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**FR-A- 2 388 042
GB-A- 1 452 513
US-A- 3 370 007
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Description

This invention relates to a lubricant composition containing a metallic phosphorus chalcogenide as a crystal powder having a layered structure or an intercalation compound of the metallic phosphorus chalcogenide, and more particularly to a solid lubricant containing an intercalation compound in which a metallic phosphorus chalcogenide is a host layer and an alkylamine, an aromatic amine, pyridine or an alkylammonium chloride is a guest and having an excellent extreme pressure property as well as extreme pressure lubricant or extreme pressure grease containing the above solid lubricant dispersed therein.

The lubricant is a general term for substances having such physical and chemical properties that it is placed between two solid surfaces of relative movement to reduce friction and wear on the solid surface, decrease dynamic loss and prevent seizing, fatigue failure and the like, and is morphologically classified into liquid lubricant, semi-solid lubricant and solid lubricant. For example, the liquid lubricant includes petroleum lubricating oil (mineral oil) and synthetic lubricating oil, and the semi-solid lubricant includes grease and compound, and the solid lubricant includes layered structure crystal powders such as graphite and molybdenum disulfide.

These lubricants are considered to have the following five functions, i.e. (1) cooling function, (2) sealing function, (3) rust preventing function, (4) anti-seizing function and (5) lubricating function. Among these functions, the lubricating function (5) is a most important function in the lubricant, which is satisfied in any of the liquid lubricants, semi-solid lubricant and solid lubricant. However, the liquid lubricant is excellent in the cooling function (1), but is poor in the sealing function (2) as well as the rust preventing function (3) and the anti-seizing function (4). The functions (2), (3) and (4) can be reinforced by the addition of additives. The semi-solid lubricant is poor in the cooling function (1), but is excellent in the sealing function (2) and the rust preventing function (3). Further, the anti-seizing function (4) is poor, but can be reinforced by the addition of additives.

The solid lubricant is poor in all of the cooling function (1), sealing function (2), rust preventing function (3) and anti-seizing function (4) in form of single powder. Therefore, the solid lubricant is usually used in combination with the liquid lubricant or the semi-solid lubricant while utilizing the merit of the latter lubricant. That is, the above functions are reinforced by the addition of extreme pressure additive at the present.

On the other hand, it is favorable to reduce the number of components in the lubricant composition as far as possible from viewpoints of the simplification of production steps and material maintenance and the reduction of cost. For this end, the use of multi-purpose component has hitherto been considered. As a result, there has been examined the use of an extreme pressure lubricating oil such as phosphate ester oil and an extreme pressure thickener such as chlorinated fatty acid metallic soap. The former has a property of swelling rubbery material such as packing and a property of lowering the rust preventing property due to the incorporation of water, and is expensive in the cost, while the latter is poor in the thickening ability, so that they are not widely used up to the present.

As the solid lubricant, crystal powder having a layered structure such as graphite, molybdenum disulfide or the like has been widely used, in which it is expected to develop an effect of conducting the lubrication by slipping of an interlaminar portion having a small shearing strength. Similarly, mica and bentonite have a layered structure. And also, an intercalation compound as a reaction product obtained by invading another molecule, atom or ion (guest) into the interlaminar portion and reacting with crystal layer (host layer) is used as a lubricant.

For example, graphite fluoride obtained by reacting graphite layer with fluorine invaded between the layers is used as a solid lubricant, while an organic bentonite by reacting bentonite layer with quaternary ammonium salt invaded between the layers is used as a thickener for grease.

All of them develop the lubrication function through the slipping between the layers, and cannot expect such an extreme pressure action as conducted in sulfur series extreme pressure additive or sulfur-phosphorus extreme pressure additive that sulfur reacts with local friction portion to produce an iron sulfide film having a melting point of about 1000°C for the prevention of metal contact or an eutectic body of iron phosphoride and iron having a low melting point is produced thereon to give an action smoothening the friction surface.

Lubricant compositions containing metallis phosphorus chalcogenides are disclosed in FR-A-2388042 and compositions containing metallic sulphides, e.g. ZnS, as host with organic amine as guest are disclosed in US-A-3763043.

It is an object of the invention to develop a solid lubricant having excellent extreme pressure property and improved anti-seizing function and wear resistance, whereby the structure of the lubricant composition is simplified and the cost is reduced.

According to the invention, it has been found that the metallic phosphorus chalcogenide contains phosphorus (P) and a chalcogen element such as sulfur (S), selenium (Se) or tellurium (Te) in its molecule and fur-

ther includes a metallic element such as Zn, Mg or Pb. Further, it has been found that this substance is a crystal of layered structure and is a solid lubricant having excellent extreme pressure property and anti-seizuring function. Moreover, intercalation compounds can be formed by intercalating various guests between layers of the metallic phosphorus chalcogenide. In this connection, the inventors have repeated experiments using various guests and made studies and further found that when an alkylamine, an aromatic amine, pyridine or a quaternary alkylammonium salt is used as a guest, the resulting crystal powder of the intercalation compound itself develops most excellent extreme pressure property and anti-seizuring function and is considerably effective as a solid lubricant having an extreme pressure property.

