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Abe et al.

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[54] **SOLID LUBRICANT**

[75] Inventors: **Wataru Abe,** Chigasaki; **Yasuyuki Terada,** Kamakura; **Akira Sugafuji,** Fujisawa, all of Japan

[73] Assignee: **Oiles Kogyo Kabushiki Kaisha,** Tokyo, Japan

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[30] **Foreign Application Priority Data**

Aug. 19, 1971 Japan 46-62609

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[51] **Int. Cl.** **C10m 7/06,** C10m 7/04, C10m 7/02

[58] **Field of Search** 252/12, 12.2, 12.4, 12.6; 75/156, 163

[56] **References Cited**

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Primary Examiner—Daniel E. Wyman
Assistant Examiner—I. Vaughn
Attorney, Agent, or Firm—Oldham & Oldham Co.

[57] **ABSTRACT**

This invention is based on a finding in which an addition of 10 — 30 wt percent of alloy powders to the solid lubricant of graphite-sodium fluoride or graphite-sodium fluoride-tungsten disulfide suitable for use at high temperature contributes to improvements of the mechanical strength as well as the friction coefficient, the preferable alloy being that of the composition of 77Cu-23Pb or 90Cu-5Sn-5Pb.

While the addition of 10 – 30 wt percent of a metal salt of tungstate contributes to the formation of strong film or coatings at a high temperature and to prolongation of bearing life.

7 Claims, 3 Drawing Figures

FIG. 1

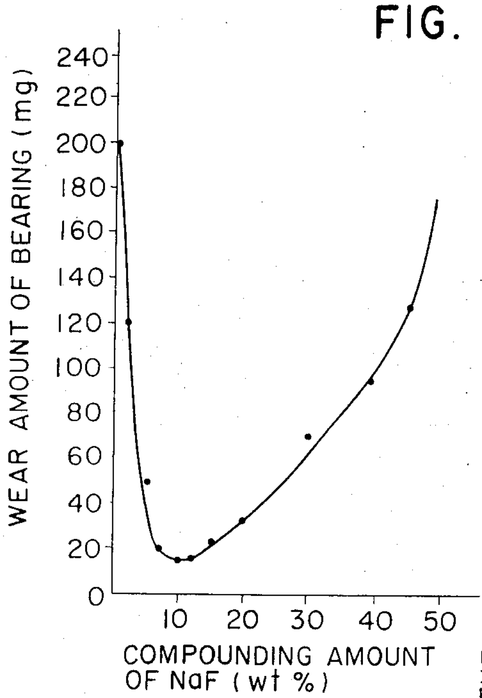


FIG. 3

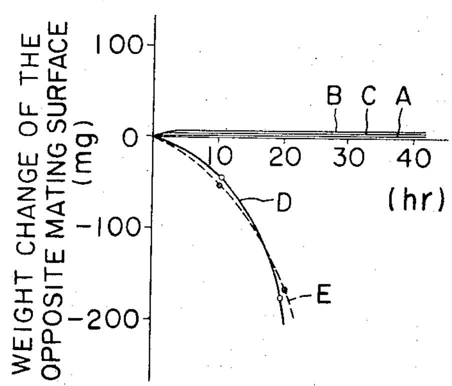
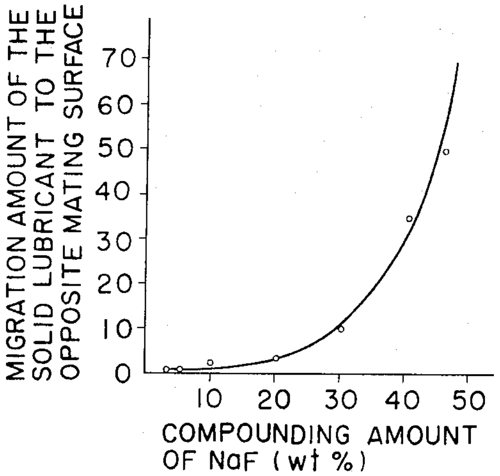


FIG. 2



SOLID LUBRICANT

It has been used heretofore a solid lubricant comprising graphite and molybdenum disulfide as a representative solid lubricant.

