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(54) A solid film lubricant system useful in coating a metal, ceramic or polymeric material 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.

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

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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] European patent application 0 452 189 relates to a solid material for dry lubrication of the contact between a first surface made of a first material and a second surface made of ceramic material wherein it comprises at lease one rare-earth fluoride. From this document is known a process for dry lubrication of the contact between two surfaces one of which is made of ceramic material wherein it consists in interposing between the two surfaces to be lubricated a layer of a lubricating material comprising at least one rare-earth fluoride. This document does not disclose a film as lubricating coating.

[0004] International application WO 00/53702 relates to an aqueous coating composition for providing a dry film lubricant coating to a substrate, comprising 10-70% by weight alkaline earth metal fluoride, 2-65% by weight of a silicon resin binder, and water, wherein the silicon resin is an alkyl silicone resin emulsion in water and is used primarily to hold the lubricating powders on the surface of the substrate.

[0005] European patent application 0 217 138 relates to a low friction support member comprising a compacted body formed from an intercalated graphite powder, which is stable in air and at an elevated temperature. The intercalated graphite is compressed uniaxially such as in a mold or dye, or isostatically such as in a pressurized fluid to form a compact body of the desired shape. This document does not relate to a solid film lubricant system useful in coating a metal, ceramic or polymeric material wear surface.

[0006] French patent application 2 684 684 relates to self-lubricating dense articles, consisting essentially of sintered rare-earth fluorides and exhibiting a fine-grained uniform microstructure. These self-lubricating dense articles are obtained by a process consisting of sintering, in a non-oxidizing and/or reducing atmosphere, a submicron and very pure powder of rare-earth fluorides in the presence of a carbonaceous sintering additive. These articles can be employed as self-supporting components or as insert components, but they cannot be regarded as a solid film lubricant system useful in coating a metal, ceramic or polymeric material wear surface.

[0007] U.S. patent 3,756,982 relates to a method of producing antifriction materials for dry friction units, consisting of curing a mixture of polyphenylene oligomers in combination with various fillers. Pulverulent fillers are added into a mixture of oligomers in an alcohol, with which a fabric is then impregnated. The result of the impregnation procedure is an impregnated fabric which is then dried at a temperature of 130 °C, and the mass thus obtained is placed into cold compression molds, heated up to 180 °C, the compression mold is then closed and a pressure is built up therein with a view towards obtaining an article of adjustable density. The resulting articles are work pieces which can be finished to a required size on metal working machines. This document does not relate to a solid film lubricant system useful in coating a metal, ceramic or polymeric material wear surface.

[0008] U.S. patent 6,228,815 relates to solid lubricants containing bismuth sulfide for use in friction linings for applications such as brake disk pads, brake drums and clutch disks. The friction material matrix comprises at least one solid lubricant, the solid lubricant containing bismuth sulfide and at least one binder system.

[0009] Japanese publication No. 04 004293 relates to a solid lubricant having good lubricating characteristics by blending a graphite based solid lubricant with a graphite intercalation compound and thermally treating. This document does not relate to a solid film lubricant system useful in coating a metal, ceramic or polymeric material wear surface.

[0010] 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. Under European legalisation, the use of the

heavy metals lead and cadmium in automobiles will be forbidden as from 2003, whilst the use of Cr(VI) in automobiles will be banned as from the middle of 2007. 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. The present lubricant system is furthermore less sensitive to dust, dirt, moisture and chemical influences and it exhibits greater resistance against radiation in comparison with lubricant systems that are already commercially available and, in addition, it is easy to apply to pre-treated surfaces of workpieces.

[0011] The AF coatings that are known from the prior art, for example from US patent No 5,554,020, can be considered to be suspensions of solid lubricants having a very small particle size, such as MoS_2, graphite or PTFE in inorganic and organic binders and solvents.

[0012] 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.

[0013] Another object of the present invention is to provide a solid lubricant system which does not comprise any environmentally objectionable solid components.

[0014] 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.

[0015] 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.

[0016] According to the present invention, the solid lubricant system as referred to in the introduction is characterized in that said ii) solid lubricant components are comprised of at least two ingredients 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.

[0017] The aforesaid objectives will be accomplished if one or more of the aforesaid solid lubricant components are used in the present solid lubricant system.

[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 hil-

lebrandite ($Ca_2SiO_2.H_2$), 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] Suitable additives are selected from the group consisting of Na-, K- and NH_3-salts, of polyaspargic acid and N-alkyl morpholines, lecithin, sodium olefin copolymers, ethylene diamine terminated polytetraalkylene glycol, succinimide, (bismuth (>C_6 alkylene dithiocarbamates) and bimethylene bis dibutyl dithiocarbamates, methylamino acetic acid or its sodium salt, butylamino ethanol and urea, or mixtures thereof.

[0028] 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 ii) solid lubricant components are comprised of at least two ingredients 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.

2. A solid film lubricant system according to claim 1, **characterized in that** said ii) solid lubricant components are present in said system in an amount of less than 70 wt.%.

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

4. A solid film lubricant system according to claim 3, **characterized in that** said ii) solid lubricant components have a particle size in the range of 15-300 nm.

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

6. A solid film lubricant system according to claim 1, **characterized in that** as phyllosilicates the group of Serpentine having a density of 2.2-2.6 g/cm^2 is used.

7. A solid film lubricant system according to any one of the preceding claims, **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.

8. A solid film lubricant system according to any one of the preceding claims, **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 9001

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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	26 February 2004	Rotsaert, L

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EUROPEAN SEARCH REPORT

Application Number
EP 03 07 9001

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