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(54) **USE OF INORGANIC PHOSPHORUS COMPOUNDS AS FRICTION IMPROVERS IN WET CLUTCH OR WET BRAKE LUBRICANT COMPOSITIONS**

VERWENDUNG VON ANORGANISCHEN PHOSPHORVERBINDUNGEN ALS FRIKTIONSVERBESSERER IN SCHMIERMITTELZUSAMMENSETZUNGEN FÜR FLÜSSIGKEITSKUPPLUNGEN ODER FLÜSSIGKEITSBREMSEN

UTILISATION DE COMPOSES PHOSPHORIQUES INORGANIQUES POUR AMELIORER LES PROPRIETES FRICTIONNELLES DE LUBRIFIANTS POUR EMBRAYAGES OU FREINS A DISQUE HUMIDE UNE HUILE LUBRIFIANTE POUR EMBRAYAGES OU FREINS A DISQUE HUMIDE

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Description

[0001] The present invention relates to the use of an inorganic phosphorus compound to improve the frictional properties of a wet-clutch or wet-brake lubricant composition.

5 [0002] A wet clutch or a wet brake of a power transmission device such as an automatic transmission for an automobile, an agricultural machine, a construction machine, or other industrial machines transmits a driving force by regulating the frictional properties of a plate on the driving side and a plate on the driven side, wherein the frictional properties of a lubricant employed for lubrication have a very important bearing. A wet clutch is taken up for explanation as a representative in the following description. Since inappropriate frictional properties cause a power transmission loss in the clutch and greatly affect the comfort on operating the machine, it is important for the lubricant to have appropriate frictional properties.

10 [0003] The friction control of a wet clutch of this type involves three friction coefficients, i.e. dynamic friction coefficient, break-away friction coefficient, and static friction coefficient, and it is conventionally required for the regulation of the friction in a wet clutch of this type to raise the power transmission torque (called as dynamic friction coefficient in view of the friction coefficient and usually expressed as μ_d ; hereinafter referred to as μ_d), and at the same time, to lower the friction transmission torque at the engaging point of the wet clutch (called as break-away friction coefficient in view of the friction coefficient and usually expressed as μ_0 ; hereinafter referred to as μ_0). If the ratio of μ_0/μ_d exceeds 1, a transmission shock is produced to arouse discomfort at the change of speed (when the clutch is operated). If the ratio is 1 or less, no such a transmission shock is produced and the transmission properties which do not impair the comfort are obtained.

20 [0004] The power transmitting capacity of the wet clutch is also of importance, and in this connection, it is important to increase the static friction torque (called as static friction coefficient and expressed as μ_s to be distinguished from the break-away friction coefficient; hereinafter referred to as μ_s).

25 [0005] Since these friction coefficients depend largely upon the lubricant employed, for improving the transmission shock, the use of a friction modifier, etc. has usually been practiced to reduce the ratio of μ_0/μ_d to 1 or less, however, the addition of the friction modifier, etc. causes at the same time a problem of lowering in μ_s . It is, therefore, important in lubricating machines under consideration to obtain a lubricant capable of reducing the μ_0/μ_d ratio to 1 or less and increasing μ_s as much as possible, thereby eliminating the transmission shock and attaining a high transmitting capacity.

30 [0006] The lubricant is required to show good durability in a long-time use while undergoing little aging change in the friction coefficient and to suppress the transmission shock over a long period of time, however, the addition of a large amount of a friction modifier, etc. to obtain this effect is associated with a problem of lowering in μ_s . The μ_0/μ_d ratio and the μ_s are in a trade-off relation with each other as described heretofore, and accordingly, a variety of designs and inventions have hitherto been made as will be described below.

35 [0007] A lock-up clutch has recently come to be used in an automatic transmission for an automobile to reduce the fuel consumption and to reduce the power loss in a torque converter and thus, the lubricant has been imposed with a still more complicated factor. Specifically, the problem in the lock-up clutch case is a vibration called shudder. The frictional properties at different rotations have an important bearing on the suppression of the vibration and the lubricant composition need be designed to have a ratio of the change in friction coefficient (μ) to the change in slipping velocity (v) at the time when the speed of rotation is changed, i.e., $d\mu/dv \geq 0$.

40 [0008] The addition of the friction modifier, etc. for achieving $d\mu/dv \geq 0$, however, usually results in the reduction of static friction coefficient (μ_s). Moreover, the vibration is more likely to occur at a relatively low temperature, and therefore, the above-described $d\mu/dv \geq 0$ need be achieved at a low temperature, however, the friction coefficient is usually so dependent on temperature as to drop along with an elevation in lubricant temperature. Even though the prevention of vibration at a low temperature, for example, 40°C, is achieved by blending a large amount of friction modifier, etc., or by blending a very effective friction modifier with too much care to the prevention of vibration, the friction coefficient in a working temperature range of 80°C to 120°C lowers excessively and thereby the torque transmitting capacity in the lock-up clutch decreases, leading to a problem of easy slipping. The friction coefficient is, therefore, desired to be free from the temperature dependence. And also, the durability is required for the suppression of vibration in the lock-up clutch. Accordingly, blending of a large amount of friction modifier, etc. is required in the prior art, which gives rise to the reduction in static friction coefficient (μ_s).

