

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 349 093
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89201758.3

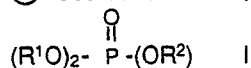
(51) Int. Cl.4: **C10M 105/74 , //C10N40:04**

(22) Date of filing: 30.06.89

(30) Priority: 01.07.88 GB 8815754

(43) Date of publication of application:
03.01.90 Bulletin 90/01(84) Designated Contracting States:
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NL-2501 CH The Hague(NL)(54) **Phosphate ester lubricants.**

(57) Use as lubricants, especially for traction drives, of organophosphate esters of the general formula I:-



wherein each group R¹ individually represents a saturated alicyclic group, preferably cyclohexyl, optionally substituted by one or more alkyl, especially methyl groups, and R² represents R¹ or an alkyl or aryl group.

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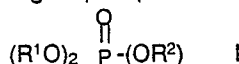
PHOSPHATE ESTER LUBRICANTS

The present process relates to the use of certain phosphate ester compounds as lubricants, in particular their use in traction drives.

These lubricants can be used in a variety of engineering applications, being of particular value in traction drives. Traction is broadly defined as the adhesive friction of a body on a surface on which it moves. A traction drive is a device in which torque is transmitted from an input element to an output element through nominal point or line contact typically with a rolling action by virtue of the traction between the contacting elements. While traction elements are commonly spoken of as being in contact, it is generally accepted that a fluid film is present therebetween. Almost all traction drives require fluids to remove heat, to prevent wear at the contact surfaces and to lubricate bearings and other moving parts associated with the drive. Thus, instead of metal to metal rolling contact there is a film of fluid introduced into the contact zone and interposed between the metal elements. The nature of this fluid determines to a large extent the limits in performance and the capacity of the drive. Most traction drives are designed to operate with a traction fluid which preferably has a coefficient of traction above about 0.06, a viscosity in the range of about 4-20,000 mPa.s over a temperature range of 40 °C to -20 °C and good thermal and oxidative stability. The fluid should also be noncorrosive to common materials of construction and have good load-bearing and low wear-rate properties.

Mineral base oils are rather unsatisfactory lubricants for traction drives since in general their traction (friction) coefficient is low, which means that for any given load applied to the gears the maximal tangential force that may be transmitted by the friction wheels is low.

It has now been found that certain organophosphate esters constitute good lubricants and traction fluids. Accordingly, the present invention provides the use as lubricants, and especially as traction fluids, of organophosphate esters of the general formula I



wherein each group R^1 individually represents a saturated alicyclic group, preferably a C_5 - 7 cycloalkyl group, optionally substituted by one or more alkyl groups, and R^2 represents R^1 or an alkyl or aryl group. The alkyl groups as substituent(s) on group R^1 , may be linear or branched and preferably contain 1 to 6 carbon atoms, groups having up to 4 carbon atoms providing a particularly suitable combination of physical properties and material costs. When R^2 is alkyl or aryl, the preferred groups are C_1 - 6 alkyl, preferably C_4 - 6 branched alkyl, e.g. neopentyl, or phenyl groups optionally bearing one or more alkyl substituents, e.g. methylphenyl groups.

Preferred organophosphate esters of formula I are those compounds wherein R^1 represents an optionally alkyl-substituted cyclohexyl group. Advantageously R^1 is cyclohexyl or methylcyclohexyl, and R^2 is cyclohexyl, methylcyclohexyl, methylphenyl or a branched C_4 - 6 alkyl group. Especially preferred esters of formula I are those wherein R^1 and R^2 are independently selected from 2-methylcyclohexyl and 3-methylcyclohexyl groups.

Organophosphate esters are known compounds, and therefore may be prepared by known procedures, such as the reaction of phosphoryl chloride with the appropriate alcohol in the presence of a base, such as pyridine or triethylamine, and suitably also a solvent. Naturally, the optimal reaction conditions vary in detail according to the alcohol used. In the case where cyclohexanol is reacted with phosphoryl chloride, it was found that good results were obtained by carrying out the reaction in dichloromethane solvent and at a temperature not exceeding 25 °C, with the product being purified by crystallisation from diethyl ether. For the methylcyclohexyl analogues, comparable reaction conditions can be used, with the purification being effected by a thin-film evaporator.