The inventors have made further studies and found that when the above intercalation compound is dispersed in a lubricating oil, the improved thickening function is developed in accordance with the kind of the organic substance as a guest.

That is, multi-purpose substances as a solid lubricant having an excellent extreme pressure property and a thickening agent are obtained from the above intercalation compounds, whereby the invention has been accomplished.

Therefore, the metallic phosphorus chalcogenides of the layered structure and their intercalation compounds according to the invention can be used as a solid lubricant having an excellent extreme pressure property in form of powder, and also some intercalation compounds among the above intercalation compounds provide an extreme pressure grease by dispersing into a lubricating oil, which can particularly exhibit excellent extreme pressure property and anti-seizuring function without adding an extreme pressure additive.

That is, the invention is concerned with a lubricant containing not less than 0.1% by weight of at least one intercalation compound consisting of a metallic phosphorus chalcogenide as a host layer and an alkylamine, an aromatic amine, pyridine or an alkyl ammonium chloride as a guest. When the amount of the metallic phosphorus chalcogenide or the intercalation compound is less than 0.1% by weight, the effect of considerably improving the lubrication property is not obtained, while when the amount is 100% by weight or the composition consists of the metallic phosphorus chalcogenide or the intercalation compound itself, it can be used as a powdery solid lubricant, so that the upper limit is not particularly critical.

The metallic phosphorus chalcogenide used in the invention is a compound having a molecular formula (1) of MPX_3 (wherein M is a metallic element selected from Mg, Ca, V, Mn, Fe, Co, Ni, Pb, Zn, Cd, Hg, Sn and Nb and X is a chalcogen element selected from S, Se and Te) and can be produced by reacting a metal, phosphorus and a chalcogen element or a metallic sulfide, phosphorus and a chalcogen element under heating according to the well-known method.

As the metallic phosphorus chalcogenide, mention may be made of $ZnPS_3$, $ZnPSe_3$, $ZnPTe_3$, $NiPS_3$, $FePSe_3$, $MnPS_3$, $MgPS_3$ and $MgPSe_3$.

All of these chalcogenides have a layered crystal structure and form the intercalation compounds through intercalation of the guest.

The alkylamine used as the guest in the invention is a compound having the following molecular formula (2):

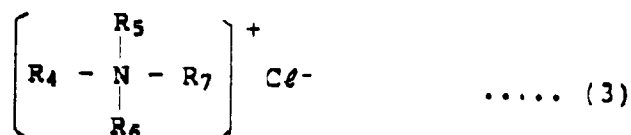


(wherein R_1 , R_2 and R_3 are hydrogen atom or straight or branched chain alkyl group having a carbon number of 1-24, respectively). Concretely, it includes n-butylamine, octylamine, 2-octylamine, dodecylamine, hexadecylamine, octadecylamine, oleylamine, N-methyl octadecylamine and N,N-dimethyl octadecylamine

As the aromatic amine, mention may be made of aniline, p-dodecylaniline and N-ethylene toluidine.

As a nitrogen-containing heterocyclic compound, pyridine may be used.

The alkylammonium chloride used in the intercalation compound according to the invention is a compound having the following molecular formula (3):



(wherein two of R_4 , R_5 , R_6 and R_7 are methyl group or straight or branched chain alkyl group having a carbon number of 4-24, respectively and the remaining two are methyl group, respectively). Concretely, it includes trimethylhexadecyl ammonium chloride, trimethyloctadecyl ammonium chloride and dimethyloctadecyl ammonium chloride.

5 The intercalation compound according to the invention is obtained by contacting the compound of the formula (1) with the compound of the formula (2) or (3), so that it is not particularly required to specify the production method. For example, there are a vapor phase reaction method in which the compound of the formula (2) or (3) vaporized by heating under a reduced pressure is contacted with the compound of the formula (1), a mixing method in which both the compounds are directly mixed and agitated and, if necessary, heated, a
10 pressurization method in which both the compounds are mixed and pressurized and, if necessary, heated, a solvation method in which the compound of the formula (2) or (3) is dissolved in water or an organic solvent and contacted with the compound of the formula (1) and so on. Furthermore, the alkylamine having a small molecular weight such as n-butylamine is intercalated into the compound of the formula (1) and then added to a solution formed by dissolving an alkylamine having a large molecular weight, an aromatic amine, pyridine
15 or an alkyl ammonium chloride in an adequate solvent, whereby the large molecular weight alkylamine, aromatic amine, pyridine or alkyl ammonium chloride can be intercalated into the compound of the formula (1).