45 [0009] The frictional properties are mutually contradictory as stated above, and therefore, a variety of friction modifiers, detergents, phosphoric esters, etc. have hitherto been used. Japanese Patent Application (Laid-Open) No. 173097/1985 (corresponding to Japanese Patent Publication No. 46635/1990), for example, proposes a lubricant composition comprising (A) a phosphoric ester having from 4 to 30 carbon atoms or an amine salt thereof, and (B) one compound selected from the group consisting of a sorbitan fatty acid ester, a glycerol fatty acid ester, a palm kernel oil fatty acid, a coconut oil fatty acid, a compound represented by the general formula $(RCOO)_2Zn$, a mixture of a fat and oil and a fatty acid, and a reaction product of a polyalkylenepolyamine and a fatty acid.

[0010] A series of Japanese Patent Application (Laid-Open) Nos. 39395/1991, 39396/1991, 39397/1992, 39398/1991 and 39399/1991 propose the use of a combination of (A) one compound selected from a phosphoric ester, a phosphorous ester, and an amine salt thereof each having from 4 to 30 carbon atoms, and (B) a tertiary amine, an aliphatic dicarboxylic acid, a primary zinc thiophosphate, a succinimide, an overbased magnesium, calcium sulfonate, or the like to improve frictional properties.

[0011] All of these techniques employ an amine salt of an organic phosphoric acid having from 4 to 30 carbon atoms to improve the friction behaviour.

[0012] These conventional lubricant compositions are, however, still unsatisfactory not only in the friction behaviour but also in durability and need to be improved. More specifically, in the prior techniques, a very effective compound is used as a friction modifier or a large amount of friction modifier is used to prevent the vibration of a lock-up clutch. The use of such a friction modifier, however, impairs a static friction coefficient (μ_s), or the friction control power cannot be maintained by the deterioration or consumption of friction modifier, resulting in the failure to provide satisfactory durability. Moreover, satisfactory performance is not provided with respect to oxidation stability and corrosiveness to copper.

[0013] Accordingly, the present invention provides the use of an inorganic phosphorus compound which may contain sulfur atoms and/or oxygen atoms as its constituent elements, or an amine salt thereof, to improve the frictional properties of a wet-clutch or wet-brake lubricant composition as defined in claim 1.

[0014] The lubricant composition used in accordance with the present invention preferably satisfies the following conditions: (1) the μ_0/μ_d ratio is reduced to eliminate any shock arising from a speed change, (2) the μ_s is increased as high as possible to enhance a torque transmitting property, and (3) the vibration of a lock-up clutch is prevented, while all friction coefficients are free from the temperature dependence.

[0015] The lubricant composition is excellent not only in initial properties but is also durable in view of the prevention of vibration of a lock-up clutch.

[0016] The inorganic phosphorus compound used in accordance with the invention preferably contains a sulfur atom and/or an oxygen atom as its constituent elements, or is an amine salt thereof.

[0017] The lubricant used in the present invention contains at least one organic polyol compound having at least two hydroxyl groups in one molecule.

[0018] The above-described lubricant composition for a wet-clutch or a wet-brake may further comprise an ashless dispersing agent containing a nitrogen atom.

[0019] The lubricant composition used in the present invention typically comprises, as a principal component, a base oil. The base oil is not particularly restricted as far as it is a base oil usually employed for a lubricant, and may be a synthetic oil, a mineral oil, or a mixture thereof. The base oil preferably has a kinematic viscosity of 1×10^{-6} to 8×10^{-5} m^2/s (1 to 80 cSt (centisokes)), more preferably 2×10^{-6} to 5×10^{-5} m^2/s (2 to 50 cSt), at $100^\circ C$. Examples of the mineral oil include a paraffin-based mineral oil, a naphthene-based mineral oil, and a paraffin-naphthene-based mineral oil, and further, a mineral oil dewaxed by a usual method or a mineral oil modified to have a high viscosity index may be used.

[0020] Examples of the synthetic lubricant oil include various synthetic oils such as poly- α -olefin, a low-molecular ethylene- α -olefin copolymer, polybutene, a dibasic acid ester, polyglycol, a hindered ester, alkylbenzene, and polyether. A mixed oil of the above-described mineral oil and synthetic oil may also be used.

[0021] The inorganic phosphorus compound which may contain an oxygen atom and/or a sulfur atom as its constituent elements includes the followings.

[0022] Examples are phosphorous acid, phosphoric acid, hypophosphoric acid, phosphorus trioxide, phosphorus tetroxide, phosphorus pentoxide, phosphorotetrathionic acid (H_3PS_4), phosphoromonothionic acid (H_3PO_3S), phosphorodithionic acid ($H_3PO_2S_2$), phosphorotrithionic acid ($H_3PO_2S_3$), and P_2S_5 . Among these, phosphorous acid and phosphoric acid are preferred. An amine salt of an inorganic phosphorus compound can also be preferably used. Examples of the amine for use in the amine salt include primary, secondary and tertiary amines, and, in particular, amines containing a tertiary alkyl group, for example, those containing tertiary carbon atoms as carbon atoms adjacent to nitrogen atoms, more specifically, those represented by $R-C(CH_3)_2-NH_2$ (wherein R is an alkyl group having from 16 to 22 carbon atoms), are preferred. It is also possible to use a plurality of inorganic phosphorus compounds of these together.