It has been found that the viscosity characteristics of the above ester compounds are very suitable for use in e.g. friction wheel gears (traction drives) in which application they may be admixed with conventional grease thickeners. Such thickeners can be of any number of materials commonly used to thicken mineral oils to lubricating viscosity, including both organic and inorganic compositions such as metallic soaps, synthetic polymers, organosiloxanes, clays, bentonite, and colloidal silica. Suitably, the viscosity properties of compounds to be used in traction drives are such that the compounds are operable between -30 and 150 °C. To achieve this it is advantageous that the ester compounds in the lubricants according to the invention have a viscosity of at most 1000, preferably 250 mm²/s at 40 °C and at least 1, preferably 3 mm²/s at 100 °C.

The compounds can be used as lubricants in various engineering applications. Since the above ester compounds show excellent lubricating performance in traction drives, the invention in particular provides the

use of these ester compounds as traction fluids, and also the operation of a traction drive wherein such esters form the traction fluid.

The ester compounds of the present invention can be used per se as lubricants. They can be mixed with other lubricants such as mineral or synthetic oils, and various additives can be added to the ester compounds, such as VI-improvers, pour point depressants, dispersants, detergents, anti-oxidants and the like. A mixture that can be of particular interest for traction fluid applications is a blend with a polyolefin, in particular a poly-alpha-olefin, especially polyisobutylene, since the presence of the polymer can usefully enhance the traction coefficient of the fluid blend. The molecular weight of such polyolefin blend components is conveniently in the range 500-10,000, a specific example of a suitable polyisobutylene being "Hyvis", and the proportion of polyolefin may vary from zero to 70% by weight.

The following Examples illustrate the preparation of representative compounds used in the present invention, together with their frictional and other physical properties.

15 Example I Tricyclohexyl phosphate

A solution of cyclohexanol (751.2g, 7.5m) and pyridine (595.0g, 7.5m) in dichloromethane (3.5L) was stirred under an atmosphere of dry nitrogen and phosphoryl chloride (382.5g, 2.5m) was added dropwise over 1-2 hours, whilst maintaining the temperature of the reaction mixture at between 15 and 25 °C throughout the addition period. On completion of the addition, stirring was continued at ambient temperature for a further 18 hours, and then the resultant mixture was filtered. The organic solution was washed with water (3 x 5L) and dried (over MgSO₄), and the solvent was evaporated off in vacuo at 30 °C to give a pale-yellow viscous oil (730.3g) which slowly solidified on standing. The crude oil was dissolved with stirring in diethyl ether (750ml) and cooled with stirring to -40 to -50 °C in a dry ice/acetone cooling bath. The precipitate was filtered and dried in vacuo at 25 °C to give tri(cyclohexyl) phosphate (520.0g) as an off-white solid, m.p. 48-50 °C.

30 Example II Tri(methylcyclohexyl) phosphate

A solution of methylcyclohexanol (technical grade, containing a mixture of isomers; 2.08 kg, 18.2m) and pyridine (1.44 kg, 18.2m) in dichloromethane (10L) was stirred under an atmosphere of dry nitrogen and phosphoryl chloride (930.2g, 6.07m) added dropwise over 1.5 hours, whilst maintaining the temperature of the stirred reaction mixture at between 15 and 25 °C throughout the addition period. On completion of the addition, stirring was continued at ambient temperature for a further 18 hours, and then the resultant mixture was filtered, washed with water (4 x 6L) and dried (over MgSO₄), and the solvent was evaporated off in vacuo at 30 °C to give the crude product as a viscous oil. The crude oil was allowed to stand at room temperature overnight, was then filtered and unreacted methylcyclohexanol and other volatile impurities were removed by evaporation on a KDL-4 thin-film evaporator (at 85 °C and 0.8mmHg (107 Pa)) to give the product as a clear viscous oil (1.75 kg) containing a mixture of different isomers.