Graphite tends to bring an increase of a friction coefficient at an atmoshpere of about 400°C and also to be inferior to a film forming ability, while molybdenum disulfide is superior to a film forming ability and a migration property to the mating bearing surface, but molybdenum disulfide comes into question as a lubricating material at the high temperature since an oxidative wear of bearing becomes excessive in an atmospheric temperature of more than about 350°C.

Many attempts, have been effected to improve the lubricating property, one of which is a method for coating metallic surface with a paste consisting of molybdenum disulfide and grease resulting in making unbearable to a repeated sliding motion on the bearing surface, another of which is a method for burying and setting into cavities provided on the bearing surface, the solid lubricant together with a binder of a synthetic resin resulting in limitting an use temperature of the bearing owing to a heat resistance property of the binder.

In order to overcome said disadvantages, various methods, namely methods for adding metal oxide to graphite or adding metal sulfide to molybdenum disulfide have been attempted.

However, it has not been found the solid lubricant capable of bearing at high temperature of about 400° – 500°C.

This invention relates to the solid lubricant suitable for the use of high temperature atmosphere having the following compositions, namely

a. 55 – 97 wt percent of graphite and 3 – 45 wt percent of sodium fluoride,

b. less than 30 wt percent of tungsten disulfide, 3 – 45 wt percent of sodium fluoride and a residual amount of graphite,

c. 55 – 97 wt percent of graphite, 3 – 45 wt percent of sodium fluoride and 5 – 20 wt percent of sodium meta-phosphate as the binder on the basis of the total weight of graphite and sodium fluoride,

d. less than 30 wt percent of tungsten disulfide, 3 – 45 wt percent of sodium fluoride and the residual amount of graphite and 5 – 20 wt percent of sodium meta-phosphate as the binder on the basis of the total weight of tungsten disulfide, sodium fluoride and graphite,

e. 3 – 45 wt percent of sodium fluoride and 55 – 97 wt percent of graphite and 10 – 30 wt percent of 77Cu-23Pb alloy powder or 90Cu-5Sn-5Pb alloy powder as the binder on the basis of the total weight of sodium fluoride and graphite,

f. less than 30 wt percent of tungsten disulfide, 3 – 45 wt percent of sodium fluoride and the residual amount of graphite and 10 – 30 wt percent of 77Cu-23Pb alloy powder or 90Cu-5Sn-5Pb alloy powder as the binder on the basis of the total weight of tungsten disulfide, sodium fluoride and graphite,

g. 3 – 45 wt percent sodium fluoride and 55 – 97 wt percent of graphite and 10 – 30 wt percent of 77Cu-23Pb alloy powder or 90Cu-5Sn-5Pb alloy powder on the basis of the total weight of graphite and sodium fluoride as the binder and also 5 – 20 wt percent of metal salt of tungstate on the basis of the total weight of graphite, sodium fluoride and said metal alloy,

h. less than 30 wt percent of tungsten disulfide, 3 – 45 wt percent of sodium fluoride and the residual amount of graphite and 10 – 30 wt percent of 77Cu-23Pb alloy powder or 90Cu-5Sn-5Pb alloy powder on the basis of the total weight of graphite, tungsten disulfide and sodium fluoride as the binder and also 5 – 20 wt percent of metal salt of tungstate on the basis of the total weight of graphite, tungsten disulfide, sodium fluoride and said metal alloy.

The solid lubricant of this invention possesses the properties of bearing to the use of high temperature atmosphere (room temperature to about 500°C) and various other properties of protecting the oxidative wear, enhancing the film forming ability and prolonging a film life.

FIG. **1** is a graph of showing an interrelationship between the compounding ratio of sodium fluoride to graphite and a wear rate of the bearing.