[0023] The inorganic phosphorus compound is preferably contained in an amount of from 0.005 wt% to 0.1 wt%, preferably from 0.01 wt% to 0.05 wt%, in terms of the molar amount of phosphorus, based on the total lubricant oil composition, and within this range, the effect of the present invention can be achieved.

[0024] Examples of the organic polyol compound having at least two hydroxyl groups in one molecule include 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,2-hexanediol, 2,4-hexanediol, 2,4-octanediol, and 1,3-dodecanediol.

[0025] A triol, tetraol, or higher alcohol can be used as a simple substance, or as a partially esterified compound of the alcohol, such as a monoester, diester, or triester compound. Specifically, when glycerol or trimethylolpropane formed from triol is used, an ester with a carboxylic acid having from 1 to 40 carbon atoms, preferably with a fatty acid having from 1 to 24 carbon atoms is used. Industrially, the ester is usually a mixture of mono-, di- and triesters, and it is

preferred to distill and refine it by molecular distillation, etc. to convert it into a mixture of diester and monoester, or preferably a monoester of higher purity. An ester of a polyhydric alcohol such as tetraol can also be used, and a mixture of di-, tri-, and tetraesters formed with the above-described acids can also be used to leave at least two hydroxyl groups in one molecule. When using a polyhydric alcohol, an alkylaryl group may be used or a carboxylic ester having an alkylaryl group may be formed to increase solubility in the base oil. A polyhydric alcohol having an ester group may be in the form of a thioester. In the polyol containing hydroxyl groups, one of the hydroxyl groups is preferably in the α , β , or γ -position relative to the other hydroxyl group. Two or more of various compounds containing these hydroxyl groups may also be used.

[0026] The polyol compound containing at least two hydroxyl groups in one molecule is preferably contained in an amount of from 0.01 wt% to 4 wt%, preferably from 0.1 wt% to 1 wt% based on the total lubricant composition, and within this range, the effects of the present invention can be achieved.

[0027] In addition to the above-described essential components, the lubricant composition may contain, for the purpose of improving performance as a lubricant, additives usually employed, if desire, such as an antioxidant, a detergent-dispersant, an extreme-pressure agent, a friction modifier, an oiliness improver, an anti-wear agent, a corrosion inhibitor, a rust preventing agent, a rubber swelling agent, a defoaming agent, a pour-point depressant, and a viscosity index improver.

[0028] As the antioxidant, a phenol-based antioxidant, an aromatic amine-based antioxidant, a zinc dithiophosphate, etc., is used, and specific examples thereof include 2,6-di-t-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-t-butylphenol), phenyl- α -naphthylamine, dialkyldiphenylamine, zinc di-2-ethylhexyldithiophosphate, zinc diamyldithiocarbamate, and pinene pentasulfide. The antioxidant is added in an amount of from 0.01 wt% to 2 wt%, preferably from 0.05 wt% to 1 wt%, based on the lubricant composition.

[0029] The detergent-dispersant may be an ashless dispersant, a metallic detergent, or an ashless dispersant containing boron. Specific examples thereof include alkenyl succinimide- and benzylamine-type ashless dispersants, boronized polyisobutenyl succinimide- and boronized benzylamine-type ashless dispersants, metal sulfonate, metal phenate and metal salicylate. The metallic detergent indicates those containing a metal such as magnesium, calcium, or barium. The detergent-dispersant is added in an amount of from 0.01 wt% to 10 wt%, preferably from 0.5 wt% to 5 wt%, based on the lubricant composition.

[0030] Examples of the friction modifier include an amine compound such as oleyldiethanolamine, dodecyldiethanolamine, dodecyldipropanolamine, oleylamine, hexadecylamine, dodecyldiethylamine, dodecylethanolamine, and a mixture thereof, an amide such as oleic amide, dodecylcarboxylic acid diethanolamide, dodecylcarboxylic acid propanolamide, oleic acid diethanolamide, oleic acid propanolamide, hexadecylcarboxylic acid diethanolamide, hexadecylcarboxylic acid propanolamide, and a mixture thereof, and N-hydroxyethyl oleylimidazoline.

[0031] The above-described additives other than the antioxidant, the detergent-dispersant and the friction modifier are added in such an amount as in the addition for modifying a lubricant for a wet clutch or a wet brake.

[0032] The present invention will now be described with reference to Examples. The addition amount in Examples are in wt%.

EXAMPLES

[0033] The evaluation on performance of the lubricant composition described below is conducted in accordance with the following test method.

(1) SAE No. 2 Friction Tester

[0034] Evaluation was conducted by using this tester under the following conditions:

Disk	Paper disk for automatic transmission
Plate	Steel plate for automatic transmission
Motor rotating speed	3000 rpm

[0035] Measurement was carried out taking the value of 1200 rpm (shown as μ 1200 in the tables below) as the dynamic friction coefficient (μ_d) and the friction coefficient at the engaging point of the clutch as the break-away friction coefficient (μ_0).

Piston pressure	276 kPa (40 psi)
Lubricant temperature	120°C

[0036] The maximum friction coefficient at the engaging point at 0.7 rpm was measured as the static friction coefficient (μ_s).

