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(54) BORON-FREE WATER-BASED LUBRICANT FOR PLASTIC WORKING

(57) The present disclosure is directed to an aqueous lubricating composition having utility in the cold working of metallic substrate, said aqueous lubricating composition comprising, based on the weight of the composition:
from 1 to 20 wt.% of a) at least one water-soluble inorganic salt, said inorganic salt or salts being in a dissolved state;
b) at least one particulate solid lubricant;
from 0.1 to 5 wt.% of c) at least one rheological control agent;
from 0.1 to 5 wt.% of d) at least one base; and,
from 0.1 to 5 wt.% of e) at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants and zwitterionic surfactants,
wherein said composition is free from boron and boron compounds and is further characterized in that the ratio by weight of b) said at least one solid lubricant to a) said at least one water-soluble inorganic salt [(b):(a)] is from 0.1:1 to 1:1.

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Description

FIELD OF THE INVENTION

[0001] The present disclosure is directed to an aqueous lubricating composition which is to be used in the cold working of metallic substrates. More particularly, the present disclosure is directed to an aqueous lubricating composition in which is dispersed a particulate solid lubricant which is to be deposited on a surface of the metallic substrate, which aqueous lubricating composition is free from boron compounds.

BACKGROUND TO THE INVENTION

[0002] The practice of cold working refers to the plastic deformation of metals which is performed below the recrystallization temperature. In most manufacturing environments, this cold working is performed at room temperature but the employment of slightly higher temperatures - but still below the recrystallization temperature - can provide increased ductility and reduced strength in the metal to be worked.

[0003] Broadly, the major cold-working operations can be classified under four heading: squeezing; bending; shearing; and, drawing, which drawing encompasses tube, bar, wire and shell drawing and also spinning and ironing. Focusing on squeezing processes, as these account for the greatest tonnage of worked products, these are commonly processes which have hot-working counterparts and include: cold rolling; swaging; cold forging; and extrusion.

[0004] When compared to hot-working, these cold working processes do present a number of advantages. Most obviously the energetic expenditure of heating is not required but additional benefits include: the obtainment of better surface finishes to the worked metal; superior dimensional control of the worked metal; minimization of directional properties of the worked metal; improved strength of the worked metal; and the superior reproducibility of cold working processes.

[0005] There are, however, disadvantages associated with cold-working processes which include: the need to generate high forces for metal deformation - particularly where limited metal ductility is available - promotes a need for heavier and more powerful processing equipment; the metal surfaces must be clean and scale-free; strain hardening may occur; and undesirable residual stresses may be present in the worked metal.

[0006] Given these disadvantages, it is somewhat commonplace in the art to provide the metal to be coldworked with a lubricating film at the interface between the metal and cold-working tool. An effectively applied lubricating film - which is free from defects and which has a consistent and sufficient thickness - can serve to reduce friction at this interface and suppress the occurrence of seizures. Experience in the art has demonstrated that lubricating oils are difficult to apply and handle in a manner which provides effective films on metallic substrates. As such, the use of solid lubricating films has become ubiquitous. These films may be deposited from solvent-borne or water-borne compositions in which a solid lubricant is dispersed.

[0007] GB2003923A (Foseco Int.) discloses a metal working lubricant composition comprising: (i) a water-soluble metallic soap; and, (ii) an alkali metal chloride, an alkali metal sulphate and an alkali metal borate.

[0008] WO00/63324 A1 (Chevron Chemical Co.) discloses a lubricant composition having a base oil of lubricating viscosity, a dispersed hydrated alkali metal borate, and a polyalkylene succinic anhydride or non-nitrogen derivative thereof.

[0009] EP 917559 A (Henkel Corporation) describes a waterborne lubricant for the cold plastic working of metals, said waterborne lubricant comprising, in addition to water: (a) a component of water-soluble inorganic salt; (b) a homogeneously dispersed component of solid lubricant; (c) a homogeneously emulsified component of at least one substance selected from the group consisting of mineral oils, animal and plant oils and fats, and synthetic oils; and, (d) surfactant, in which the solid lubricant to water-soluble inorganic salt weight ratio ((b)/(a)) is from 0.05:1 to 2:1 and the weight ratio of the oily component to the sum of the water-soluble inorganic salt and the solid lubricant ((c):(a+b)) is from 0.05:1 to 1:1.

[0010] EP 2450423 A (Henkel AG & Co. KGaA) discloses a water-based lubricant for plastic working, comprising a resin component containing a copolymer or homopolymer of monomers having an ethylenically unsaturated bond, including at least maleic anhydride (a), an inorganic component (b), and a solid lubricating component (c), wherein maleic anhydride moieties of the resin component (a) are blocked with a nitrogen-containing compound at a blocking ratio of 10 to 80%, and unblocked of maleic anhydride moieties are neutralized with an alkaline component at a degree of neutralization of 40 to 100%.

[0011] JP2011246684A (Nihon Parkerizing) discloses an aqueous lubricant for plastic working of a metallic material, said lubricant comprising: alkaline metal borate salts (a), wherein the alkaline metal borate salts (a) contain lithium borate and wherein the molar ratio of lithium to all the alkaline metals in the alkaline metal borate salts (a) is 0.1 to 1.0; and, wherein the molar ratio (B/M) of boron (b) to alkaline metals M in the alkaline metal borate salts (a) is 1.5 to 4.0.

[0012] CN107805541A (Maanshan Tuori Metal Surface Tech Co. Ltd) provides a lubricant for plastic working, said lubricant comprising by weight: 10-50% of stearic acid; 1-10% of borate; 1-10% of a rust inhibitor; 1-10% of an inorganic alkali; 0.1-0.5% of an antifoaming agent; and, the balance of water.

[0013] It will be noted that many of these prior art citations share the commonality of using boron compounds. This is considered disadvantageous. Boron compounds are irritants to humans and animals, irritating in particular the nose, throat and eyes of humans. A high exposure to boron in humans can cause infections of the stomach, kidney and brain. Further, boron compounds which are released into soil from industrial run-off can supplement the levels of natural boron in soils to the point of toxicity, which point is reached quite facilely for phloem-immobile plants. Such boron toxicity in soils is difficult to ameliorate.

[0014] There is considered to be a need in the art to develop aqueous lubricating compositions which are free from boron and boron compounds but which retain effective utility in the cold working of metallic substrates.