Although all of these methods can be used, when the compound being easily modified through heating and hardly vaporized such as amine, ammonium compound or the like is used as a guest and it is intended to prevent the bad influence of the solvent through adsorption, it is desirable to conduct the mixing method or
20 the pressurization method without heating. The amount of the compound of the formula (2) or (3) to be reacted with the compound of the formula (1) is within a range of about 0.1-5 mol.

The metallic phosphorus chalcogenide and its intercalation compound are powdery and are used as a solid lubricant for supplying to a lubricating surface. Furthermore, they are added to lubricating oil or grease or to form an extreme pressure lubricating oil or an extreme pressure grease developing an excellent effect.

25 As previously mentioned, the metallic phosphorus chalcogenide and the intercalation compound according to the invention have a layered structure of repeatedly laminating thin crystal layers one upon the other. Particularly, the guest substance of the formula (2) having a long chain alkyl group, aryl group or alkylaryl group and a polar group or ion group and having excellent lubricity and reactivity is intercalated between host layers of the compound of the formula (1) and strongly bonded to the host layer to widen the basal spacing,
30 whereby the host layers in the intercalation compound are easily slipped with each other.

Therefore, the intercalation compound is excellent in the lubricating function through the slipping between the layers. Furthermore, the metallic phosphorus chalcogenide used as a host layer in the invention contains a greater amount in total of phosphorus having an effect known as an extreme pressure agent, sulfur, selenium and tellurium. Moreover, the metallic phosphorus chalcogenide contains zinc (Zn), lead (Pb), tin (Sn) and mag-
35 nesium (Mg) having a good lubricity as a metal, so that it is excellent in the properties under extreme pressure. And also, the intercalation compound in which the amine having a long chain alkyl group is existent between the host layers is an improved extreme pressure lubricant itself. Thus, the intercalation compound according to the invention possessing the extreme pressure lubricity and excellent sliding friction property can be said to be a most ideal lubricant. According to the inventors' studies, it could be found that the aforementioned inter-
40 calation compounds are excellent in the effect of thickening the lubricating oil. In the grease containing the above intercalation compound as a thickening agent, therefore, the intercalation compound serves as an extreme pressure additive different from the usual extreme pressure grease, so that the grease itself becomes an excellent extreme pressure grease without separately adding an extreme pressure additive.

When the intercalation compound according to the invention is used together with an oiliness agent such
45 as acetylated fatty oil or fatty acid amide, the resulting product can be adapted to wider lubricating conditions by the synergistic action of the extreme pressure lubricity and interlaminar sliding lubricity in the former compound and the oiliness in the latter compound. In this case, the intercalation compound may be adapted to widest lubricating conditions together with both the soft acetylated fatty oil having a lower melting point and the hard fatty acid amide having a higher melting point and adaptable for light lubricating condition.

50 Fig. 1 is a schematic front view of a vibration friction testing machine for the measurement of friction coefficient in the lubricant.

The following examples are given in illustration of the invention and are not intended as limitations thereof.

55 1. Synthesis of metallic phosphorus chalcogenides

The metallic phosphorus chalcogenides of Examples 1a-4b having a composition as shown in Table 1 were synthesized as follows:

(1) Synthesis of ZnPS_3 in Examples 1a, 1b

Commercially available zinc sulfide, red phosphorus and powdery sulfur were mixed at a given mol ratio and heated in a sealed tube to synthesize the object compound.

5 That is, these components were weighed in the following amounts and fully mixed in a mortar.

			Mol ratio
10	Zinc sulfide	5.06 parts by weight	1
	Red phosphorus	1.61	1
	Powdery sulfur	3.33	2

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After the resulting mixture was placed in a glass tube sealed at its one end, the opening portion of the glass tube was connected to a suction port of a vacuum pump to deareate the inside of the tube. Then, the opening portion of the glass tube was fused by means of a gas burner for sealing.

20 The thus sealed glass tube was placed in a lateral tubular furnace and gradually heated up to $450^\circ\text{C}\pm 5^\circ\text{C}$ and maintained at this temperature for 1 week to obtain a light grayish brown product.

The resulting product was ground in a mortar and its crystal structure was examined by X-ray diffractometry, whereby it had been confirmed to be ZnPS_3 of layered crystal structure having a diffraction peak inherent to basal spacing of $6.46\text{\AA}$.

25 (2) Synthesis of MgPS_3 in Examples 2a, 2b

30 Magnesium powder (reagent), red phosphorus and powdery sulfur were mixed at the following ratio and then heated in a sealed tube in the same manner as in the synthesis procedure of the above item (1). In this case, a quartz tube was used instead of the glass tube of the item (1) and the heating temperature was $800\pm 5^\circ\text{C}$.

			Mol ratio
35	Magnesium powder	1.61 parts by weight	1
	Red phosphorus	2.04	1
	Powdery sulfur	6.35	3

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The thus obtained product was confirmed to be MgPS_3 having a diffraction peak inherent to basal spacing of $6.75\text{\AA}$ from X-ray diffraction pattern.