[0037] The higher values of μ_d and μ_s were judged the better. Those satisfying $\mu_0/\mu_d \leq 1.0$ were more preferred.

5 [0038] The lubricant which underwent aging change in the friction coefficient was not preferred, and for indexing this, the following equation was used with the μ_s at 500 cycles being defined as $\mu_s(500)$ and the μ_s at 10,000 cycles being defined as $\mu_s(10,000)$:

$$\mu_s(10,000) - \mu_s(500) = \Delta\mu_s$$

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The $\Delta\mu_d$ was likewise adopted as for μ_d .

[0039] The lower $\Delta\mu_s$ and $\Delta\mu_d$ were accordingly judged the better.

(2) LVFA (Single-Plate Low-Velocity Friction Tester)

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[0040] The evaluation was conducted on the prevention of vibration of a lock-up clutch by using a single-plate low-velocity friction tester. The relation of the friction coefficient-the slip velocity (hereinafter referred to as μ -v characteristics) at a fixed temperature was obtained.

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Disk	Paper disk for automatic transmission (1 disk)
Plate	Steel plate for automatic transmission (1 plate)
Surface pressure	10 kg/cm ²
Lubricant temp.	40°C, 100°C

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Motor rotating speed:

[0041] The rotating speed was intermittently varied in a range of from 1 to 100 rpm.

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[0042] The rotating speed was varied to determine the friction coefficient (μ) versus the slip velocity (v), and when $d\mu/dv \geq 0$, the vibration was prevented and judgement was good.

[0043] For the sake of convenience, the friction coefficient at the rotation speed of 1 rpm was defined as μ_1 and the friction coefficient at 50 rpm was defined as μ_{50} . The μ_1/μ_{50} ratio was employed as the index. The lubricant satisfying $\mu_1/\mu_{50} \leq 1$ was concluded as having a preferred ability of preventing vibration.

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[0044] In LVFA, the lower the lubricant temperature, the more difficult the prevention of vibration, and the μ_1/μ_{50} ratio as an index of frictional properties is likely to become $\mu_1/\mu_{50} \geq 1$. On the other hand, although $\mu_1/\mu_{50} \leq 1$ is easily achieved in the vicinity of a practical working temperature range of from 80°C to 120°C, the reduction in the absolute value of μ_1 disadvantageously causes the slipping of the clutch. The value of μ generally shows the temperature dependence and becomes smaller as the temperature is elevated, and a lubricant free of the temperature dependence is demanded. Therefore, the ratio of $\mu_l(40^\circ\text{C})/\mu_l(100^\circ\text{C}) = \mu_1(T)$ was employed as the index showing the temperature dependence, by taking the friction coefficient at 1 rpm and 40°C as $\mu_l(40^\circ\text{C})$, and the friction coefficient at 1 rpm and 100°C as $\mu_l(100^\circ\text{C})$, with the value of $\mu_l(T)$ close to 1 being concluded as good.

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[0045] For evaluating the durability on the prevention of vibration, the evaluation of μ -v characteristics was conducted in LVFA for the tested lubricant after 10,000 cycles in the SAE No. 2 friction test using a new disk and a new plate. The μ_1/μ_{50} ratio of the new lubricant and the μ_l/μ_{50} ratio of the used lubricant were compared and the lubricant which showed little difference in the ratio value was concluded as having good durability.

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(3) Oxidation Stability Test:

[0046] The test was conducted at 165.5°C for 120 hours in accordance with the oxidation stability test of a lubricant for an internal combustion engine (JIS K-2514).

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(4) Copper Corrosion Test:

[0047] The amount of copper eluted after the processing at 150°C for 16 hours in accordance with JIS K-2513 was measured and the evaluation was made for judging the corrosion thereafter.

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EXAMPLE 1 AND COMPARATIVE EXAMPLES 1 TO 6

[0048] Samples each having the following composition were prepared by further adding thereto, in addition to the additives set forth below and additives described in respective tables, a paraffin-based mineral oil having a kinematic viscosity of 4.2×10^{-6} m²/s (4.2 cSt) at 100°C as the rest to make up 100 wt% in total, in which the phosphorus was added so that the molar amounts of the phosphorus in the compositions became equal, and the above-described evaluation was conducted. The evaluation results are shown in Table 1 and Table 2. In Tables, the overall characteristics as a lubricant composition are expressed by as excellent, O as good, Δ as acceptable, and × as unacceptable.

Formulation of Lubricant Composition	(wt%)
Polybutenyl succinimide (HiTEC 644: produced by Ethyl Petroleum Additives Inc.)	4.0
Phenol-based antioxidant (HiTEC 4728: produced by Ethyl Petroleum Additives Inc.)	0.5
N-Hydroxyethyl oleylimidazoline	0.02
Hydroxyethyl long-chained amine (Ethomeen T-12: produced by Akzo Chem. Inc.)	0.1
Sulfurized fats and oils (Sulperm 10S: produced by Keil Products Division of Ferro Corporation)	0.5
Tolyltriazole	0.04
Caprylic acid	0.05
Calcium phenate (Oloa 216: produced by Chevron Chemical Co.)	0.05
Silicone-based defoaming agent (added to account for 8 ppm in the test oil in terms of silicon element)	
Acrylate copolymer (PC-1244: produced by Monsanto Co.)	0.02
Dispersion-type polymethacrylate	6.0
Compounds shown in each Table shown	amounts
Table	in each
Paraffin-based mineral oil (kinematic viscosity at 100°C: 4.2×10^{-6} m ² /s (4.2 cSt))	the rest (100 in total)

[0049] In Examples, orthophosphorous acid was used as an inorganic phosphorus compound and monolauryl glyceride as a polyol.