STATEMENT OF THE INVENTION

[0015] In accordance with a first aspect of the invention, there is provided an aqueous lubricating composition comprising, based on the weight of the composition:

from 1 to 20 wt.% of a) at least one water-soluble inorganic salt, said inorganic salt or salts being in a dissolved state;
b) at least one particulate solid lubricant;
from 0.1 to 5 wt.% of c) at least one rheological control agent;
from 0.1 to 5 wt.% d) at least one base; and,
from 0.1 to 5 wt.% of e) at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants and zwitterionic surfactants,

wherein said composition is free from boron and boron compounds and is further characterized in that the ratio by weight of b) said at least one solid lubricant to a) said at least one water-soluble inorganic salt [(b):(a)] is from 0.1:1 to 1:1.

[0016] In an important embodiment of the invention, the aqueous lubricating composition comprises, based on the weight of the composition

from 2 to 20 wt.%, preferably from 5 to 20 wt.% of a) said at least one water-soluble inorganic salt, said inorganic salt or salts being in a dissolved state;
b) said least one particulate solid lubricant;
from 0.1 to 2.5 wt.%, preferably from 0.1 to 2 wt.% of c) said least one rheological control agent;
from 0.1 to 2.5 wt.%, preferably from 0.1 to 2 wt.% of d) said least one base; and,
from 0.1 to 2.5 wt.%, preferably from 0.1 to 2 wt.% of e) at least one surfactant selected
from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants and zwitterionic surfactants,

wherein said composition is free from boron and boron compounds and is further characterized in that the ratio by weight of b) said at least one solid lubricant to a) said at least one water-soluble inorganic salt [(b):(a)] is from 0.1:1 to 1:1, preferably from 0.2:1 to 1:1.

[0017] The aqueous lubricating composition may, optionally, have a pH of from 7 to 10, preferably from 7 to 9.

[0018] The aqueous lubricating composition will conventionally comprise from 60 to 90 wt.%, preferably from 65 to 85 wt.%, more preferably from 65 to 80 wt.% of water, based on the weight of the composition. The aqueous lubricating composition may, alternatively or additionally to the water content characterization, be characterized by a viscosity of from 0.005 to 1 Pa·s, as measured using a Brookfield viscometer at 25°C.

[0019] The total amount of rheological control agent(s) c) included in the composition should be from 1 to 10 wt.%, preferably from 2 to 8 wt.% of the total amount by weight of components a) and b). It is preferred that the or each rheological control agent included in the composition is a thixotrope.

[0020] An exemplary aqueous lubricating composition in accordance with the present invention comprises, based on the weight of the composition:

as part a) from 5 to 20 wt.% of a mixture of sodium sulphate, potassium tripolyphosphate and sodium tripolyphosphate, wherein each of the salts of this mixture is in the dissolved state;
a solid lubricant b) comprising or consisting of:

  at least one phosphate salt selected from the group consisting of zinc phosphate, zinc calcium phosphate and manganese phosphate; and,
  at least one wax selected from the group consisting of: polyethylene waxes; oxidized polyethylene waxes; polypropylene waxes; oxidized polypropylene waxes; and, co-polymeric waxes based on ethylene or propylene

as the majority monomers, further wherein said at least one wax is characterized by a number average molecular weight (Mn) of from 400 to 30,000 g/mol, preferably from 1000 to 25,000 g/mol;

as part c) from 0.1 to 2 wt.% of at least one thixotrope selected from the group consisting of: cellulose derivatives; and, polysaccharides;
as part d) from 0.1 to 2 wt.% of at least one base selected from the group consisting of: bis(2-(N,N'-dimethylamino)ethyl)ether; bis-(t-butylaminoethyl)ether, 1,2-bis-(t-butylaminoethoxy)ethane; 1,2-bis-(t-butylaminoethoxyethoxy)ethane; bis[2-(isopropylamino)propyl]ether; 1,2-[2-isopropylamino)-propoxy]ethane; and,
as part e) from 0.1 to 2 wt.% of at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants and zwitterionic surfactants,

wherein said composition is free from boron and boron compounds and is further characterized in that the ratio by weight of b) said at least one solid lubricant to a) said mixture of water-soluble inorganic salts [(b):(a)] is from 0.2:1 to 1:1, preferably from 0.4:1 to 1:1.

[0021] In accordance with a second aspect of the invention, there is provided the use of the aqueous waterborne lubricating composition as defined herein above and in the appended claims or of the dried film obtained therefrom in the plastic cold working of metallic substrates.

[0022] The invention further provides a process for the plastic cold working of a solid metallic substrate by mechanically forcing said solid metallic substrate through an aperture bounded by at least one solid surface of at least one metal working tool, said process comprising the steps of:

i) applying the aqueous lubricating composition as defined herein above and in the appended claims to at least one solid surface of said metallic substrate, which surface or surfaces would, if not coated, directly contact a solid metal working tool surface during the process;
ii) drying the applied aqueous lubricating composition to form a film on said at least one solid surface of said metallic substrate; and
iii) mechanically forcing the metallic substrate formed in step ii) through said aperture bounded by at least one metal working tool surface, so that the metallic substrate is cold worked.

DEFINITIONS

[0023] As used herein, the singular forms "a", *"an"* and *"the"* include plural referents unless the context clearly dictates otherwise.

[0024] The terms *"comprising", "comprises"* and *"comprised* of" as used herein are synonymous with *"including", "includes", "containing"* or *"contains",* and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. If used, the phrase *"consisting of'* is closed, and excludes all additional elements. Further, the phrase *"consisting essentially of* excludes additional material elements, but allows the inclusions of non-material elements that do not substantially change the nature of the invention.

[0025] When amounts, concentrations, dimensions and other parameters are expressed in the form of a range, a preferable range, an upper limit value, a lower limit value or preferable upper and limit values, it should be understood that any ranges obtainable by combining any upper limit or preferable value with any lower limit or preferable value are also specifically disclosed, irrespective of whether the obtained ranges are clearly mentioned in the context.

[0026] The words *"preferable", "preferred", "preferably", "particularly"* and *"desirably"* and synonyms thereof are used frequently herein to refer to embodiments of the disclosure that may afford particular benefits, under certain circumstances. However, the recitation of one or more preferable, preferred, particular or desirable embodiments does not imply that other embodiments are not useful and is not intended to exclude those other embodiments from the scope of the disclosure.

[0027] As used throughout this application, the word *"may"* is used in a permissive sense - that is meaning to have the potential to - rather than in the mandatory sense.

[0028] As used herein, room temperature is 23°C plus or minus 2°C.

