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(54) A solid film lubrican system useful in coating a metal, ceramic or polymericmaterial wear surface.

(57) The present invention relates to a solid film lubricant system useful in coating a metal, ceramic or polymeric material wear surface, comprising

i) a carrier,
ii) solid lubricant components,
iii) additives.

Such AF coatings, being high-grade lubricants, generally provide maintenance-free, permanent lubrication, and they are capable of meeting extreme requirements which the usual lubricants cannot meet.

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Description

[0001] A solid film lubricant system useful in coating a metal, ceramic or polymeric material wear surface.

[0002] The present invention relates to a solid film lubricant system useful in coating a metal, ceramic or polymeric material wear surface, comprising

i) a carrier,
ii) solid lubricant components,
iii) additives.

[0003] The lubricant system referred to in the introduction is also known as so-called AF coatings (anti-friction coatings), which coatings, being high-grade solid or dry lubricants, generally provide maintenance-free, permanent lubrication, and they are capable of meeting extreme requirements which the usual liquid or consistent lubricants cannot meet. For anti-friction coatings it is not necessary to build up a hydrodynamically carrying film via the hydrodynamically acting speed for separating the base member and the counter member, so that parts which only reach low speeds upon being subjected to high loads or which make oscillating movements have an active separating solid film present between the surfaces from the moment the movement starts. AF coatings are used in the case of extreme operating conditions, for example high temperatures and pressures or no access for liquid lubricants. The AF coatings referred to in the introduction exhibit excellent properties also in the field of corrosion protection, in combination with reduction of wear, pressure loading capacity and resistance against environmental influences. In combination with the addition of corrosion protection additives it is possible to substitute the known coatings on metal, which are hazardous to the environment and which generally have a base of chromium, nickel or cadmium. Such coatings, which mainly contain Cr(VI), function to obtain the required lubricating properties after galvanising, passivating and greasing. In addition to that, lead-containing compounds and other heavy metal compounds are frequently used, which is dubious, however, in view of the carcinogenic properties of said components. The lubricant systems referred to in the present introduction are used for dry, durable lubrication of connecting materials, such as nuts, washers and bolts, hinges, lock parts, such as catches, pins, housings and handles, magnetos, bearings, bushes, shafts and the like, with a constant coefficient of friction, a wide temperature range and a contact pressure loading capacity which exceeds the yield limit of most metallic materials. Ageing or resinification does not occur in the present lubricant system. Moreover, the effect of the present lubricant system is retained even after a prolonged period of rest. Another aspect of the present lubricant system is the fact that it provides a long-lasting corrosion protection film exhibiting an excellent adhesion, even in the case of extreme deformation of the workpiece, without exhibiting any signs of flaking. In addition, the present lubricant system is insensitive to dust, dirt, moisture and chemical influences, it is radiation-proof and easy to apply to pre-treated surfaces of workpieces.

[0004] The AF coatings that are known from the prior art, for example from US patent No 5,482,637, can be considered to be suspensions of solid lubricants having a very small particle size, such as MoS_2, LiF_3, CaF_6, WS_2, graphite or BN in inorganic and organic binders and solvents, such as a matrix resin selected from the group of alkyd polyester, epoxy and vinyl butyryl, with the suspension further containing an active amount of moisturiser, defoaming agent and surfactant, such as xanthane.

[0005] The object of the present invention is to provide a lubricant system which enables the preparation of tailor-made AF coatings for industrial application through careful selection of the suitable solid lubricant components.

[0006] Another object of the present invention is to provide a solid lubricant system which does not comprise any environmentally objectionable components.

[0007] Another object of the present invention is to provide the lubricant system which does not require the use of Cr(VI)-containing precoatings in order to obtain the lubricating properties aimed at.

[0008] Yet another object of the present invention is to provide a solid lubricant system which covers a broad temperature range, which provides a pressure loading capacity that exceeds the yield limit of the metals that are used in practice and which moreover exhibits adequate protection against corrosion.

[0009] Another object of the present invention is to provide a group of additives for use in solid lubricant systems, which additives lead to a stable suspension not exhibiting any or low sedimentation and/or phase separation and if, no coagulation of the solid particles whilst keeping it uncured for a long time, both during storage and during transport.