FIG. **2** is a graph of showing the interrelationship between the migrating amount of the solid lubricant to the mating surface under the same conditions as those of the FIG. **1.**

FiG. **3** is a graph of showing the interrelationship between the migrating amount of the solid lubricant to the mating surface and a friction time under the same conditions as those of the FIG. **1.** The invention is based on the provision of the solid lubricant suitable for the use of high temperature having the compositions a – h as mentioned above.

These and other objects, features and advantages of the present invention will become apparent from the following examples.

Various types of the solid lubricants have been manufactured according to the methods as mentioned below.

1. The solid lubricant of buried type manufactured by uniformly mixing a graphite flake having a particle size of less than 150 mesh of Tyler standard slieve with fine powders of sodium fluoride having a particle size of less than 200 mesh and then pressure molding the mixture into a metallic mold under a pressure of about 1,000 Kg/cm^2.
2. The solid lubricant of buried type manufactured by uniformly mixing the graphite flake having the particle size of less than 150 mesh with fine powders of tungsten disulfide having a mean particle size of 2 microns and sodium fluoride having the particle size of less than 200 mesh and then molding the mixture obtained into the metallic mold under the pressure of 1,000 Kg/cm^2.
3. The solid lubricant of the paste type manufactured by uniformly mixing the graphite flake having the particle size of less than 150 mesh with fine powders of sodium fluoride having particle size of less than 200 mesh and then further mixing an aqueous solution of sodium meta-phosphate ($NaPO_3$) as the binder into the resulting mixture to form the solid lubricant suitable for covering the sliding surface of the bearing.
4. The solid lubricant of the paste type manufactured by uniformly mixing the graphite flake having the particle size of less than 150 mesh with fine powders of tungsten disulfide having the mean particle

size of 2 microns and sodium fluoride having the particle size of less than 200 mesh and then further mixing the aqueous solution of sodium meta-phosphate ($NaPO_3$) as the binder into the resulting mixture to form the solid lubricant suitable for covering the sliding surface of the bearing.

5. The solid lubricant having high strength manufactured by heating the paste obtained from the methods of said items 3 and 4 to remove most of water contained therein and then molding said paste into the metallic mold under the pressure of 1,000 Kg/cm^2 and further heating said paste into an oven at about 200°C.
6. A cylinderical solid lubricant of buried type manufactured by uniformly mixing the graphite flake having the particle size of less than 150 mesh with sodium fluoride having the particle size of less than 200 mesh and adding to said mixture, alloy powders of less than 150 mesh consisting 90 wt percent Cu, 5 wt percent Sn and 5 wt percent Pb and after uniformly mixing, premolding under the pressure of 1,000 Kg/cm^2 and then sintering the mixture obtained at the temperature of about 800°C in N_2 gas atmosphere.
7. The cylinderical solid lubricant of buried type manufactured by uniformly mixing the graphite flake having the particle size of less than 150 mesh with fine powders of tungsten disulfide having the mean particle size of 2 microns and sodium fluoride having the particle size of less than 200 mesh and adding to said mixture, alloy powders of less than 150 mesh consisting 90 wt percent Cu, 5 wt percent Sn and 5 wt percent Pb and after uniformly mixing, premolding under the pressure of 1,000 Kg/cm^2 and then sintering the mixture obtained at the temperature of about 800°C in N_2 gas atmosphere.
8. The cylinderical solid lubricant of buried type manufactured by uniformly mixing the graphite flake having the particle size of less than 150 mesh with sodium fluoride having the particle size of less than 200 mesh alloy powders having the particle size of less than 150 mesh and consisting 90 wt percent Cu, 5 wt percent Sn and 5 wt percent Pb and sodium tungstenate (Na_2WO_4) having the particle size of less than 200 mesh and premolding the mixture obtained, under the pressure of 1,000 Kg/cm^2 and then sintering said mixture at the temperature of about 800°C in N_2 gas atmosphere.
9. The cylinderical solid lubricant of buried type manufactured by uniformly mixing the graphite flake having the particle size of less than 150 mesh with fine powders of tungsten disulfide having the mean particle size of 2 microns, sodium fluoride having the particle size of less than 200 mesh, alloy powders having the particle size of less than 150 mesh and consisting 90 wt percent Cu, 5 wt percent Sn and 5 wt percent Pb and sodium tungstenate (Na_2WO_4) having the particle size of less than 200 mesh and premolding the mixture obtained, under the pressure of 1,000 Kg/cm^2 and then sintering said mixture at the temperature of about 800°C in N_2 gas atmosphere.