[0029] As used herein, number average molecular weight (Mn) and weight average molecular weight (Mw) are determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent in accordance with DIN 55672-1:2007-08. The term polydispersity (PD) is derived from Mw and Mn and is calculated as (Mw/Mn).

[0030] As used herein, by "d_{50} *particle size"* is meant that the particle size distribution is such that at least 50% of the particles by weight have a particle size diameter of less than the specified value. Unless otherwise stated, that particle size is determined by laser diffraction.

[0031] The term *"aqueous lubricating composition"* as used herein refers to that composition which actually contacts the metallic substrate. As is known in the art, such contacting can occur in a socalled *"bath"* which is shaped, sized and disposed to enable at least part of the substrate to be immersed therein. The bath should moreover be sized to allow for movement of the aqueous lubricating composition around and throughout the loaded substrate, which movement can be further enhanced with recirculation and / or ultrasonics. The pH of the composition within the bath, the temperature of the bath, and contact time of the substrate are result effective variables which should be monitored either manually or automatically, whenever possible.

[0032] As used herein, the term *"alloy"* refers to a substance composed of two or more metals or of a metal and a non-metal which have been intimately united, usually by being fused together and dissolved in each other when molten. The term *"X alloy"* therefore denotes an alloy of which the metal X is the majority constituent component and wherein X will generally comprise at least 40 wt.% - more typically at least 50 wt.% or at least 60 wt.% - of the alloy, on a metals basis.

[0033] As used herein, "C_1-C_n *alkyl"* group refers to a monovalent group that contains 1 to n carbons atoms, that is a radical of an alkane and includes straight-chain and branched organic groups. As such, a "C_1-C_{18} *alkyl*" group refers to a monovalent group that contains from 1 to 18 carbons atoms, that is a radical of an alkane and includes straight-chain and branched organic groups. Examples of alkyl groups include, but are not limited to: methyl; ethyl; propyl; isopropyl; n-butyl; isobutyl; secbutyl; tert-butyl; n-pentyl; n-hexyl; n-heptyl; and, 2-ethylhexyl. In the present invention, such alkyl groups may be unsubstituted or may be substituted with one or more halogen. Where applicable for a given moiety (R), a tolerance for one or more non-halogen substituents within an alkyl group will be noted in the specification.

[0034] The term "C_1-C_n *hydroxyalkyl*" as used herein refers to a HO-(alkyl) group having from 1 to n carbon atoms, where the point of attachment of the substituent is through the oxygen-atom and the alkyl group is as defined above.

[0035] An *"alkoxy group"* refers to a monovalent group represented by -OA where A is an alkyl group: non-limiting examples thereof are a methoxy group, an ethoxy group and an iso-propyloxy group. The term "C_1-C_{12} *alkoxyalkyl*" as used herein refers to an alkyl group having an alkoxy substituent as defined above and wherein the moiety *(alkyl-O-alkyl)* comprises in total from 1 to 12 carbon atoms: such groups include methoxymethyl ($—CH_2OCH_3$), 2-methoxyethyl ($—CH_2CH_2OCH_3$) and 2-ethoxyethyl.

[0036] The term *"alkylene"* as used herein, is defined as a saturated, divalent hydrocarbon radical. In general in the present disclosure, such alkylene groups may be unsubstituted or may be substituted with one or more halogen.

[0037] The term "C_3 —C_{30} *cycloalkyl*" is understood to mean a saturated, mono- or polycyclic hydrocarbon group having from 3 to 30 carbon atoms. In the present invention, such cycloalkyl groups may be unsubstituted or may be substituted with one or more halogen. Where applicable for a given moiety (R), a tolerance for one or more non-halogen substituents within a cycloalkyl group will be noted in the specification. Examples of cycloalkyl groups include: cyclopropyl; cyclobutyl; cyclopentyl; cyclohexyl; cycloheptyl; cyclooctyl; adamantane; and, norbornane.

[0038] As used herein, *"cycloalkylene"* means a divalent radical formed by the removal of two hydrogen atoms from one or more rings of a cycloalkyl group.

[0039] As used herein, an "C_6-C_{18} *aryl*" group used alone or as part of a larger moiety - as in *"aralkyl group"* - refers to monocyclic, bicyclic and tricyclic ring systems in which the monocyclic ring system is aromatic or at least one of the rings in a bicyclic or tricyclic ring system is aromatic. The bicyclic and tricyclic ring systems include benzofused 2-3 membered carbocyclic rings. In the present invention, such aryl groups may be unsubstituted or may be substituted with one or more halogen. Where applicable for a given moiety (R), a tolerance for one or more non-halogen substituents within an aryl group will be noted in the specification. Exemplary aryl groups include: phenyl; (C_1-C_4)alkylphenyl, such as tolyl and ethylphenyl; indenyl; naphthalenyl, tetrahydronaphthyl, tetrahydroindenyl; tetrahydroanthracenyl; and, anthracenyl. And a preference for phenyl groups may be noted.

[0040] The *"arylene"* - when used independently or with respect to a combined moiety such as alkarylene

- means a divalent group formed by the removal of two hydrogen atoms from one or more rings of an aryl group as defined above, wherein hydrogen atoms may be removed from the same or different rings. Nominative examples include phenylene and napthylene.

[0041] As used herein, "C_2-C_{20} *alkenyl*" refers to hydrocarbyl groups having from 2 to 20 carbon atoms and at least one unit of ethylenic unsaturation. The alkenyl group can be straight chained, branched or cyclic and may optionally be substituted with one or more halogen. Where applicable for a given moiety (R), a tolerance for one or more non-halogen substituents within an alkenyl group will be noted in the specification. The term *"alkenyl"* also encompasses radicals having *"cis"* and *"trans"* configurations, or alternatively, "*E*" and "Z' configurations, as appreciated by those of ordinary skill in the art. Examples of said C_2-C_{20} alkenyl groups include, but are not limited to: $— CH=CH_2$; $—CH=CHCH_3$; $—CH_2CH=CH_2$; $—C(=CH_2)(CH_3)$; $—CH=CHCH_2CH_3$; $— CH_2CH=CHCH_3$; $—CH_2CH_2CH=CH_2$; $—CH=C(CH_3)_2$; $—CH_2C(=CH_2)(CH_3)$; $—C(=CH_2)CH_2CH_3$; $—C(CH_3)=CHCH_3$; $—C(CH_3)CH=CH_2$; $—CH=CHCH_2CH_2CH_3$; $—CH_2CH=CHCH_2CH_3$; $— CH_2CH_2CH=CHCH_3$; $—CH_2CH_2CH_2CH=CH_2$; $—C(=CH_2)CH_2CH_2CH_3$; $—C(CH_3)=CHCH_2CH_3$; $— CH(CH_3)CH=CHCH$; $—CH(CH_3)CH_2CH=CH_2$; $—CH_2CH=C(CH_3)_2$; 1-cyclopent-1-enyl; 1-cyclopent-2-enyl; 1-cyclopent-3-enyl; 1-cyclohex-1-enyl; 1-cyclohex-2-enyl; and, 1-cyclohexyl-3-enyl.