Examples III to V

45 By using the process of Example II, but substituting respectively 2-methylcyclohexanol, 3-methylcyclohexanol and 4-methylcyclohexanol (in each case mixtures of cis- and trans-isomers) in place of the technical grade methylcyclohexanol, there were prepared:-

III - Tri-(2-methylcyclohexyl)phosphate (oil)

IV - Tri-(3-methylcyclohexyl)phosphate (oil)

50 V - Tri-(4-methylcyclohexyl)phosphate (oil)

Example VI Bis(methylcyclohexyl) mono(methylphenyl) phosphate

55 A mixture of phosphoryl chloride (115.0g, 0.75m) and cresol (industrial-mixture of isomers) (81.1g, 0.75m) in dichloromethane (750ml) was stirred at 15 °C under an atmosphere of dry nitrogen. Pyridine (59.3g, 0.75m) was added dropwise over 20-30 minutes, whilst maintaining the temperature of the reaction mixture at below 20 °C throughout this period. The mixture was stirred at ambient temperature for 18 hours

after which more pyridine (118.7g, 1.5m) was added. The mixture was cooled to 10-15 °C and methylcyclohexanol (technical grade as in Example II) (205.5g, 1.8m) was added over 30 minutes, whilst maintaining the temperature of the reaction mixture at 15-20 °C throughout this period. Stirring was continued overnight and the mixture was then washed with water (4 x 500ml) and dried (over magnesium sulphate), and the solvent was evaporated off in vacuo. The resultant crude oil (315g) was passed down a thin-film evaporator (at 150 °C and 0.8mm Hg pressure (107 Pa)) to remove volatile impurities to give the required bis(methylcyclohexyl) mono(methylphenyl) phosphate (230g), as a brown oil, containing a mixture of different isomers.

Example VII Bis(methylcyclohexyl) mononeopentyl phosphate

A solution of phosphoryl chloride (76.7g, 0.5m) in dichloromethane (500ml) was stirred at 15 °C under an atmosphere of dry nitrogen and neopentyl alcohol (44.1g, 0.5m) was then added over 15 minutes, whilst maintaining the temperature of the reaction mixture at below 20 °C throughout the addition period. The mixture was stirred for 24 hours and then pyridine (130.5g, 1.65m) was added dropwise with cooling to 10-15 °C. Methylcyclohexanol (technical grade as in Example II) (137.1g 1.2m) was then added, whilst maintaining the temperature of the stirred mixture at between 10 and 20 °C throughout the addition period. Stirring was then continued for 18 hours at 15-20 °C after which the resultant solution was washed with water (4 x 500ml), dried (over magnesium sulphate) and evaporated in vacuo to give the crude product (200.3g) as a yellow oil. The crude oil was purified by evaporation on a thin-film evaporator (at 150 °C and 0.7mm Hg pressure (93 Pa)) to give bis(methylcyclohexyl) mononeopentyl phosphate (131.0g), as a viscous yellow oil containing a mixture of different isomers.

Example VIII Friction coefficient measurement

All friction measurements were performed on a two-disc machine. Hardened steel discs are fixed on the ends of two shafts so as to make tangential contact with each other. Radial forces may be applied to press the discs together with loads of 0-200 kgf. Each disc is driven by an electric motor. The speeds of rotation of the two discs are different, such that there is a slip.

Between the electric motor and the shaft carrying the lower test specimen, a measuring device is fitted which indicates the transmitted friction torque. The measuring device is a gear dynamometer with a pendulum which is swung out of its vertical balanced position when power is transmitted, the sine of the angle of inclination being a measure of the torque. The torque measurement is pre-calibrated through the design and dimensions of the instrument. The friction coefficient is defined by the torque measured divided by the product of the radial force times the radius of the lower disc.

Both discs used had a diameter of 50.0mm, the upper disc having a width of 3mm, the lower one having a width of 10mm. The top shaft speed was 606rpm, and the mean tangential (or surface) velocity was 1.48 ms⁻¹. The slip employed was 9.1%.