[0010] According to the present invention, the solid lubricant system as referred to in the introduction is characterized in that said iii) additives are selected from the group consisting of Na-, K- and NH_3-salt, of polyaspargic acid and N-alkyl morpholines, polyanilines, lecithine, sodium olefin copolymers, ethylene diamine terminated polytetraalkylene glycol, succinimide, bismuthtris (>C_6 alkylenedithio carbamates) and bi-methylenebisdibutyldithio carbamates, methylamino acetic acid or its sodium salt, butylamino ethanol and urea, or mixtures thereof.

[0011] The aforesaid objectives will be accomplished if one or more of the aforesaid additives are used in the present solid lubricant system.

[0012] The preferred amount of carrier or binder is less than 10 wt.%, preferably less than 3 wt.%, based on the total amount of solid lubricant system.

[0013] Polyanilines (poly-p-phenylene amine imine, Pani) comprise amine and imine groups. Polyaniline is

to be regarded as a benzene rings and chinon groups conjugated polymer, chinoide-imine structures and benzeneamine groups respectively. Pani becomes electrically conductive by paratoluene sulphonic acid. The maximum temperature of application is 220 °C, wherein, however, a temperature of about 260 °C is allowable during a short period of time. Experimental data have shown that ≤ 20 wt.% polyaniline particles having a dimension of < 500 nm will shift the corrosion potential with a value of + 800 mV, which shift is in particular favourable for anticorrosion objectives. It is preferred to disperse 3-10 wt.% electrically conductive polyanilines having a average particle size of about 20-30 nm in the present lubricant system. In the group of polyanilines several oxidation steps are possible which determine the amount of N-H-bindings, as well as the ratio of benzene rings and chinon groups, on which several reversible redox reactions are based. Therefore, several compounds can be mentioned like leucomeraldine (completely reduced Pani), emeraldine-base (a partially oxidized Pani) and pernigraline base (a completely oxidized Pani). These compounds can be converted in each other by proton delivery, reaction of amine groups with radicals, respectively, and the salts thereof can be formed.

[0014] In particular lecithin-based compounds, such as commercially available technical lecithin consists of lecithin (more than 60%), the remainder being soybean oil, or sodium olefin copolymers, viz. anionic dispersing agents for aqueous systems, are added as additives to the present lubricant system.

[0015] The use of PIB-succinimide (mono-, bis- en trisuccinimide) or salts of polyaspargic acid is in particular desirable if graphite compounds are used as solid lubricant components. Moreover, ethylene diamine grafted polytetralkene glycol is suitable for use as an anti-sedimentation and dispersing agent. In addition (bismuth ($>C_6$ alkylene dithiocarbamates) and bimethylene bis dibutyl dithiocarbamates can be used as molybdenum or zinc salts.

[0016] The group of N-alkylmorpholines is in particular suitable for use as an anti-corrosion agent in water-based solid lubricant systems. In addition to that, said group exhibits very good properties under extreme pressure conditions, stabilizing the pH-value as a buffer. From a toxicologic point of view, the alkyl derivatives with a base of CH_3 and C_6H_{13} are preferred, because such compounds are quickly biodegradable and exhibit a favourable toxicity. In addition to that, polymers of polyaspargic acid are suitable on account of their biodegradability, in combination with a low toxicity value. Moreover, polymers of polyaspargic acid surprisingly have multifunctional properties, because polyaspargic acid is dipolar, on account of the COOH and C=O groups, and adsorbs on surfaces, so that said molecule has multifunctional anti-wear and high-pressure properties. In addition, polyaspargic acid has a dispersing effect and prohibits coagulation on the solid lubricant components of the present lubricant system, whilst also having a favourable influence as regards the prevention of calcification. The molecule can be considered to be strongly anionic and functions as a strong regulator or stabiliser. According to the present invention, all types of D-, L- and DL-polyaspargic acid, preferably L-polyaspargic acid, with potassium, sodium or lithium, as well as ammonium, having a molecular weight of 1000 - 10.000 g/mol are suitable.

[0017] Suitable solid lubricant components are: Zr $(OH)_4$, $Zr(OH)_4.nH_2O$, $ZrO_2.nH_2O$, Bi_2S_3, graphite intercalation compounds, graphite inhibited compounds, phyllosilicates and CeF_3, or a combination thereof

[0018] Cerium fluoride (CeF_3) is a white crystal having a hexagonal crystal structure, it is characterized by high-pressure properties which surpass the properties of MoS_2 to a significant degree, because CeF_3 is thermally stable in air conditions above 600 °C and because it is resistant against oxidation.