[0042] The term *"alkenylene"* means a divalent group formed by the removal of two hydrogen atoms from al alkenyl group as defined above.

[0043] As used herein, "*alkylaryl"* refers to alkyl-substituted aryl groups, both groups being defined as above. Further, as used herein "*aralkyl*" means an alkyl group substituted with an aryl radical as defined above.

[0044] The term *"hetero"* as used herein refers to groups or moieties containing one or more heteroatoms, such as N, O, Si and S. Thus, for example *"heterocyclic"* refers to cyclic groups having, for example, N, O, Si or S as part of the ring structure. "*Heteroalkyl*", *"heterocycloalkyl"* and "*heteroaryl*" moieties are alkyl, cycloalkyl and aryl groups as defined hereinabove, respectively, containing N, O, Si or S as part of their structure.

[0045] The term *"base"* as used herein refers to a species: which is capable of abstracting a proton in either a polar or non-polar solvent; or, which is capable of donating a hydroxide anion (OH^-).

[0046] The term *"amine"* is used in accordance with its ordinary meaning in the art and broadly refers to a compound containing a nitrogen atom with a lone pair.

[0047] As used herein "*C_1-C_9 heteroaryl amine"* refers to a compound wherein at least one carbon atom of an aromatic ring - which may be present in a monocyclic or polycyclic ring system - is substituted with a nitrogen atom. Preferably, a C_1-C_9 heteroaryl amine has from 1 to 3 carbon atoms of the aromatic ring substituted with nitrogen atoms. The heteroaryl amine may be unsubstituted or substituted with one or more C_1-C_4 alkyl groups at any position of the heteroaryl ring. In addition to having at least one carbon atom of the hydrocarbon ring substituted with a nitrogen atom, a heteroaryl amine can also have one or more carbon atoms substituted with other heteroatoms. Examples of heteroaryl amines include, but are not limited to pyridine, pyrrole, pyrimidine, imidazole, quinazoline, purine, pyrazole, and triazole.

[0048] As used herein, the term "*C_1-C_9 heterocyclic amine"* refers to an aliphatic compound which may be monocyclic or polycyclic, wherein at least one carbon atom - and preferably 1 or 2 carbon atoms - of a given hydrocarbon ring is substituted with a nitrogen atom. The number of ring carbon atoms is in toto from 1 to 9. A heterocyclic amine can be unsubstituted or substituted with one or more C_1-C_4 alkyl groups, as defined above, at any position of the heterocycle, including the one or more nitrogen atoms. In addition to having at least one carbon atom of a hydrocarbon ring substituted with a nitrogen atom, a heterocyclic amine can also have one or more carbon atoms substituted with other heteroatoms. Examples of heterocyclic amines include, but are not limited to, piperazine, pyrrolidine, and morpholine.

[0049] An *"amino acid"* is an organic acid having one or more than one alkaline radical such as amino, guanidino, imino or hydrazine radicals attached at any carbon atom other than that of the carboxyl group. As used herein, the term *"basic amino acid"* refers to an amino acid having an additional alkaline radical that can accept a proton. Examples of basic amino acids include, but are not limited to arginine and lysine, including both the L- and D- forms of each.

[0050] As used herein, the term *"amino sugar"* refers to a monosaccharide unit having one or more hydroxyl groups substituted with an $—NR_2$ group, wherein each R is independently selected from H or C_1-C_4 alkyl. Examples of amino sugars include, but are not limited to glucosamine and N-methylglucamine.

[0051] Viscosities of the composition compositions may be determined using the Brookfield Viscometer, Model RVT at standard conditions of 20°C and 50% Relative Humidity (RH). The viscometer is calibrated using silicone oils of known viscosities, which vary from 5,000 cps to 50,000 cps. A set of RV spindles that attach to the viscometer are used for the calibration. Measurements of the aqueous lubricating compositions are done using the No. 6 spindle at a speed of 20 revolutions per minute for 1 minute until the viscometer equilibrates. The viscosity corresponding to the equilibrium reading is then calculated using the calibration.

[0052] The present compositions are defined herein as being *"substantially free"* of certain compounds, elements, ions or other like components. The term *"substantially free"* is intended to mean that the compound, element, ion or other like component is not deliberately added to the composition and is present, at most, in only trace amounts which will have no (adverse) affect on the desired properties of the coating. An exemplary trace amount is less than 1000 ppm by weight of the composition. The term *"substantially free"* encompasses the term "free", the latter term indicating those embodiments where the specified compound, element, ion, or other like component is completely absent from the composition or is not present in any amount measurable by techniques generally used in the art.

DETAILED DESCRIPTION OF THE INVENTION

a) Water Soluble Inorganic Salt

[0053] The aqueous lubricating composition of the present disclosure comprises from 1 to 20 wt.%, based on the weight of the composition of a) at least one water-soluble inorganic salt. The aqueous lubricating composition should preferably comprise from 2 to 20 wt.%, for example from 5 to 20 wt.% of a) said at least one water-soluble inorganic salt. The or each included water-soluble inorganic salt is in the dissolved state in the aqueous lubricating composition.

[0054] The chemical nature of the salt(s) is not critical save for the fact that inorganic salts containing boron - such as borate salts - are precluded. The water-soluble inorganic salt should form a coating upon the metallic substrate which is to be cold worked.

[0055] Non-limiting examples of suitable water-soluble inorganic salts, which may be used alone or in combination in the present disclosure, include: phosphate salts, such as calcium phosphate; polyphosphate salts including alkali metal polyphosphates; alkali metal silicates, in particular sodium and potassium silicate; alkali metal tungstates, in particular sodium tungstate; molybdate salts including ammonium molybdate and alkali metal molybdates, in particular sodium molybdate; sulphate salts including alkali metal sulphates, in particular sodium sulphate and potassium sulphate; and, carbonate salts including alkali metal carbonates, in particular sodium or potassium carbonate.