45 (3) Synthesis of CaPS_3 in Example 3a, 3b

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Calcium sulfide (reagent), red phosphorus and powdery sulfur were mixed at the following ratio and then heated in a sealed tube in the same manner as in the synthesis procedure of the above item (1). In this case, a quartz tube was used instead of the glass tube of the item (1) and the heating temperature was $750\pm 5^\circ\text{C}$.

			Mol ratio
50	Calcium sulfide	4.31 parts by weight	1
	Red phosphorus	1.85	1
55	Powdery sulfur	3.83	2

The thus obtained product was confirmed to be CaPS_3 having a diffraction peak inherent to basal spacing of $6.00\text{\AA}$ from X-ray diffraction pattern.

(4) Synthesis of $\text{Zn}_{0.7}\text{Ca}_{0.3}\text{PS}_3$ in Examples 4a, 4b

Zinc sulfide, calcium sulfide, red phosphorus and powdery sulfur were mixed at the following ratio and then heated in a sealed tube in the same manner as in the synthesis procedure of the above item (1). In this case, a quartz tube was used instead of the glass tube of the item (1) and the heating temperature was $750\pm 5^\circ\text{C}$.

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		Mol ratio
	Zinc sulfide	3.68 parts by weight
		0.7
	Calcium sulfide	1.17
		0.3
	Red phosphorus	1
	Powdery sulfur	2

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The thus obtained product was confirmed to be $\text{Zn}_{0.7}\text{Ca}_{0.3}\text{PS}_3$ having a diffraction peak inherent to basal spacing of $6.46\text{\AA}$ from X-ray diffraction pattern.

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2. Preparation of intercalation compounds

Intercalation compounds of Examples 5-9 having a composition as shown in Table 2 were prepared as follows.

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Example 5: ZnPS_3 and n-butylamine were mixed at a mol ratio of 1:2.5 and uniformly ground in a mortar to form a sample.

Example 6: ZnPS_3 and octylamine were mixed at a mol ratio of 1:1.5 and uniformly ground in a mortar to form a sample.

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Example 7: A hydrogenated tallow amine (consisting essentially of octadecylamine) was dissolved in ethyl alcohol in an amount corresponding to a mol ratio of ZnPS_3 to octadecylamine of 1:0.3, which was mixed with the sample prepared in Example 5.

The resulting mixture was left to stand over a night, which was filtered, washed, dried and uniformly ground in a mortar to form a sample.

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Example 8: N,N-dimethyl dioctadecyl ammonium chloride was dissolved in isopropyl alcohol in an amount corresponding to a mol ratio of 1:0.2 with respect to ZnPS_3 , which was mixed with the sample prepared in Example 5. The resulting mixture was left to stand over a night, which was filtered, washed, dried and uniformly ground in a mortar to form a sample.

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Example 9: In ethyl alcohol was dissolved p-dodecyl aniline in an amount corresponding to a mol ratio of 1:0.5 with respect to ZnPS_3 , which was mixed with the sample prepared in Example 5. The resulting mixture was left to stand over a night, which was filtered, washed, dried and uniformly ground in a mortar to form a sample.

3. Test for extreme pressure property and test for wear resistance

3.1 Test for extreme pressure property:

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The seizing load was measured with respect to each sample by a Falex method defined according to ASTM D2625B.

3.2 Test for wear resistance:

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The kinetic friction coefficient of each sample and the worn depth of test specimen were measured by means of a vibration wear testing machine (made by Optimol in Germany).

This testing machine can realize the friction state under conditions of a combination of metals and/or syn-

thetic resins (metal/metal, metal/synthetic resin, synthetic resin/synthetic resin) and presence or absence of lubricant through vibration slipping motion under high load.

A main part of this machine is shown in Fig. 1. A fixed support for sample 10 is connected to a fixed holder for specimen 3 being a movable interchange holder through upper and lower specimens (5, 9). These support and holder are pressed by means of an electronic control loading device. Vibrations produced from a moving-coil are transferred to the fixed holder 3. Various friction tests of point contact, face contact, line contact and the like can be conducted by properly selecting the specimen 9.

In this example, the point contact test was conducted. The result can be evaluated by using a disc as the specimen 5 and a ball as the specimen 9. Thus, a steel disc of 24 mm (diameter)x7.85 mm was used as the specimen 5 on the support 10, and a steel ball of 10 mm in diameter was used as the specimen 9 on the holder 3.

In Fig. 1, numeral 1 is a nut for fixation (against the holder provided with screw threads), numeral 2 a fixing screw, numeral 4 a vibration stroke cylinder provided with a fixing chuck (female), numeral 6 a pushing member on the front face of the specimen 5, numeral 7 a pushing member on the specimen 9 (ball), and numeral 8 a chuck (male) for the fixed holder.