The components to be added to the solid lubricant are shown as follows:

a. Sodium fluoride powder.

Said powders of Moh's hardness of more than 5 are used as the additives.

Sodium fluoride does not give any influence to the lubricating property of graphite but protects a change of the friction coefficient even if the temperature change of the solid lubricant occur in the compounding amount of about 1 wt percent of sodium fluoride and also improves the film forming ability in the dry friction when about 3 wt percent of sodium fluoride is mixed into graphite.

When about 10 wt percent of sodium fluoride is mixed into graphite, the effect of addition will remarkably increase. The more the compounding amount of sodium fluoride increases for example to more than 50 wt percent, the more the migrating amount of solid lubricant to the mating surface will increase thereby indicating a reverse effect.

Therefore, it has been found that a preferable amount of mixing sodium fluoride is less than 45 percent by weight. The additive effect of sodium fluoride to the solid lubricant of graphite-WS_2 compositions is similar to that of the graphite composition.

b. Tungsten disulfide powder.

Said powders show a superior lubricating effect but, possess an inferior heat resistance property.

The additive effect of tungsten disulfide will bring an increase of the lubricating property and an improvement of the film forming ability in a relatively low temperature region.

The heat resistance property of tungsten disulfide itself is improved to such extent that the solid lubricant may be used in the high temperature such as 400° – 500°C or more than one by the addition of sodium fluoride.

The additional range or extent of tungsten disulfide is preferable to be less than 30 wt percent.

Tungsten disulfide may be added in an upper limited amount of said range in the use of relatively low temperature. The compounding amount of tungsten disulfide may gradually decrease according to the increase of the use temperature. By the reason of that in a high temperature of about 400° – 500°C, the durability of film becomes more important than the decrease of friction, the addition of tungsten disulfide attributes to the depression of the friction coefficient but the durability of film will decrease.

In order to overcome said disadvantages, the addition of tungsten disulfide will have to be controlled in lesser extent. In view of said matter, the solid lubricant not containing any tungsten disulfide is applicable in rather high temperature. The table 1 shows the solid lubricant of the present invention having various compositions.

c. Sodium meta-phosphate.

Sodium meta-phosphate may be used for forming the film of the solid lubricant on the mating surface of the bearing as the binder.

Sodium meta-phosphate may be used for forming a block type solid lubricant by heating the paste to remove the most of water contained in the paste, and then molding it into the metallic mold and then sintering and further may be used for forming the film of the solid lubricant on the mating surface of bearing by coating said surface with the paste of the solid lubricant and heating it to about 200°C to remove the most of water contained therein and then backing the molded article into the oven at the temperature of 200°C or molding into the hot press under a high temperature and a high pressure. As sodium meta-phosphate itself does not give any lubricating property, it is preferable to add 5 – 10 wt percent of sodium meta-phosphate in the film forming use, while to add less than 20 wt percent of sodium meta-phosphate in the block type solid lubricant use.

The bearing properties of the solid lubricants containing graphite and sodium fluoride or graphite, tungsten disulfide and sodium fluoride are shown in the FIGS. 1 – 3.

In FIG. 1, an abrasion amount of the bearing was measured about the solid lubricants containing various amounts of sodium fluoride by burying it into the mating surface of a cylindrical bronze casting (JIS BS 6) using an opposite mating bearing of S45C under the test conditions of the temperature of 500°C, the sliding rate of 3.5 m/min and the surface pressure of 30 Kg/cm^2 at every 20 hours.

The composition of said bronze casting corresponds to 81.0 – 87.0 wt percent Cu, 4.0 – 6.0 wt percent Sn, 4.0 – 7.0 wt percent Zn and 3.0 – 6.0 wt percent Pb.