Table 1

Additives	Comparative Example						Example 1
	1	2	3	4	5	6	
Octyl acid phosphate	0.30	0.30					
Diethylhydrodiene phosphite			0.35	0.35			
Amine salt of octyl acid phosphate					0.90	0.90	
Inorganic phosphorus acid							0.10
Monolauryl glyceride	0.50		0.50		0.50		0.50
Other additives + base oil	99.20	99.70	99.15	99.65	98.60	99.10	99.40
Results of SAE NO. 2 test							
$\mu 0$	0.137	0.140	0.151	0.154	0.139	0.145	0.146
μd	0.123	0.124	0.130	0.129	0.119	0.120	0.143
μs	0.116	0.117	0.117	0.118	0.120	0.120	0.125
$\mu 0/\mu d$	1.11	1.13	1.16	1.19	1.17	1.21	1.02
$\Delta \mu d$	0.007	0.009	0.015	0.016	0.004	0.005	0.004
$\Delta \mu s$	0.011	0.014	0.025	0.024	0.012	0.014	0.000
Overall Judgement	x	x	x	x	x	x	o

Table 2

LVFA Test Results		Comparative Example						Example 1
		1	2	3	4	5	6	
Fresh Oil	μ_1	0.115	0.120	0.116	0.123	0.117	0.119	0.125
	μ_{50}	0.140	0.138	0.141	0.138	0.140	0.139	0.140
	μ_1/μ_{50}	0.82	0.87	0.82	0.89	0.84	0.86	0.89
	$\mu_1(T)$	1.10	1.12	1.10	1.13	1.08	1.13	1.01
	Overall judgement	Δ	x	Δ	x	Δ	x	\bullet
Used Oil	μ_1	0.125	0.165	0.119	0.168	0.120	0.164	0.126
	μ_{50}	0.144	0.137	0.140	0.138	0.140	0.137	0.140
	μ_1/μ_{50}	0.87	1.20	0.85	1.22	0.86	1.20	0.90
	$\mu_1(T)$	1.09	1.25	1.08	1.21	1.09	1.20	0.99
	Overall judgement	Δ	x	Δ	x	Δ	x	\bullet

[0050] As is apparent from comparison of Example 1 with Comparative Examples 1, 3 and 5, the samples containing the inorganic phosphorus compound show high μ_d and μ_s , the lowest μ_0/μ_d ratio, and low $\Delta\mu_s$ and $\Delta\mu_d$ indicating the aging change of the friction coefficient, revealing to be best. Other samples show high μ_0/μ_d ratio and also high $\Delta\mu_s$ and $\Delta\mu_d$, revealing to be bad.

[0051] The effect of monoalanyl glyceride as a polyol is confirmed by the evaluation in LVFA of the lubricants used in the SAE No. 2 friction test, that is, without monoalanyl glyceride, the μ_1/μ_{50} ratio exceeds 1, and the temperature dependence appears as seen from $\mu_1(T)$.

[0052] In conclusion, it is found that, when the inorganic phosphorus compound and monoalanyl glyceride are present

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together, ideal frictional properties are obtained such as high μ_d and μ_s and a low μ_0/μ_d ratio in the SAE NO. 2 frictional properties, and μ_l/μ_{50} below 1 and $\mu_l(T)$ closest to 1 in the μ -v characteristics by LVFA for the used oil.

EXAMPLES 2 AND COMPARATIVE EXAMPLE 7 TO 10

5 **[0053]** Lubricant compositions were prepared in the same manner as the lubricant compositions in Example 1 and Comparative Examples 1 to 6, except for adding 0.1 wt% of boric acid.

10 **[0054]** The composition of each sample is shown in Table 3, and the evaluation as a lubricant composition was conducted in the same manner as above, which results are shown in Tables 3 and 4.

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Table 3

Additives	Comparative Example				Example 2
	7	8	9	10	
Octyl acid phosphate	0.30	0.30			
Amine salt of octyl acid phosphate			0.90	0.90	
Inorganic phosphorus acid					0.10
Monolauryl glyceride	0.50		0.50		0.50
Other additives + base oil	99.20	99.70	98.60	99.10	99.40
Results of SAE NO. 2 test					
$\mu 0$	0.137	0.140	0.134	0.136	0.147
μd	0.123	0.122	0.121	0.120	0.142
μs	0.116	0.115	0.113	0.115	0.122
$\mu 0/\mu d$	1.11	1.15	1.11	1.13	1.04
$\Delta \mu d$	0.007	0.010	0.008	0.007	0.005
$\Delta \mu s$	0.011	0.013	0.009	0.012	0.001
Overall Judgement	x	x	x	x	o