The operating conditions of the testing machine were set as follows:

Load	200N
Amplitude	1.0 mm
Frequency	50 Hz
Running time	30 minutes

Under these conditions, the test was carried out by interposing each sample of Examples and Comparative Examples between both the specimens, during which the kinetic friction coefficient was measured by means of a recorder. After the test, the worn depth produced on the surface of the disc was measured by means of a roughness meter. In this way, the wear resistance every sample was evaluated. The friction coefficient was represented by an average value in the running time, and particularly a maximum peak value was shown in parenthesis when variation is large.

4. Comparison of effects

4.1 Examples in Table 1:

Each lubricant composition of Examples 1a, 2a, 3a, 4a is obtained by mixing 3% by weight of a given metallic phosphorus chalcogenide with petroleum lubricating oil of Comparative Example 1 (bright stock ISO-VG 450 grade), adding 0.1% by weight of α -olefin-maleic acid copolymer as a dispersing agent and then uniformly dispersing them through three-stage roll mill. Lubricant compositions of Comparative Examples 3a and 4a are obtained by the same method as in Example 1a except that graphite and molybdenum disulfide widely used as a solid lubricant having usually a layered crystal structure are used instead of the metallic phosphorus chalcogenide, respectively.

Each lubricant composition of Examples 1b, 2b, 3b, 4b is obtained by adding 5% by weight of a given metallic phosphorus chalcogenide to lithium soap-based grease of Comparative Example 2 and then uniformly dispersing them through three-stage roll mill. Lubricant compositions of Comparative Examples 3b and 4b are obtained by the same method as in Example 1b except that graphite and molybdenum disulfide are used instead of the metallic phosphorus chalcogenide, respectively.

As compared with Comparative Example 1, in Examples 1a, 2a, 3a and 4a, the extreme pressure property is considerably improved, while the friction coefficient and worn depth in the vibration friction test are small, whereby the wear resistance is confirmed to be considerably improved.

As compared with Examples 1a, 2a, 3a and 4a, Comparative Example 4a is excellent in the extreme pressure property but poor in the wear resistance, while Comparative Example 3a is poor in the extreme pressure property and the wear resistance.

Furthermore, it has been confirmed that in Examples 1b, 2b, 3b and 4b, the extreme pressure property and the wear resistance are considerably improved as compared with Comparative Example 2.

In Examples 1b, 2b, 3b and 4b, the extreme pressure property is equal to that in Comparative Example 4b but is excellent in the wear resistance. On the other hand, Examples 1b, 2b, 3b and 4b are superior to Comparative Example 3b in the extreme pressure property and the wear resistance.

When the lubricant powder as in Examples 1a, 2a, 3a, 4a and Comparative Examples 3a and 4a is dispersed in the mineral lubricating oil, the settlement of powder occurs only in the mechanical kneading through three-stage roll mill and hence the resulting composition is lacking in the practical use. However, when a small amount of a dispersing agent such as methacrylate, diethylaminoethyl methacrylate copolymer, α -olefin-male-

ic acid copolymer or the like is added, the settlement of powder can be suppressed to an extent of practically using without trouble, so that the compositions of Examples 1a, 2a, 3a and 4a can be used as a lubricant.

The compositions of Comparative Examples 3a-4b are black in the appearance and are difficult to peel off when they have been adhered to cloth or skin, so that the use of these compositions is required to take many labors in order to maintain good working environment strongly demanding amenity, and consequently it is desirable to develop white solid lubricant. The solid lubricants according to the invention properly meet with such a demand in the art and are widely adapted to new applications such as robots comprised of precise parts, copying machine and the like extremely disliking the pollution with molybdenum disulfide, graphite or the like.

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Table 1(a)

Example									
	1a	1b	2a	2b	3a	3b	4a	4b	
ZnPS ₃	3.0	5.0							
MgPS ₃			3.0	5.0					
CaPS ₃					3.0	5.0			
Zn _{0.7} Ca _{0.3} PS ₃							3.0	5.0	
Mineral lubricating oil	96.9		96.9		96.9		96.9		
Lithium soap-based grease		95.0		95.0		95.0		95.0	
Dispersing agent (α -olefin-maleic acid copolymer)	0.1		0.1		0.1		0.1		
Graphite									
Molybdenum disulfide									
Appearance	light yellowish white fluid	grayish white paste	light yellowish white fluid	grayish white paste	light yellowish white fluid	grayish white paste	light yellowish white fluid	grayish white paste	grayish white paste
Extreme pressure test (Falex method) (according to ASTM D2625B) Seizuring load (pound)	1000	1500	1000	1500	1500	1750	2000	1500	
Vibration friction test	friction coefficient	0.095	0.096	0.095	0.095	0.095	0.095	0.095	0.095
	worn depth μm	0.4	0.4	0.7	0.6	0.5	0.3	0.6	0.6

Table 1(b)