The area of the solid lubricant to the total area of the mating surface corresponds to 30 wt percent.

From the test results of FIG. 1, it has been found that the effect of adding sodium fluoride appears when about 3 wt percent of sodium fluoride are added to the solid lubricant, on the contrary, the wear amount of bearing increases when more than 50 wt percent of sodium fluoride are added.

In FIG. 2, it has been found that the migrating amount of solid lubricant remarkably increases when the compounding amount of sodium fluoride reaches more than 50 wt percent and that the friction coefficient does not change remarkably showing a value of about 0.2 when said compounding amount reaches less than 45 wt percent and also that the friction coefficient reaches to the value of 0.4 when the compounding amount of sodium fluoride reaches to 50 wt percent of sodium fluoride.

As mentioned above, if the migrating amount is too much, it is celar that any satisfactory result will not be obtained in the effects of the friction and the wear.

In FIG. 3, curve (A) shows the test result of the solid lubricant having the composition of test No. 5 of table 1, curve (B) shows that of the solid lubricant having the composition of test No. 18 of table 1 and curve (C) shows that of a film of the solid lubricant having the composition of test No. 18 mixed with 8 wt percent of $NaPO_3$ as the binder.

Curves (D) and (E) show comparative test results of graphite or graphite containing 10 wt percent of tungsten disulfide respectively.

It has been found that a good film of the solid lubricant is formed by migrating the solid lubricant to the mating surface of the bearing thereby resulting in the increase of the weight.

The film formed on the mating surface of the bearing has clearly observed by a nacked eyes to be a smooth and glossy black film.

The friction coefficient after 40 hours has been equal in the solid lubricants having the compositions as shown in curves (A) and (B).

The friction coefficient having the compositions as shown in the curves (A) and (B) was 0.15 – 0.20, until a lapse of 20 hours, 0.20 – 0.25 after 40 hours, while the friction coefficient having the composition as shown in the curve (C) was 0.08 – 0.10 until the lapse of 20 hours observing a relative and smooth migration to the mating surface of the bearing.

On the contrary, it has been observed that the migration of film is almost null in the solid lubricants having the compositions as shown in the curves (D) and (E), and that many scratches were formed on the mating surface of bearing thereby reducing the weight of bearing.

In the experiments of FIGS. 2 and 3, the mean value of thickness of the migrated coatings amounts to 4 – 6 microns when the weight increase of the mating surface reaches 50 mg, while said value amounts to less than 1 micron when said weight increase reaches to 10 mg. A.

The bearing properties of the solid lubricant suitable for a pellet type containing graphite, tungsten disulfide, sodium fluoride and the metallic powders as the binder are explained as follows.

In case that the metal powders, especially the mixture of Cu and Pb powders or the mixture of Cu, Sn and Pb powders are used as the binder, the mechanical strength, hardness, antifriction property and antiwearing property of the molded solid lubricant are remarkably improved without any depression of an inherent lubricating property of graphite, tungsten disulfide and sodium fluoride.

It is a reason for selecting Cu, Sn and Pb powders as the alloy powders suitable for the binder that said powders are low melting point metal powders having lower temperature than the oxidative temperature or the melting point of the solid lubricant namely graphite, WS_2 and NaF and capable of forming a solid solution thereof and also having a similar component to that of a base metal of bronze castings (JIS BC6). In the present invention, it is preferable to use the alloy of 77Cu-23Pb or 90Cu-5Sn-5Pb.

The composition and the bearing property are shown in the table 2.

In the table 2, the solid libricant having the composition of 75 graphite - 15 tungsten disulfide - 10 sodium fluoride was used compounding the alloy powders as the binder.

The test conditions are shown as follows.

The pellets of the solid lubricant having the composition of table 2 were buried on the sliding surface of the cylindrical bronze castings (JIS BC6).

The area of the solid lubricant buried corresponds to 30 wt percent of the total area of the sliding surface.

While the opposite mating material is 13 Cr steel, and the temperature of a heat treatment for forming the pellet is 700° – 850°C.