Table 4

LVFA Test Results	Comparative Example				Example	
	7	8	9	10		
Fresh Oil	$\mu 1$	0.120	0.121	0.124	0.123	0.119
	$\mu 50$	0.145	0.140	0.144	0.143	0.143
	$\mu 1/\mu 50$	0.83	0.86	0.86	0.86	0.83
	$\mu 1(T)$	1.11	1.14	1.15	1.14	0.96
	Overall judgement	Δ	x	Δ	x	\bullet
Used Oil	$\mu 1$	0.123	0.165	0.118	0.160	0.123
	$\mu 50$	0.142	0.137	0.140	0.137	0.140
	$\mu 1/\mu 50$	0.87	1.20	0.84	1.17	0.88
	$\mu 1(T)$	1.10	1.25	1.09	1.19	1.00
	Overall judgement	Δ	x	Δ	x	\bullet

[0055] As is apparent from comparison between Example 2 and Comparative Examples 7 to 10, when the inorganic phosphorus compound and monolauryl glyceride are present together as in Example 2, the samples satisfying both the frictional properties in SAE No. 2 test and the durability and temperature dependence in LVFA test are obtained.

EXAMPLES 3 TO 8

[0056] Lubricant compositions were prepared in the same manner as the lubricant compositions in Example 2 and Comparative Examples 7 to 10 above, except for changing the friction modifier to the polyol compound variously. The composition of each lubricant composition is shown in Table 5, and the results are shown in Tables 5 and 6.

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Table 5

Additives	Example							
	3	4	5	6	7	8		
1,3-Butanediol	0.20							
2,4-Hexanediol		0.50						
Monobutyl glyceride			0.50					
Monolauryl glyceride				0.50				
Monocoleyl glyceride					0.50			
Dioleyl pentaerythritol ester							0.50	
Other additives + base oil	99.70	99.40	99.40	99.40	99.40	99.40	99.40	99.40
Results of SAE NO. 2 test								
$\mu 0$	0.153	0.155	0.160	0.152	0.151	0.152		0.152
μd	0.146	0.147	0.149	0.146	0.145	0.144		0.144
μs	0.129	0.130	0.130	0.126	0.127	0.124		0.124
$\mu 0/\mu d$	1.05	1.05	1.07	1.04	1.04	1.06		1.06

Table 6

LVFA Test Results		Example					
		3	4	5	6	7	8
Fresh Oil	μ l	0.128	0.132	0.130	0.124	0.126	0.128
	μ 50	0.145	0.144	0.145	0.143	0.140	0.148
	μ l/ μ 50	0.88	0.92	0.90	0.87	0.90	0.86
	μ l(T)	0.99	0.99	0.98	0.96	1.02	1.05
Used Oil	μ l	0.129	0.134	0.131	0.124	0.127	0.143
	μ 50	0.143	0.145	0.144	0.142	0.141	0.150
	μ l/ μ 50	0.90	0.92	0.91	0.87	0.90	0.95
	μ l(T)	1.01	0.99	1.00	1.02	0.99	1.11

[0057] As is apparent from Examples 3 to 8, the samples containing an inorganic phosphorus compound of the present invention and 2,4-hexanediol, 2,4-octanediol, monobutyl glyceride, monolauryl glyceride, or dioleypentaerythritol ester show a low μ 0/ μ d ratio, while maintaining a high μ s. Moreover, the μ l/ μ 50 ratio in LVFA of the lubricant used in the SAE NO. 2 friction test is low and no temperature dependence appears.

EXAMPLES 9 COMPARATIVE EXAMPLES 11 to 14

[0058] The lubricant compositions shown in Table 3 were compared in respect of oxidation stability by ISOT. The composition of each sample and the results are shown in Table 7 below.

Table 7

Additives	Comparative Example				Example 9
	11	12	13	14	
Octyl acid phosphate	0.30	0.30			
Amine salt of octyl acid phosphate			0.90	0.90	0.10
Inorganic phosphorus acid					0.50
Monolauryl glyceride	0.50		0.50		
Other additives + base oil	99.20	99.70	98.60	99.10	99.40
Test results					
Increase in viscosity at 40°C %	60	63	54	51	12
TAN Increase	5.6	5.4	5.3	5.5	1.0
Extinction coefficient of carbonyl	0.39	0.40	0.41	0.42	0.18
Undissolved B %	0.01	0.01	0.01	0.01	0.01
Eluted copper (ppm)	132	125	113	128	38

[0059] As is apparent from the Table, when the inorganic phosphorus compound is added, the oxidation stability is good with a small increase in kinematic viscosity and total acid number. The less the eluted copper amount, the better, and samples containing the phosphorus compound showed good results.

EXAMPLE 10 AND COMPARATIVE EXAMPLES 15 to 18

[0060] The same lubricant compositions as in Examples 9 and Comparative Examples 11 to 14 were subjected to

a corrosion test of copper plates.

[0061] The composition of each lubricant composition and the test results are shown in Table 8 below.

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Table 8

Additives	Comparative Example				Example 10
	15	16	17	18	
Octyl acid phosphate	0.30	0.30			
Amine salt of octyl acid phosphate			0.90	0.90	
Inorganic phosphorus acid					0.10
Monolauryl glyceride	0.50		0.50		0.50
Other additives + base oil	99.20	99.70	98.60	99.10	99.40
Test results					
Eluted copper (ppm)	115	130	136	129	14

55 [0062] Also in the corrosion test of copper plate, the eluted amount of copper is small when added the inorganic phosphorus compound, revealing the superiority of the addition.