[0056] For completeness, the term *"polyphosphate"* refers to a group comprising at least 2, for example from 2 to 6, tetrahedral phosphate (PO_4) units linked together via shared oxygen atoms: the polyphosphate may be linear or cyclic. Exemplary alkali metal polyphosphates having utility in the present disclosure include but are not limited to: tetrasodium pyrophosphate; tetrapotassium pyrophosphate; sodium tripolyphosphate; potassium tripolyphosphate; sodium metaphosphate; potassium metaphosphate; sodium hexametaphosphate; potassium hexametaphosphate; lithium hexametaphosphate; and, mixtures thereof.

[0057] Good results have been obtained in the present disclosure where component a) comprise a mixture of sodium sulphate, potassium tripolyphosphate and sodium tripolyphosphate.

b) Solid Lubricant

[0058] The aqueous lubricating composition comprises b) at least one particulate solid lubricant. The particles of the lubricant are conventionally dispersed within the composition: when that composition is applied to the surface of the substate to be worked and is subsequently dried thereon, the particles become deposited on that surface. Depending on the nature of the solid lubricant, some coalescence of the deposited particles may occur upon drying, leading to the development of a lubricating film on the substrate surface.

[0059] The ratio by weight of b) said at least one particulate solid lubricant to a) said at least one water-soluble inorganic salt [(b):(a)] in the waterborne lubricant should be in the range from 0.1:1 to 1:1. Preferably, said weight ratio [(b):(a)] is in the range from 0.2:1 to 1:1, in particular from 0.4:1 to 1:1 or from 0.4:1 to 0.8:1. The particular value of this ratio should be selected based on *inter alia* the specific shape of the metal stock to be subjected to plastic working, the working conditions and the working device. When the weight ratio has a value below 0.1:1, the resulting coating will have diminished lubricating properties and, as such, scuffing and seizure of the metal workpiece can occur. A weight ratio in excess of 1:1 can result in a reduced coating hardness and in a reduced adhesion between the substrate and the coating: when the metal is introduced to the mouth of the tool under these circumstances, the dried coating formed on the surface is very prone to debonding, which results in impaired lubricating properties.

[0060] Without intention to limit the present disclosure, the particulate solid lubricant will conventionally be selected from: i) lamellar solids, including talc, micas, graphite, zinc sulphide (ZnS), cadmium sulphide (CdS), molybdenum disulfide (MoS_2), molybdenum selenide ($MoSe_2$); tungsten disulfide (WS_2), selenium disulfide (SeS_2), calcium fluoride (CaF_2) and sodium-aluminum fluorides, such as cryolite and modified cryolite as disclosed in US Patent No. 3,377,279; iii) metal soaps including the metal salts of fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, hydroxystearic acid and behenic acid; iii) lubricious oxides, including titanium oxide, cadmium oxide, cobalt oxide, zinc oxide and silica (SiO_2); iv) non-lamellar, lubricious metallic compounds such as cerium fluoride (CeF_3), calcium hydroxide, calcium carbonate, zinc phosphate, zinc calcium phosphate and manganese phosphate; v) soft elemental metals including gold, silver, lead, tin, indium and barium; vi) solid polymeric lubricants including polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), polyacetals, polyimides, polyether ether ketone (PEEK) and ultra-high molecular weight polyethylene (UHWPE); and, vii) waxes. Such particulate lubricants may be utilized alone or in combination.

[0061] For completeness, the term *"mica"* above encompasses both synthetic mica and natural micas such as sericite and muscovite. Further, the metal soaps will conventionally include calcium, aluminum, magnesium, barium, zinc, lead, lithium or potassium as the constituent metals; a preference for the use of calcium stearate as the metal soap may be mentioned.

[0062] Without intention to limit the present invention, exemplary waxes having utility in the aqueous lubricating compositions include: paraffin wax [CAS No. 8002-74-2]; polyethylene wax [CAS No. 9002-88-4]; polyethylene-polypropylene waxes; co-polymeric polyethylene waxes, for example copolymers of ethylene with at least one monomer selected from (meth)acrylic acid, maleic anhydride, vinyl acetate and vinyl alcohol, which copolymers are available under, for instance CAS Nos. 38531-18-9, 104912-80-3 and 219843-86-4; polybutene waxes; Fischer-Tropsch waxes; oxidized waxes, for example oxidized polyethylene wax [CAS No. 68441-17-8]; polar modified polypropylene waxes; microcrystalline waxes, for example microcrystalline paraffin waxes [CAS No. 63231-60-7]; montan wax and montan wax raffinates; montanic acids and salts and esters thereof; fatty acid amides such as erucamide [CAS No. 112-84-5], oleamide [CAS No. 301-02-0] and 1,2-ethylenebis(stearamide) [CAS No. 110-30-5]; and, carnauba wax.

[0063] It is preferred that any waxes included in the present composition meet at least one of the following conditions: i) an acid number of less than 200 mg KOH/g, preferably less than 100 mg KOH/g; ii) a melting point of from 40 to 200°C, preferably from 60 to 180°C; and, iii) a number average molecular weight (Mn) of at least 200 g/mol, preferably at least 400 g/mol. For completeness, these conditions are not intended to be mutually exclusive: waxes may meet one, two or desirably three of these conditions.

[0064] A particular preference may be noted for the use of at least one wax selected from polyethylene waxes, oxidized polyethylene waxes, polypropylene waxes, oxidized polypropylene waxes and co-polymeric waxes based on ethylene or propylene as the majority monomers. For instance, in an exemplary embodiment, the solid lubricant comprises or consists of: at least one phosphate salt selected from the group consisting of zinc phosphate, zinc calcium phosphate and manganese phosphate; and, at least one wax selected from polyethylene waxes, oxidized polyethylene waxes, polypropylene waxes, oxidized polypropylene waxes and co-polymeric waxes based on ethylene or propylene as the majority monomers. In these embodiments, the or each wax included in the composition should be further characterized by a number average molecular weight (Mn) of from 400 to 30,000 g/mol, preferably from 1000 to 25,000 g/mol.

[0065] To facilitate their inclusion in the aqueous compositions of the present invention, the or each solid particulate lubricant may be initially provided: i) in finely divided powder form, in particular in a micronized form characterized by a dso particle size of less than 5 microns, as measured by laser diffraction; and / or, ii) as an aqueous dispersion, the particles of which dispersion may desirably be characterized by a dso particle size of less than 5 microns, as measured by dynamic light scattering. In exemplary embodiments, the or each solid particulate lubricant included in the aqueous composition may have a dso particle of less than 2 microns, preferably less than 1 micron, as measured by laser diffraction.

c) Rheological Control Agent

[0066] The aqueous lubricating composition of the present disclosure comprises from 0.1 to 5 wt.%, based on the weight of the composition of c) at least one rheological control agent. The aqueous composition may preferably comprise from 0.1 to 2.5 wt.%, for example from 0.1 to 2 wt.% of c) said least one rheological control agent.