The test was effected under the conditions of the surface pressure of 50 Kg/cm^2 and the sliding rate of 3.5 m/min at the temperature of 500°C for 20 hours.

As shown in the Table 2, the compounding ratio of the metal powders to the solid lubricant is preferable to be 10 – 30 wt percent. If the compounding ratio of the metal powders is less than said range, the mechanical strength of the solid lubricant formed, decreases whereby the solid lubricant buried tends to break during sliding and to increase the friction coefficient. While if e said ratio is more than said range, the mechanical strength of the solid lubricant increases but the friction coefficient increases whereby the friction will increase. The friction coefficient and the abrasion amount of the solid lubricant of the pellet type depend on the treating temperature even if the composition of the solid lubricant is same.

Therefore, it is important to select an appropriate temperature for heat-treating of the solid lubricant, the temperature of about 700° – 850°C is preferable. It has been found in the table 2 that the allowable limitation in the abrasion amount of the solid lubricant amounts to 0.10 mm and that if the abrasion amount of the solid lubricant is beyond the said limitation, a scuffing abrasion will suddenly increase whereby the friction coefficient reaches to more than 0.30.

The similar results have been obtained in the solid lubricant comprising 70 – 90 wt percent of the base lubricant having the compositions of 55 – 97 graphite and 3 – 45 sodium fluoride, and 10 – 30 wt percent of said alloy powders as well as the solid lubricant comprising 70 – 90 wt percent of the base lubricant having 3 – 45 wt percent of sodium fluoride, less than 30 wt percent of tungsten disulfide and residual amount of graphite, and 10 – 30 wt percent of said alloy powders.

The satisfactory results were obtained showing the abrasion amount of 0.050 – 0.095 mm and the friction coefficient of 0.20 – 0.30.

B.

The bearing properties of the solid lubricant having the composition of graphite, tungsten disulfide, sodium fluoride and the said alloy powders as the binder and also metal salt of tungstate are explained as follows.

Said alloy powder comprises Cu and Pb powders or Cu, Sn and Pb powders, while said tungstate comprises alkali salts of tungstate such as sodium tungstate (Na_2WO_4), potassium tungstate (K_2WO_4) alkali earthmetal of tungstate such as barium tungstate ($BaWO_4$) and metal salt of tungstate such as lead tungstate ($PbWO_4$), zinc tungstate ($ZnWO_4$), copper tungstate ($CuWO_4$) and cadmium tungstate ($CdWO_4$).

It has been found that a strong film or coatings is formed on the friction surface of the bearing in especially a high temperature thereby protecting a base metal and assisting the lubricating property of graphite, tungsten disulfide and sodium fluoride, and also prolonging the bearing life.

In the table 3, the solid lubricants having the composition of 90 (75 graphite - 15 tungsten disulfide — 10 sodium fluoride) — 10 (90Cu-5Sn-5Pb) and various sorts of metal salts of tungstate were tested.

It has been found in the table 3 that the solid lubricant having low friction coefficient is manufactured by adding 5 – 20 wt percent of lead tungstate to the said lubricant.

In table 3, the test was carried out using 5 percent by weight of another metal salts of tungstate whereby similar results were obtained.

The friction coefficient and the abrasion amount of said lubricant depend on the treating temperature of the solid lubricant of the pellet type even if the composition of solid lubricant is same.

Therefore, it is important to select an appropriate temperature for the heat treatment, said temperature is preferable to be about 700° – 850°C.

The similar good results have been obtained in the solid lubricant having the composition of 70 – 90 wt percent of (55 – 97 graphite – 3 – 45 NaF) – 10 – 30 wt percent of (77Cu-23Pb or 90Cu-5Sn-5Pb) and also the solid lubricant comprising 5 – 20 wt percent of the metal salt of tungstate and 80 – 95 wt percent of the base lubricant having the composition of 70 – 90 wt percent of less than 30 wt percent of WS_2, 3 – 45 wt percent of NaF residual amount of graphite - 10 – 30 wt percent of said metal powders respectively.