POSSIBILITY OF UTILIZATION IN INDUSTRY

[0063] The lubricant composition used in the present invention exhibits excellent frictional properties in a wet clutch and a wet brake, in particular, provides a high μ_d (dynamic friction coefficient) and a high μ_s (static friction coefficient), shows good prevention of vibration in a lock-up clutch used for an automatic transmission, is imparted with good durability for preventing the vibration, thus showing excellent properties as a lubricant composition for a wet clutch or a wet brake, further, has friction coefficients free from the temperature dependence, and works sufficiently effectively as a shock absorber oil, a power steering oil, a hydraulic suspension oil, etc.

Claims

1. Use of an inorganic phosphorus compound which may contain sulfur atoms and/or oxygen atoms as its constituent elements, or an amine salt thereof, to increase the static friction coefficient (μ_s)¹ to 0.122 or above ², and to reduce the ratio of the breakaway friction coefficient (μ_s) to the dynamic friction coefficient (μ_d)³ such that $\mu_o/\mu_d^4 \leq 1.15$, as measured at 120°C⁶ in the SAE No 2 Frictions Test as hereinbefore described⁷ of a wet-clutch or wet-brake lubricant composition comprising at least one organic polyol compound having at least two hydroxyl groups in one molecule.
2. Use according to claim 1 wherein the lubricant composition comprises a base oil which is at least one mineral oil and/or at least one synthetic lubricant oil selected from poly- α -olefins, low-molecular weight ethylene- α -olefin copolymers, polybutenes, dibasic acid esters, polyglycols, hindered esters, alkylbenzenes and polyethers.
3. Use according to claim 1 wherein the polyol compound(s) containing at least two hydroxyl groups in one molecule is/are contained in an amount of from 0.01 wt% to 4 wt%.
4. Use according to any one of the preceding claims wherein the lubricant composition contains an ashless dispersant containing nitrogen atoms.
5. Use according to any one of claims 2 to 4 wherein the base oil has a kinematic viscosity of 1×10^{-6} to 8×10^{-5} m²/s (1 to 80 cst (centistokes)) at 100°C.
6. Use according to any one of the preceding claims wherein the inorganic phosphorus compound is selected from phosphorous acid, phosphoric acid, hypophosphoric acid, phosphorus trioxide, phosphorus tetroxide, phosphorus pentoxide, phosphorotetrathionic acid (H₃PS₄), phosphoromonothionic acid (H₃PO₃S), phosphorodithionic acid (H₃PO₂S₃), phosphorotrithionic acid (H₃PO₂S₃) and phosphorus pentasulfide (P₂S₅).
7. Use according to any one of the preceding claims wherein the amine salt of an inorganic phosphorus compound is used.
8. Use according to any one of the preceding claims wherein the lubricant composition additionally comprises at least one additive selected from antioxidants, detergent-dispersants, extreme-pressure agents, friction modifiers, oiliness improvers, anti-wear agents, corrosion inhibitors, rust preventing agents, rubber swelling agents, defoaming agents, pour-point depressants, and viscosity index improvers.
9. Use according to any one of the preceding claims wherein the amount of the inorganic phosphorus compound is from 0.005 wt% to 0.1 wt% in terms of the molar amount of phosphorus, based on the total composition.

Patentansprüche

1. Verwendung einer anorganischen Phosphorverbindung, die Schwefelatome und/oder Sauerstoffatome als Be-

¹ p2 para [004]

² lowest μ_s of any invention Example 3, p 10 (max μ_s in any comparative Example is 0.120, C Ex 11, p 13)

³ p2 para [003]

⁴ p2 para [006]

⁵ p5 line 1

⁶ p4 56

⁷ see page 4 ll 44 to 57 for details

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standteile enthalten kann, oder eines ihrer Aminalsalze, zur Erhöhung des Haftreibungskoeffizienten (μ_s) auf 0,122 oder darüber, und zur Verringerung des Verhältnisses des Friktionskoeffizienten des Losbrechens (μ_o) zum dynamischen Friktionskoeffizienten (μ_d), so dass $\mu_o/\mu_d \leq 1,1$ von Schmiermittelzusammensetzungen für Flüssigkeitskupplungen oder Flüssigkeitsbremsen, umfassend mindestens eine organische Polyolverbindung, die mindestens