[0067] In certain embodiments, the total amount of rheological control agent(s) c) included in the composition should be from 1 to 10 wt.%, for example from 2 to 8 wt.% of the total amount by weight of components a) and b).

[0068] The term *"rheological control agent'* as used herein references a compound which is capable of absorbing liquid, such as but not limited to water, physically swell and thereby alter the liquid viscometric and flow properties. A rheological control agent may also function as a thickening agent and serve to keep the components of the composition - in particular the solid lubricant - in a dispersed form, typically by creating a continuous phase matrix. This agent may further function to modify the drying characteristics of the composition.

[0069] It is mentioned, in particular, that the or each rheological control agent included in the composition should be a thixotrope. In accordance with its standard definition, a thixotrope is a substance which

- either *per se* on when dispersed in solvent, herein water - exhibits a *viscosity that decreases when* a *stress is applied, such as when stirred.*

[0070] Without intention to limit the present invention, said at least one rheological agent should be selected from the group consisting of: clays, such as smectite clays, synthetic hectorite clays, colloidal montmorillonites, silicoaluminate clays and collidal magnesium aluminium silicate derived from natural smectic clay; fumed silica *(pyrogenic silica);* carboxyl vinyl polymers; polyvinylpyrrolidone (PVP) polymers and copolymers, such as PVP/vinyl acetate co-polymers; polyacrylates; cellulose derivatives, such as carboxymethycellulose (CMC), carboxyhydroxymethylcellulose, ethoxymethylcellulose, hydroxyethylcellulose and hydroxypropylcellulose; natural thickeners, such as alginate, guar gum, starch, gum tragacanth and locust bean gum; polysaccharides, such as xanthan gum; and, proteins, such as caseine, collagen and albumin.

[0071] When particulate rheological control agents are included in the composition, these should preferably be initially provided in a micronized form characterized by a d_{50} particle size of less than 5 microns, in particular less than 2 microns, as measured by laser diffraction. For example, fumed silicas, natural clays and synthetic clays should - as provided for inclusion in the composition - be characterized by a dso particle size of from 5 to 100 nm, for example from 5 to 40 nm, as measured by laser diffraction.

[0072] The above aside, a preference may be noted for the use of cellulose derivatives and / or polysaccharides as the rheological control agent. For instance, good results with regard to the stability and shelf-life of the aqueous lubricating compositions have been obtained where the aqueous composition comprises at least one of, and preferably both of, carboxymethycellulose (CMC) and xanthan gum.

d) Base

[0073] In order to provide biostability and rust resistance, the aqueous lubricating composition of the present disclosure comprises from 0.1 to 5 wt.%, based on the weight of the composition of d) at least one base. The aqueous lubricating composition may preferably comprise from 0.1 to 2.5 wt.%, for example from 0.1 to 2 wt.% of d) said least one base.

[0074] In certain embodiments, which are not intended to be mutually exclusive of the preferred weight ranges given above, the added amount of base should be such that the aqueous lubricating composition has a pH of from 7 to 10, for example from 7 to 9.

[0075] Typically the or each base included in the composition will be selected from the group consisting of:

alkali metal alkoxides;
ammonia;
quaternary ammonium hydroxide compounds having the general formula $(NR^a_4)^+(OH)^-$, wherein each R^a is independently selected from C_1-C_4 alkyl;
aliphatic, aromatic or mixed aliphatic-aromatic monoamines having the general formula $N(R^b)(R^c)(R^d)$ wherein: R^b is C_1-C_{12} alkyl, C_1-C_{12} hydroxyalkyl, C_2-C_{12} alkoxyalkyl, C_3-C_{18} cycloalkyl, C2-C12 alkenyl, C_6-C_{10} aryl, C_7-C_{18} aralkyl or C_7-C_{18} alkylaryl; and, R^c and R^d are independently selected from hydrogen, C_1-C_{12} alkyl, C_1-C_{12} hydroxyalkyl, C_2-C_{12} alkoxyalkyl, C_3-C_{18} cycloalkyl, C_2-C_{12} alkenyl, C_6-C_{10} aryl, C_7-C_{18} aralkyl or C_7-C_{18} alkylaryl;
aliphatic, aromatic or mixed aliphatic-aromatic polyamines wherein two or more amino groups $-N(R^c)(R^d)$, which amino groups may be the same or different and of which R^c and R^d are as defined above, are linked by an alkylene, hydroxyalkylene, alkoxyalkylene, cycloalkylene, alkenylene, arylene, aralkylene or alkylarylene group;
C_1-C_9 heterocyclic amines;
C_1-C_9 heteroaryl amines;
basic amino acids, such as arginine and lysine; and,
amino sugars.

[0076] Suitable alkali metal alkoxides will conventionally be selected from aliphatic, aromatic or araliphatic alkoxides of lithium, sodium or potassium. Non-limiting examples thereof are lithium, sodium or potassium methoxide, ethoxide, n-propoxide, isopropoxide, n-butoxide, sec-butoxide, tert-butoxide, n-pentoxide, isopentoxide, hexoxide, amyl alkoxide, 3,7-dimethyl-3-octoxide, phenoxide, 2,4-di-tert-butylphenoxide, 2,6-di-tert-butylphenoxide, 3,5-di-tert-butylphenoxide and 2,4-di-tert-butyl-4-methylphenoxide. Preference is given to using the aliphatic $(C_1$-$C_4)$alkoxides, in particular methoxides, ethoxides, n-propoxides, isopropoxides, n-butoxides, sec-butoxides and tert-butoxides of sodium, potassium or lithium.

[0077] As noted, the composition may optionally comprise ammonia (NH_3) as a base, either independently or in combination with other of the listed bases. For completeness, the constituent weight of ammonia included in the composition is to be calculated on the basis of NH_3. The ammonia will be present in the aqueous compositions of the present invention as an ammonia solution $NH_3(aq)$ which encompasses weakly basic solutions of ammonia in water which may referred to in the art as ammonium hydroxide, ammonia water, ammonia liquor, aqua ammonia, aqueous ammonia, or simply ammonia. While the term *"ammonium hydroxide"* suggests a base with the composition $[NH_4^+][OH^-]$, it is virtually impossible to isolate samples of NH_4OH, insomuch as these ions do not comprise a significant fraction of the total amount of ammonia in an ammonia solution, except in the case of extremely dilute ammonia solutions.