The test results showing the wear amount of 0.025 – 0.050 mm and the friction coefficient of 0.15 – 0.30 have been obtained.

Table 1

Composition No.	Graphite (wt%)	WS_2 (wt%)	NaF (wt%)
1	99		1
2	97		3
3	95		5
4	93		7
5	90		10
6	88	0	12
7	85		15
8	80		20
9	75		25
10	70		30
11	65		35
12	60		40
13	55		45
14	50		50
15	89	1	
16	85	5	
17	80	10	
18	75	15	10
19	70	20	
20	65	25	
21	60	30	
22	50	40	

Table 2

No.	75-Graphite-15WS_2 -10NaF (wt%)	77Cu-23Pb (wt%)	90Cu-5Sn -5Pb (wt%)	Wear amount of bearing (mm)	Friction coefficient
23	95	5		0.127	0.34 – 0.36
24	90	10		0.055	0.24 – 0.27
25	80	20		0.065	0.28 – 0.29
26	70	30		0.075	0.29 – 0.30
27	65	35		0.184	0.34 – 0.36
28	95		5	0.150	0.33 – 0.36
29	90		10	0.045	0.20 – 0.22
30	80		20	0.050	0.24 – 0.26
31	70		30	0.095	0.25 – 0.28
32	65		35	0.180	0.34 – 0.36

Table 3

No.	90(75-Graphite-15WS_2-10NaF)-10(90Cu-5Sn-5Pb) (wt%)	$PbWO_4$ (wt%)	$CuWO_4$ (wt%)	$CdWO_4$ (wt%)	K_2WO_4 (wt%)	Na_2WO_4 (wt%)	$CaWo_4$ (wt%)	Wear amount of bearing (mm)	Friction coefficient
33	98	2						0.058	0.25 – 0.28
34	95	5						0.021	0.13 – 0.15
35	85	15						0.035	0.16 – 0.18
36	80	20						0.043	0.22 – 0.25
37	75	25						0.087	0.30 – 0.32
38	95		5					0.025	0.13
39	95			5				0.038	0.15
40	95				5			0.040	0.18 – 0.24
41	95					5		0.050	0.25 – 0.30
42	95						5	0.046	0.11

What is claimed is:

1. A solid lubricant comprising 55 – 97 percent by weight of graphite, 3 – 45 percent by weight of sodium fluoride and 10 – 30 percent by weight of alloy powders of 77Cu-23Pb or 90Cu-5Sn-5Pb on the total basis of graphite and sodium fluoride.

2. A solid lubricant comprising 3 – 45 percent by weight of sodium fluoride, less than 30 percent by weight of tungsten disulfide, 25 – 97 percent by weight of graphite and 10 – 30 percent by weight of the alloy powders of 77Cu-23Pb or 90Cu-5Sn-5Pb on the total basis of graphite and sodium fluoride.

3. A solid lubricant as claimed in claim **1** in which 10 – 30 percent by weight of a metal salt of tungstate are added to the solid lubricant of the claim **1.**

4. A solid lubricant as claimed in the claim **2** in which 5 – 20 percent by weight of the metal salt of tungstate are added to the solid lubricant of the claim **2.**

5. A solid lubricant as claimed in claim **3** in which less than 30 percent by weight of tungsten disulfide is added to the solid lubricant.

6. A solid lubricant as claimed in claim **4** in which the metal salt of tungstate added is from the group consisting of sodium tungstate, potassium tungstate, barium tungstate, lead tungstate, zinc tungstate, copper tungstate, and cadmium tungstate.

7. A solid lubricant as claimed in claim **3** in which the metal salt of tungstate added is from the group consisting of sodium tungstate, potassium tungstate, barium tungstate, lead tungstate, zinc tungstate, copper tungstate, and cadmium tungstate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,821,111 Dated June 28, 1974

Inventor(s) Wataru Abe et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 42, "celar" should be -- clear --

Column 6, line 63, "e" should be -- the --

Column 7, line 33, "wo_4)" should be -- WO_4) --

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents