

DATED: 10 October 1990
PHILLIPS ORMONDE & FITZPATRICK
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MOBIL OIL CORPORATION David B Fitzpatrick