[0078] Without intention to limit the present disclosure, suitable basic amines - which may be included alone or in combination in the aqueous lubricating compositions - include: methyl amine; dimethylamine; trimethylamine; ethyl amine; diethylamine; triethylamine; cyclohexylamine; dimethylcyclohexylamine; ethanolamine; 2-(diethylamino)ethanol; N,N-dimethylethanolamine, 2,2'-dihydroxydiethylamine (diolamine); N-methylpiperidine; pyridine; 2,6-dimethylpyridine; 2,4,6-trimethylpyridine; quinoline; piperazine; pyrrolidone; 1-(2-hydroxylethyl)pyrrolidine; morpholine; N-methylmorpholine; 4-(2-hydroxyethyl)morpholine; bis(2-(N,N'-dimethylamino)ethyl)ether; bis-(t-butylaminoethyl)ether, 1,2-bis-(t-butylaminoethoxy)ethane; 1,2-bis-(t-butylaminoethoxyethoxy)ethane; bis[2-(isopropylamino)propyl]ether; 1,2-[2-isopropylamino)-propoxy]ethane; aniline; N-methylaniline; 4-methylaniline; 4-hydroxylaniline; pyrrole; pyrimidine; imidazole; quinazoline; purine; pyrazole; and, triazole.

[0079] Good results have been obtained where the composition comprises at least one base selected from the group consisting of: bis(2-(N,N'-dimethylamino)ethyl)ether; bis-(t-butylaminoethyl)ether, 1,2-bis-(t-butylaminoethoxy)ethane; 1,2-bis-(t-butylaminoethoxyethoxy)ethane; bis[2-(isopropylamino)propyl]ether; 1,2-[2-isopropylamino)-propoxy]ethane. A particular preference for the use of bis(2-(N,N'-dimethylamino)ethyl)ether may be acknowledged.

e) Surfactant

[0080] The aqueous lubricating composition comprises from 0.1 to 5 wt.%, based on the weight of the composition, of e) at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants and zwitterionic surfactants. The composition may comprise from 0.1 to 2.5 wt.%, for example from 0.1 to 2 wt.%, of e) said at least one surfactant, based on the weight of the composition.

[0081] Suitable nonionic surfactants having utility in the present disclosure include: the condensation products of C_5 to C_{25} aliphatic alcohols with from 1 to 25 moles of ethylene oxide per mole of said alcohol, wherein the alkylene chain of the aliphatic alcohol can either be straight or branched, primary or secondary; alkylpolyglycosides; alkyl glycerol ethers; sorbitan esters; and, fatty acid amide surfactants. Exemplary commercial nonionic surfactants include: Neodol™ 91-5, Neodol™ 91-8 and Neodol™ 23-5, available from Shell International Research Maatschappij BV;, Lutensol A7N, Lutensol XP 50, Lutensol XL150, Lutensol™ XL70, Lutensol™ T07 and Lutensol™ ON50, available from BASF; Novel 1412-7, Isalchem™, Lial™ and Marlipal™ O13/70 available from Sasol.

[0082] Suitable amphoteric and zwitterionic surfactants include: amine oxides of the general formula ($R^mR^nR^oN$-O), wherein R^m is C_1-C_{18} alkyl and R^n and R° are independently selected from C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl and C_1-C_6 alkoxyalkyl; and, betaines such as alkyl betaines, carbobetaines, alkyl amidobetaines, amidazoliniumbetaines, sulfobetaines and phosphobetaines. Exemplary betaines includes: Examples of suitable betaines include but are not limited to: behenamidopropyl betaines; canolamidopropyl betaines; capramidopropyl betaines; cocamidoethyl betaine; cocamidopropyl betaine; cocamidopropyl hydroxysultaine; oleamidopropyl betaine; isostearamidopropyl betaine; lauramidopropyl betaine; lauryl betaine; lauryl hydroxysultaine; lauryl sultaine; myristamidopropyl betaine; myristyl betaine; oleamidopropyl betaine; oleamidopropyl hydroxysultaine; oleyl betaine; oleylamidopropyl betaine; palmamidopropyl betaine; palmitamidopropyl betaine; ricinoleamidopropyl betaine; stearamidopropyl betaine; and, stearyl betaine.

[0083] Suitable anionic surfactants are sulphates, sulphosuccinates, sulphoacetates and / or sulphonates. Exemplary sulphonate surfactants include: C_6-C_{18} alkyl sulphonates (paraffin sulphonates); C_6-C_{18} alkyl benzene sulphonates; C_6-C_{18} alkyl glyceryl sulphonates; methyl ester sulphonate (MES); and, alpha-olefin sulphonate (AOS). As anionic surfactants, a preference may however be mentioned, either for use alone or in combination, for the water-soluble salts of C_6-C_{18} alkyl sulfates, C_6-C_{18} hydroxyalkyl sulphates and alkyl ethoxy sulfates a degree of ethyoxylation of from 1 to 5.

[0084] Suitable cationic surfactants are commonly quaternary ammonium surfactants and, in particular, quaternary ammonium surfactants selected from the group consisting of mono N-C_6-C_{18} alkyl or N-C_6-C_{18} alkenyl ammonium surfactants, wherein the remaining N positions are substituted by C_1-C_3 alkyl or C_1-C_3 hydroxyalkyl groups. Mention might also be made of C_6-C_{18} alkyl or C_6-C_{18} alkenyl esters of quaternary ammonium alcohol.

Adjunct Ingredients

[0085] The aqueous lubricating compositions of the present disclosure may further comprise adjuvants and additives that can impart improved properties to these compositions. The adjuvants and additives may, for instance, impart one or more of: enhanced boundary lubrication; reduced drying time; reduced corrosiveness; improved stability; and, longer shelf-life of the compositions. Such adjuvants and additives can be used in such combination and proportions as desired, provided they do not adversely affect the nature and essential properties of the composition. While exceptions may exist in some cases, these adjuvants and additives should not *in toto* comprise more than 5 wt.% of the total weight of the aqueous lubricating composition.

[0086] Included among such adjuvants and additives are: oils; anti-wear additives; corrosion inhibitors; antioxidants; free fatty acids, which may act to create a reacted layer for boundary lubrication; optical brighteners, in particular where confirmation of deposition of the solid lubricants under illumination may be required; and, tackifiers.