		Comparative Example					
		1	2	3a	3b	4a	4b
ZnPS ₃							
MgPS ₃							
CaPS ₃							
Zn _{0.7} Ca _{0.3} PS ₃							
Mineral lubricating oil		99.9		96.9		96.9	
Lithium soap-based grease			100		95.0		95.0
Dispersing agent (α -olefin-maleic acid copolymer)		0.1		0.1		0.1	
Graphite				3.0	5.0		
Molybdenum disulfide						3.0	5.0
Appearance		yellowish brown transparent liquid	brown paste	black fluid	black paste	black fluid	black paste
Extreme pressure test (Falex method) (according to ASTM D2625B) Seizuring load (pound)		500	500	750	750	2750	1500
Vibration friction test	friction coefficient	0.12	0.105	0.125	0.130	0.100	0.100
	worn depth μm	3.8	3.2	2.5	2.3	1.7	1.5

4.2 Examples in Table 2:

Each lubricant composition of Examples 5-9 is obtained by mixing 3% by weight of a given intercalation compound with a petroleum lubricating oil of Comparative Example 5 (bright stock ISO-VG 450 grade) and uniformly dispersing them through three-stage roll mill. Each lubricant composition of Comparative Examples 6 and 7 is obtained by the same method as in Example 5 except that molybdenum disulfide or graphite is used instead of the intercalation compound.

In Examples 5-9, the extreme pressure property is considerably improved as compared with Comparative Example 5, and also the friction coefficient and worn depth by the vibration friction test are small and hence the wear resistance is also excellent.

In Comparative Examples 6 and 7, molybdenum disulfide or graphite widely used as a solid lubricant is dispersed in the same lubricating oil as in Examples 5-9, but it is apt to cause the separation from the powder. On the contrary, the intercalation compound according to the invention has a good wettability with the mineral lubricating oil, so that the settlement of powder in the lubricating oil can sufficiently be suppressed, which is a great merit in the invention. Comparative Example 6 is higher in the extreme pressure property than Example 5 but is poor in the wear resistance. Further, Comparative Example 7 is poor in both the extreme pressure property and the wear resistance as compared with Example 5.

Table 2

			Example							Comparative Example			
	host	guest	5	6	7	8	9	5	6	7			
Inter- calation compound	ZnPS3	n-butylamine	3										
	ZnPS3	octylamine		3									
	ZnPS3	octadecylamine			3								
	ZnPS3	N,N-dioctadecyl dimethyl ammonium chloride				3							
	ZnPS3	p-dodecyl aniline					3						
Lubricat- ing oil	Mineral lubricating oil		97	97	97	97	97	100	97	97			
Solid lubricant	Molybdenum disulfide								3				
	graphite									3			
Prop- erties	appearance		light yellowish white fluid	light yellowish white fluid	light yellowish white fluid	light yellowish white fluid	light yellowish white fluid	yellowish brown transparent liquid	black fluid	black fluid			
	Settlement of powder		none	none	none	none	none	-	presence	presence			
	Extreme pressure test (Falex method) (according to ASTM D2625B) Seizuring load (pound)		1500	1000	1000	1250	1500	500	2750	750			
	Vibration friction test	friction coefficient	0.095	0.098	0.100	0.100	0.098	0.120	0.125	0.120			
	worn depth μm	0.3	0.6	1.0	0.2	1.0	3.8	4.0	4.6				

4.3 Examples in Table 3:

In Examples 10-14, the effect as an additive for grease was examined by adding 3% by weight of a given intercalation compound to lithium soap-based grease and uniformly dispersing them through three-stage roll mill.

When these examples are compared with the base grease of Comparative Example 8, the extreme pressure property and the wear resistance are considerably improved.

Comparative Examples 9 and 10 are the same compositions as in Example 10 except that molybdenum disulfide and graphite are used instead of the intercalation compound. In Comparative Example 9, the extreme pressure property is equal to or more than those of Examples 10-14 but is considerably poor in the wear resistance, while Comparative Example 10 is fairly poor in the extreme pressure property and wear resistance.

Table 3

			Example								Comparative Example		
	host	guest	10	11	12	13	14	8	9	10			
Inter-calation compound	ZnPS ₃	n-butylamine	3										
	ZnPS ₃	octylamine		3									
	ZnPS ₃	octadecylamine			3								
	ZnPS ₃	N,N-dioctadecyl dimethyl ammonium chloride				3							
	ZnPS ₃	p-dodecyl aniline					3						
		lithium soap-based grease	97	97	97	97	97	100	97	97			
Solid lubricant		molybdenum disulfide							3				
		graphite											3
	appearance		grayish white paste	grayish white paste	grayish white paste	grayish white paste	grayish white paste	brown paste	blackish brown paste	blackish brown paste			
Properties	Settlement of powder		none	none	none	none	none	none	none	none			
	Extreme pressure test (Falex method) (according to ASTM D2625B) Seizuring load (pound)		1000	1000	1000	1500	1000	500	1500	300			
	Vibration friction test	friction coefficient	0.095	0.097	0.095	0.097	0.100	0.105 (0.35)	0.135	0.105 (0.35)			
		worn depth μm	0.2	0.4	0.8	1.0	0.4	3.2	1.6	4.8			

4.4 Examples in Table 4:

In Examples 12a-13d, an effect on lubricity was examined by changing the amount of the metallic phosphorus chalcogenide or its intercalation compound added to grease. That is, the friction coefficient was measured by means of the SRV vibration friction testing machine when the amount of ZnPS_3 (Example 1) added to lithium soap-based grease of Comparative Example 11 was varied within a range of 0.1-3.0% by weight in Examples 12a-12d or the amount of the intercalation compound (Example 5) added to the same grease as above was varied within a range of 0.1-3.0% by weight in Examples 13a-14d.