[0019] Zirconium hydroxide ($Zr(OH)_4$) exhibits a high degree of stability also in high-temperature air conditions, in particular temperatures of up to about 650 °C, with zirconium hydroxide being insoluble in water. It is also possible to use $Zr(OH)_4$. nH_2O and $ZrO_2.nH_2O$ as zirconium-containing compounds.

[0020] Unlike MoS_2, which is known from the prior art, pure graphite does not have any intrinsic lubricating properties, in spite of the fact that it has a hexagonal structure, because the binding forces between the C-layers are too strong. Consequently, the graphite lattice requires a specific gaseous substance, such as water vapour or a gas, for shifting the graphite lamellae relative to each other, which substance is introduced between the layers or "intercalated" and which increases the spacing between the individual layers. When said intercalated substances are removed through the application of a vacuum or high temperatures, the coefficient of friction of graphite compounds increases to a value higher than 0.5. This actually explains the tribological sensitivity of graphite to air humidity and water vapour. According to the present invention, in order to reduce this mechanism to a minimum, one or more compounds selected from the group consisting of $FeCl_3$, $CuFeS_2$, α-Fe_2PO_5, AsF_5, $NiCl_2$, CaF_2, BaF_2, LiF, AgCl, AgF, SbF_5, $AlCl_3$, $CuCl_2$, $CoCl_2$, $MnCl_2$, $MoCl_5$, $SbCl_3$, $SbCl_5$ and hydrated compounds thereof are used in graphite in order to improve the anti-friction properties of the graphite compounds.

[0021] It is in particular preferred in the present lubricant system if said ii) solid lubricant components are present in said system in an amount of less than 70 wt. %.

[0022] The ii) solid lubricant components used in the present solid lubricant system have a particle size < 5 μm.

[0023] In a special embodiment it is desirable for said ii) solid lubricant components to have a particle size in the range of 25-300 nm.

[0024] Furthermore it can be noted that the graphite intercalation compounds and the graphite inhibited compounds have an aspect ratio of at least 6:1.

[0025] Suitable ii) solid lubricant components as used in the present lubricant system furthermore include phyllosilicates, which compounds can be defined as so-called layered silicate compounds, which are characterized by tetrahedral Si_4O_{10}-layers and octrahedral layers containing (Mg, Fe,) or Al. The aforesaid group includes kaolinite, chlorite, serpentine, biotite, muscovite, pyrophyllite/pirophillite $AlSiO_2O_5OH$ ($H_v \sim 100$ MPa) or ferripyrophyllite $Fe^{3+}{}_2Si_4(OH)_2O_{10}$, marien glass $CaSO_4$ (high plastic deformation capacity, high μ), synthetic hillebrandite ($Ca_2SiO_2.H_2$), vermiculite $Mg_3(Al, Si)_4O_{10}(OH)_2.4H_2O$, meixnerite $Mg_6Al_2(OH)_{18}.4(H_2O)$, $\rho = 1{,}95$ g/cm^3, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}26(H_2O)$) [$H_v <$ 1000 MPa], molybdenum hydroxide-hydrate [$MoO_3.nH_2O$], wherein n = 1/3, 1/2, 1 or 2 (ilsemannite, $H_v \sim$ 4600 MPa), trihydrated alumina(ATH), aluminium trihydroxide as $Al(OH)_3$, α-$Al(OH)_3$ bayerite, β-$Al(OH)_3$ nordstrandite, doyleite, γ-$Al(OH)_3$, gibbsite, hydragillite, alumina, monohydrated or oxohydroxide (Al(OOH) as γ-(Al(OOH) boehmite and α-(Al(OOH) diaspore, with especially the group of Serpentine having a density of 2.2-2.6 g/cm^2 being preferred. The following hydrates/hydroxides can be mentioned as ii) solid lubricant components belonging to the group of Serpentine:

a. Antigorite $(Mg,Fe)_3Si_2O_5(OH)_4$,
b. Clinochrysotile $Mg_3Si_2O_5(OH)_4$ (monoclinical),
c. Lizardite $Mg_3Si_2O_5(OH)_4$ (trigonal and hexagonal),
d. Orthochrysotile $Mg_3Si_2O_5(OH)_4$ (orthorhombic),
e. Parachrysotile $(Mg,Fe)_3Si_2O_5(OH)_4$ (orthorhombic), and
f. Talcum $Mg_3Si_4O_{10}(OH)_2$.

[0026] In order to protect the graphite intercalation compounds and the graphite inhibited compounds against oxidation, [CS]-surface complexes, $Zn_3P_2O_5$, zinc orthophosphate KH_2PO_4, $AlPO_4$ and $Li_2OMgOP_2O_5$, or a mixture thereof, are added to the present solid lubricant system.

[0027] A suitable carrier is selected from the group of polymineral resins, aniline resins, phosphor and boron modified phenol resins, polyaniline resins, from polyazoles, as polybenzimidazole, polypyrrolone, polyimidazolepyrrolone, poly-p-phenylene, poly-p-xylene, poly-m-phenylene isophthalamide, polyphenylene benzoxazole, polyphenylene benzothiazole, poly-tris(N-pyrrolyl) boron resins, polycarbosilanes and polysilanes as well as the mixtures thereof.

Claims

1. A solid film lubricant system useful in coating a metal, ceramic or polymeric material wear surface, comprising

i) a carrier,
ii) solid lubricant components,
iii) additives,

characterized in that said iii) additives are selected from the group consisting of Na-, K- and NH_3-salts, of polyaspargic acid and N-alkyl morpholines, polyanilines, lecithin, sodium olefin copolymers, ethylene diamine terminated polytetraalkylene glycol, succinimide, (bismuthtris (>C_6 alkylene dithiocarbamates) and bimethylene bis dibutyl dithiocarbamates, methylamino acetic acid or its sodium salt, butylamino ethanol and urea, or mixtures thereof.

2. A solid film lubricant system according to claim 1, **characterized in that** the amount of said iii) additives is less than 10 wt.%, based on the total system.

3. A solid film lubricant system according to claim 1, **characterized in that** the amount of said iii) additives is less than 3 wt.%, based on the total system.

4. A solid film lubricant system according to any one of the preceding claims, **characterized in that** said ii) solid lubricant components are comprised of an ingredient selected from the group of $Zr(OH)_4$, $Zr(OH)_4.nH_2O$, $ZrO_2.nH_2O$, Bi_2S_3, graphite intercalation compounds, graphite inhibited compounds, phyllosilicates and CeF_3, or a combination thereof.

5. A solid film lubricant system according to claim 4, **characterized in that** said ii) solid lubricant components are present in said system in an amount of less than 70 wt.%.

6. A solid film lubricant system according to any one of the claims 4-5, **characterized in that** said ii) solid lubricant components have a particle size < 5 μm.

7. A solid film lubricant system according to claim 6, **characterized in that** said ii) solid lubricant components have a particle size in the range of 15-300 nm.

8. A solid film lubricant system according to any one of the claims 4-7, **characterized in that** said graphite intercalation compounds and said graphite inhibited compounds have an aspect ratio of at least 6:1.

9. A solid film lubricant system according to claim 4, **characterized in that** as phyllosilicates the group of Serpentine having a density of 2.2-2.6 g/cm^2 is used.

10. A solid film lubricant system according to any one of the claims 4-9, **characterized in that** in said graphite intercalation compounds and said graphite inhibited compounds one or more compounds are incorporated, selected from the group consisting of $FeCl_3$, $CuFeS_2$, α-Fe_2PO_5, AsF_5, $NiCl_2$, CaF_2, BaF_2, LiF, AgCl, AgF, SbF_5, $AlCl_3$, $CuCl_2$, $CoCl_2$, $MnCl_2$, $MoCl_5$, $SbCl_3$, $SbCl_5$, and hydrated compounds thereof in order to improve the anti-friction properties of said graphite compounds.

11. A solid film lubricant system according to any one of the claims 4-10, **characterized in that** said graphite intercalation compounds and said graphite inhibited compounds are protected against oxidation by adding thereto [CS]-surface complexes, $Zn_3P_2O_5$, zinc ortho phosphate, KH_2PO_4, $AlPO_4$ and $Li_2OMgOP_2O_5$, or a mixture thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 07 8999

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	8 March 2004	Rotsaert, L

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 03 07 8999

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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 03 07 8999

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