- 5 2. Verwendung nach Anspruch 1, wobei die Schmiermittelzusammensetzung ein Basisöl umfasst, das mindestens ein Mineralöl und/oder mindestens ein synthetisches Schmieröl ist, ausgewählt aus Poly- α -olefinen, Ethylen- α -olefin-Copolymeren mit niedrigem Molekulargewicht, Polybutenen, zweibasischen Säureestern, Polyglykolen, sterisch gehinderten Estern, Alkylbenzolen und Polyethern.
- 10 3. Verwendung nach Anspruch 1, wobei die Polyolverbindung(en), die mindestens zwei Hydroxylgruppen in einem Molekül enthalten, in einer Menge von 0,01 Gew.-% bis 4 Gew.-% vorliegen.
- 15 4. Verwendung nach einem der vorstehenden Ansprüche, wobei die Schmiermittelzusammensetzung ein Stickstoffatom enthaltendes aschefreies Dispergiermittel enthält.
- 20 5. Verwendung nach einem der Ansprüche 2 bis 4, wobei das Basisöl eine kinematische Viskosität von 1×10^{-6} bis $8 \times 10^{-5} \text{ m}^2/\text{s}$ (1 bis 80 cst (Centistokes)) bei 100°C hat.
- 25 6. Verwendung nach einem der vorstehenden Ansprüche, wobei die anorganische Phosphorverbindung ausgewählt wird aus Phosphorigesäure, Phosphorsäure, Hypophosphorsäure, Phosphortrioxid, Phosphortetraoxid, Phosphorpentoxid, Phosphortetrathionsäure (H_3PS_4), Phosphormonothionsäure ($\text{H}_3\text{PO}_3\text{S}$), Phosphordithionigesäure ($\text{H}_3\text{PO}_2\text{S}_3$), Phosphortrithionigesäure ($\text{H}_3\text{PO}_2\text{S}_3$) und Phosphorpentasulfid (P_2S_5).
- 30 7. Verwendung nach einem der vorstehenden Ansprüche, wobei ein Aminsalz einer organischen Phosphorverbindung verwendet wird.
- 35 8. Verwendung nach einem der vorstehenden Ansprüche, wobei die Schmiermittelzusammensetzung zusätzlich mindestens ein Additiv umfasst, ausgewählt aus Antioxidantien, Detergensdispergiermitteln, Hochdruckmitteln, Friktionsmodifizierungsmitteln, Ölverbesserern, Mitteln zur Erhöhung der Abriebfestigkeit, Korrosionsinhibitoren, Rostverhinderungsmitteln, Gummischäumungsmitteln, Entschäumungsmitteln, Stockpunktserniedriger und Viskositätsindexverbesserern.
9. Verwendung nach einem der vorstehenden Ansprüche, wobei die Menge der anorganischen Phosphorverbindung 0,005 Gew.-% bis 0,1 Gew.-% der molaren Menge Phosphor, bezogen auf die gesamte Zubereitung, beträgt.

Revendications

- 40 1. Utilisation d'un composé de phosphore inorganique qui peut contenir des atomes de soufre et/ou des atomes d'oxygène comme éléments constitutifs, ou d'un de ses sels d'amines, pour augmenter le coefficient de frottement statique (μ_s) à une valeur égale ou supérieure à 0,122 et réduire le rapport du coefficient de frottement au démarrage (μ_o) au coefficient de frottement dynamique (μ_d), de telle sorte que $\mu_o/\mu_d \leq 1,1$, mesurés à 120°C dans l'essai de frottement SAE n° 2 tel que décrit précédemment, de frottement d'une composition de lubrifiant pour embrayage à bain d'huile ou frein à bain d'huile, comprenant au moins un polyol organique ayant au moins deux groupes hydroxyle dans la molécule.
- 45 2. Utilisation suivant la revendication 1, dans laquelle la composition de lubrifiant comprend une huile de base qui consiste en au moins une huile minérale et/ou au moins une huile lubrifiante synthétique choisie entre des poly- α -oléfinen, des copolymères éthylène- α -oléfine de bas poids moléculaire, des polybutènes, des esters de diacides, des polyglycols, des esters à encombrement stérique, des alkylbenzènes et des polyéthers.
- 50 3. Utilisation suivant la revendication 1, dans laquelle le ou les polyols contenant au moins deux groupes hydroxyle dans la molécule est/sont présent(s) en une quantité de 0,01 % en poids à 4 % en poids.
- 55 4. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la composition de lubrifiant contient un dispersant sans cendre contenant des atomes d'azote.

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5. Utilisation suivant l'une quelconque des revendications 2 à 4, dans laquelle l'huile de base a une viscosité cinématique comprise dans l'intervalle de 1×10^{-6} à 8×10^{-5} m²/s (1 à 80 cst (centistokes)) à 100°C.
- 5 6. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le composé de phosphore inorganique est choisi entre l'acide phosphoreux, l'acide phosphorique, l'acide hypophosphorique, le trioxyde de phosphore, le tétroxyde de phosphore, l'anhydride phosphorique, l'acide phosphoro-tétrathionique (H₃PS₄), l'acide phosphoromonothionique (H₃PO₃S), l'acide phosphorodithionique (H₃PO₂S₂) l'acide phosphorotrithionique (H₃PO₂S₃) et le pentasulfure de phosphore (P₂S₅).
- 10 7. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le sel d'amine d'un composé de phosphore inorganique est utilisé.
- 15 8. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la composition de lubrifiant comprend en outre au moins un additif choisi entre des anti-oxydants, des dispersants-détergents, des agents extrême-pression, des modificateurs de frottement, des agents améliorant l'onctuosité, des agents anti-usure, des inhibiteurs de corrosion, des additifs anti-rouille, des agents de gonflement des caoutchoucs, des agents anti-mousse, des agents abaissant le point d'écoulement et des agents améliorant l'indice de viscosité.
- 20 9. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la quantité de composé de phosphore inorganique est comprise dans l'intervalle de 0,005 % en poids à 0,1 % en poids en termes de la quantité molaire de phosphore, sur la base de la composition totale.

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