As compared with Comparative Example 11, the friction coefficient can be improved by adding a small amount of the metallic phosphorus chalcogenide or its intercalation compound. Moreover, the addition amount of 0.1% by weight shows substantially the addition limit because the difference in the friction coefficient becomes small between Example 12a and Comparative Example 11.

Table 4

	Sample		Addition amount	Friction coefficient by vibration friction test
Example 12a	ZnPS_3		0.1%	0.100
12b	"		0.5%	0.098
12c	"		1.0%	0.097
12d	"		3.0%	0.095
Example 13a	host	gest		
	ZnPS_3	octylamine	0.1%	0.098
	ZnPS_3	octylamine	0.5%	0.098
	ZnPS_3	octylamine	1.0%	0.097
	ZnPS_3	octylamine	3.0%	0.095
Comparative Example 11	Lithium soap-based grease		0%	0.105

4.5 Examples in Table 5

In Examples 14-18, the thickening effect on grease was examined by using the same intercalation compounds as in Examples 5-9 in an amount of 10% by weight and acetone as a dispersing agent. In this case, there were obtained samples ranging from uniform compounded (causing no separation between solid and liquid) viscous body to grease of No. 1 grade as consistency grade though there was caused a difference in the thickening effect in accordance with the kind of the organic substance as a guest intercalated between host layers. As the thickening effect of the intercalation compound, the separation from powder was caused at the addition amount of less than 1% by weight, while when the amount was more than about 70% by weight, it was difficult to obtain a uniform solid grease because it became brittle.

When these compositions are compared with commercially available greases of Comparative Examples 13 and 14, the extreme pressure property and wear resistance are excellent, and particularly it is noticed that the extreme pressure property is higher than that of the commercially available grease containing the extreme pressure additive. Furthermore, it has been found to obtain a composition having a dropping point higher than that of lithium soap-based grease by properly selecting the guest, which can be used as a heat-resistant grease.

Comparative example 12 is a case of using molybdenum disulfide instead of the intercalation compound, from which it is apparent that since molybdenum disulfide has no thickening effect, the separation of powder is caused and the composition is not suitable for practical use. Furthermore, the extreme pressure property is excellent, but the wear resistance is considerably poor as compared with Examples 14-18.

It is confirmed from the above that the intercalation compound according to the invention is a substance having three functions as a thickening agent for grease, an extreme pressure additive and a solid lubricant.

Furthermore, it has been confirmed that a grease having a heat resistance higher than that of the com-

mercially available lithium soap-based grease can be obtained by properly selecting the guest in the intercalation compound.

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Table 5

			Example						Comparative Example			
	host	guest	14	15	16	17	18	12	13	14		
Inter-calation compound	ZnPS3	n-butylamine	10									
	ZnPS3	octylamine		10								
	ZnPS3	octadecylamine			10							
	ZnPS3	N,N-dioctadecyl dimethyl ammonium chloride				10						
	ZnPS3	p-dodecyl aniline					10					
Lubricating oil	Mineral lubricating oil (MCP430) acetone		89 1	89 1	89 1	89 1	89 1	90				
Solid lubricant	Molybdenum disulfide							10				
Grease	organophilic bentonite-based grease								100			
	lithium soap-based grease No. 1 containing EP additive										100	
Prop-erties	appearance		grayish white paste	grayish white paste	grayish white paste	grayish white paste	grayish white fluid (no powder separation)	blackish brown paste (powder separation)	brown paste	reddish brown paste		
	consistency 25°C 0W 60W		440 440	439 429	338 334	434 434			320 315	328 320		
	dropping point °C		153	154	213	217			no dropping	198		
	Extreme pressure test (Falex method) (according to ASTM D2625B) Seizuring load (pound)		2000	1750	1500	2000	2000	2000	1000	750		
	Vibration friction test	friction coefficient	0.093	0.100	0.095	0.097	0.100	0.113	0.093	0.090		
	worn depth μm		0.4	0.2	0.2	0.2	0.2>	2.5	0.6	0.4		

4.6 Examples in Table 6:

5 Examples 19-21 show an embodiment of using the intercalation compound together with acetylated fatty
oil and/or fatty acid amide. In this case, the friction coefficient can be lowered as compared with Example 11
as well as Comparative Examples 15 and 16. The lubricant compositions of Examples 19-21 are adaptable
for machines requiring smooth rotation or slippage and special applications preventing occurrence of noise
and the like under relatively light lubricating conditions. Furthermore, when the compositions are subjected
to the vibration friction test on a combination of plastic - steel, they exhibit a lower friction coefficient as com-
pared with the comparative examples, from which they have been confirmed to serve as a lubricant for plas-
tics.
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Table 6