All experiments were run at ambient temperature (21 °C ± 2 °C). The friction readings are provided at loadings equivalent to Hertzian stresses of 0.69, 0.97, 1.19 and 1.38 GPa.

The friction coefficients of the compounds are indicated in the following Table. For the compound of Example I, whose m.pt. is 48-50 °C, these coefficients were determined on a supercooled fluid at 21(±2) °C.

The kinematic viscosity properties of the compounds are also included in this Table.

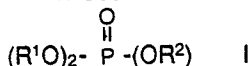
It will be noted that the friction coefficients of the compounds are all good, but that those of Examples III and IV are very surprisingly superior.

TABLE

Example -		I	II	III	IV	V	VI	VII
5	Kinematic Viscosity (40 °C) cSt (mm ² /S)	Solid	106.8	60.7	44.6	110.3	48.8	44.1
	Kinematic Viscosity (60 °C) cSt (mm ² /S)	45.62						
	Kinematic Viscosity (100 °C) cSt (mm ² /S)	9.503	7.873	6.43	5.63	8.31	5.65	5.04
	Viscosity Index	-32	-25	22	41	-7	18	-26
	Density (40 °C) g cm ⁻³	Solid	1.0310				1.073	1.002
10	Density (60 °C) g cm ⁻³	1.0585						
	Density (100 °C) g cm ⁻³	1.0295	0.9880				1.028	0.955
	Pour Point °C	48						
	Friction Coefficient (0.69GPa)	0.079	0.086	0.106	0.103	0.087	0.093	0.088
	Friction Coefficient (0.97GPa)	0.088	0.097	0.111	0.108	0.094	0.098	0.095
15	Friction Coefficient (1.19GPa)	0.098	0.102	0.113	0.111	0.099	0.100	0.098
	Friction Coefficient (1.38GPa)	0.108	0.104	0.113	0.111	0.102	0.099	0.098

Claims

1. Use as lubricants of organophosphate esters of the general formula I:-



wherein each group R¹ individually represents a saturated alicyclic group optionally substituted by one or more alkyl groups, and R² represents R¹ or an alkyl or aryl group.

2. Use according to claim 1 wherein any alkyl group present in the ester contains 1-6 carbon atoms.

3. Use according to claim 1 or 2 wherein R¹ represents an optionally alkyl substituted cyclohexyl group.

4. Use according to claim 3 wherein R² represents an alkyl group of 1 to 6 carbon atoms, an optionally alkyl substituted phenyl group, or an optionally alkyl-substituted cyclohexyl group.

5. Use according to any one of the preceding claims wherein the ester compound has a kinematic viscosity of at most 1000 mm²/s at 40 °C and at least 1mm²/s at 100 °C.

6. Use according to any one of Claims 1 to 5 wherein R¹ is cyclohexyl or methylcyclohexyl, and R² is cyclohexyl, methylcyclohexyl, methylphenyl or a branched C₄-₆ alkyl group.

7. Use according to Claim 6 wherein R¹ and R² are independently selected from 2-methylcyclohexyl and 3-methylcyclohexyl groups.

8. Lubricant composition which contains as the major component an organophosphate ester as defined in any one of claims 1-7.

9. Use as a traction fluid of an organophosphate ester as defined in any one of claims 1-7 or a composition as defined in claim 8.

10. Method of operating a traction drive wherein the traction fluid is an organophosphate ester as defined in any one of claims 1-7 or a composition as defined in claim 8.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	RESEARCH DISCLOSURE, no. 207, July 1981, pages 258-259, abstract no. 20720, Havant Hampshire, GB; "Phosphate esters as traction fluids" * Whole document *	1-4,8-10	C 10 M 105/74 // C 10 N 40:04
A	IDEM ---	6,7	
A	US-A-2 285 854 (F.B. DOWNING) * Page 1, column 2, lines 21-39; page 2, example 4; page 3, column 1, line 63; page 3, column 2, lines 14-26 * -----	1-4,6-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 M C 07 F
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	04-07-1989	HILGENGA K.J.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	