			Example					Comparative Example	
	host	guest	11	19	20	21	15	16	
Intercalation compound	ZnPS ₃	octylamine	3	2.9	2.7	2.8			
Grease	lithium soap-based grease		97	93.1	89.7	91.5	100	94	
Oiliness agent	acetylated fatty oil (Rikemal PL-008, trade name, made by Riken Vitamin K.K.)			4		2.2		3	
	fatty acid amide (Aromowax EBS, trade name, made by Kao Soap Co., Ltd.)				7.6	3.5		3	
Properties	Vibration friction test								
	I friction coefficient (steel-steel)		0.097	0.090	0.090	0.090	0.105 (0.35)	0.098	
	II friction coefficient (steel-POM) initial last		0.088 0.050	0.075 0.038	0.070 0.035	0.080 0.045	0.085 0.050	0.080 0.045	
Remarks	Conditions of vibration friction test		II						
	I		II						
	load	200 N	200N						
	amplitude	1.0 mm	1.0mm						
	frequency	50 Hz	50 Hz						
	test specimen								
	disc	steel (24 (diameter) × 7.86 mm)	polyacetal (POM) (24 (diameter) × 7.86 mm)						
	ball	steel (diameter 10 mm)	steel (diameter 10 mm)						
	time	10 minutes	10 minutes						

The lubricants according to the invention containing the metallic phosphorus chalcogenide as a crystal

powder having a particular layered structure are solid lubricants having excellent extreme pressure property and wear resistance as shown in Table 1. Furthermore, the lubricants containing the intercalation compound in which the metallic phosphorus chalcogenide is a host and the alkylamine, aromatic amine, pyridine or alkylammonium chloride is a guest are excellent in the extreme pressure property and wear resistance as shown in Tables 2 and 3. Moreover, since the intercalation compound has an improved thickening function, the combination of base oil and intercalation compound provides an excellent extreme pressure grease without adding the thickening agent as shown in Table 5.

Claims

1. A lubricant containing not less than 0.1% by weight of at least one intercalation compound in which a metallic phosphorus chalcogenide having the molecular formula MPX_3 (wherein M is a metallic element selected from Mg, Ca, V, Mn, Fe, Co, Ni, Pb, Zn, Cd, Hg, Sn and Nb; and X is a chalcogen element selected from S, Se and Te) is the host and an alkylamine, an aromatic amine, pyridine or an alkylammonium chloride is the guest.
2. A grease comprising a base oil and 1-70% by weight of an intercalation compound as defined in claim 1 as a thickening agent.
3. A lubricating oil composition obtained by dissolving or dispersing an intercalation compound as defined in claim 1 and an acetylated fatty oil into a lubricating oil.

Patentansprüche

1. Schmiermittel, enthaltend nicht weniger als 0,1 Gew.-% mindestens einer Einlagerungsverbindung, in der ein Metall- Phosphor-Chalcogenid der Molekülformel MPX_3 (worin M ein aus Mg, Ca, V, Mn, Fe, Co, Ni, Pb, Zn, Cd, Hg, Sn und Nb ausgewähltes Metallelement und X ein aus S, Se und Te ausgewähltes Chalcogen-Element ist) der Wirt und ein Alkylamin, ein aromatisches Amin, Pyridin oder ein Alkylammoniumchlorid der Gast ist.
2. Fett, umfassend ein Öl als Basis und 1 bis 70 Gew.-% einer Einlagerungsverbindung gemäß Anspruch 1 als Verdickungsmittel.
3. Schmierölzusammensetzung, erhalten durch Lösen oder Dispergieren einer Einlagerungsverbindung gemäß Anspruch 1 und eines acetylierten Fettöls in einem Schmieröl.

Revendications

1. Lubrifiant ne contenant pas moins de 0,1% en poids d'au moins un composé d'insertion dans lequel un chalcogénure métallique du phosphore ayant la formule moléculaire MPX_3 (dans laquelle M est un élément métallique choisi parmi Mg, Ca, V, Mn, Fe, Co, Ni, Pb, Zn, Cd, Hg, Sn et Nb; et X est un élément chalcogène choisi parmi S, Se et Te) est la base et une alcoylamine, une amine aromatique, de la pyridine ou un chlorure d'ammonium alcoylé est l'hôte.
2. Graisse comprenant une huile de base et de 1 - 70% en poids d'un composé d'insertion, tel que défini dans la revendication 1, comme agent d'épaississement.
3. Composition d'une huile de lubrification obtenue en dissolvant ou en dispersant un composé d'insertion, tel que défini dans la revendication 1, et une huile grasse acétylée dans une huile de lubrification.