[0087] The addition of oils may serve to form an oily surface on the substrate surface after drying of the aqueous compositions and can compensate for reduced lubricating performance in those regions of the workpieces that are characterized by non-uniform film deposition of the solid lubricant. Further, in those embodiments of the composition where the aqueous lubricating composition is applied at an elevated temperature, this is typically effected by heating the lubricant with steam tubes: the addition of oil to the aqueous lubricating composition can inhibit adhesion of the solid particulate lubricant to the heating tubes.

[0088] The oils may be used alone or in combination and may be selected from mineral oils, animal oils, animal fats, plant oils and synthetic oils. However, the or each added oil should typically be characterized by at least one of and preferably all of: a flash point in the range from 150 to 300°C; a melting point of from -20 to 20°C; and, a viscosity of from 5 to 100 centistokes stokes as determined at 40°C.

[0089] A melting point in excess of 20°C can lead to a diminished emulsifiability and re-emulsifiability by the oil in the waterborne lubricant and thus to a tendency for treatment bath stability to be reduced. An oily component having a melting point below -20°C will typically have a reduced flash point. Likewise, a viscosity below 5 centistokes will typically be associated with a low flash point, which leads to the post-working generation of large amounts of gas and hence an ignition risk. Equally, when the viscosity of the added oil is below 5 centistokes, slip between solid lubricant particles is diminished and the lubrication performance tends to decline. Conversely, a viscosity in excess of 100 centistokes usually leads to a diminished emulsifiability and re-emulsifiability of the oily component in the waterborne lubricant.

[0090] Tackifiers are utilized to improve transfer rates of the lubricant and ensure the applied and dried lubricating composition remains in place to provide the needed lubrication. The or each tackifying resin included in the composition is preferably characterized by: a softening point of from 70 to 150°C.; and, a viscosity at 150°C of less than 2000 Pa·s.

[0091] Exemplary tackifying resins which may be used alone or in combination in the present invention include: aliphatic and cycloaliphatic petroleum hydrocarbon resins; aromatic petroleum hydrocarbon resins and the hydrogenated derivatives thereof; aliphatic / aromatic petroleum derived hydrocarbon resins and the hydrogenated derivatives; polycyclopentadiene resins, hydrogenated polycyclopentadiene resins and aromatic modified hydrogenated polycyclopentediene resins; terpenes, aromatic terpenes and hydrogenated terpenes; polyterpenes, aromatic modified polyterpenes and terpene phenolics; copolymers of α-methylstyrene and a further vinyl aromatic monomer; and, gum rosins, gum rosin esters, wood rosins, wood rosin esters, tall oil rosins, tall oil rosin esters and hydrogenated rosin esters.

PREPARATION OF THE AQUEOUS COMPOSITIONS

[0092] The aqueous lubricating compositions are formulated by simple mixing of the various components as well as any adjunct ingredients. Whilst the order of mixing of the components is not intended to be limited, it may be prudent to first form an aqueous dispersion of the rheological control agent(s) (c), to which dispersion is then added the inorganic salt (a), the solid lubricants (b) and the further components under agitation. The solid lubricants (b) should desirably be added after both the rheological control agent (c) and the inorganic salt to ensure a stable, homogeneous dispersion is formed. As noted earlier, it may be advantageous for particulate components and polymeric components to be pre-prepared as aqueous dispersions - at a solids contents of from 45 to 60 wt.%, for example - to facilitate their admixture with other components of the compositions. The inorganic salts a) may also be added as a pre-prepared solution or may be added in solid form but under mixing conditions which ensure that the salts are in dissolved form in the final aqueous lubricating composition.

[0093] If necessary, the aqueous lubricating compositions may be prepared well in advance of their application. However, in an interesting alternative embodiment, a concentrated composition may first be obtained by mixing components with only a fraction of the water that would be present in the composition as applied: the concentrated composition may then be diluted with the remaining water shortly before its application. It is considered that such concentrated compositions may be prepared and stored as either single-package concentrates - that can be converted by dilution with water only - or as multi-part concentrates, two or more of which must be combined and diluted to form a complete working composition according to the invention. Any dilution can be effected simply by the addition of water, in particular deionized and / or demineralized water, under mixing. The aqueous lubricating composition might equally be prepared within a rinse stream whereby one or more streams of the concentrate(s) is injected into a continuous stream of water.

[0094] Without specific intention to limit the amount of water included in the aqueous lubricating compositions, it is preferred that said compositions contain from 60 to 90 wt.%, preferably from 65 to 85 wt.% and more preferably from 65 to 80 wt.%, based on the weight of the composition, of water. In an alternative but not mutually exclusive characterization, the aqueous lubricating composition may be defined by a viscosity of from 0.005 to 1 Pa·s (50 cps to 1000 cps), as measured using a Brookfield viscometer at 25°C.

METHODS AND APPLICATIONS

[0095] Prior to applying the compositions to a metallic substrate, it is often advisable to pre-treat the relevant surfaces to remove foreign matter there from: this step can, if applicable, facilitate the subsequent adhesion of the compositions thereto. Such treatments are known in the art and can be performed in a single or multi-stage manner constituted by, for instance, the use of one or more of: an etching treatment with an acid suitable for the substrate and optionally an oxidizing agent; sonication; plasma treatment, including chemical plasma treatment, corona treatment, atmospheric plasma treatment and flame plasma treatment; immersion in a waterborne alkaline degreasing bath; treatment with a waterborne cleaning emulsion; treatment with a cleaning solvent, such as acetone, carbon tetrachloride or trichloroethylene; and, water rinsing, preferably with deionized or demineralized water. In those instances where a waterborne alkaline degreasing bath is used, any of the degreasing agent remaining on the surface should desirably be removed by rinsing the substrate surface with deionized or demineralized water.

[0096] After said cleaning and / or degreasing, the aqueous lubricating composition is applied to the substrate. The composition may be applied at ambient temperature or the temperature of the aqueous compositions may be elevated prior to application to, for instance, a temperature in the range from 30°C to 90°C, for instance from 30°C to 70°C.

[0097] To produce a double-face plated sheet, it is conventional commercially that an operating bath as hereinbefore described is prepared and the aqueous lubricating composition is applied to the substrate by, without limitation, immersion and dipping. The contact time of the aqueous lubricating composition is not critical but should be sufficient to allow the temperature of the substate to equilibrate with the temperature of the composition in the operating bath. Exemplary contact times are from 1 minute to 15 minutes, for instance from 2 to 10 minutes.

[0098] Alternative techniques which may be used to apply the aqueous lubricating composition to either a singular surface or multiple surfaces of a substrate include but are not limited to: painting; brushing; flow coating; roll coating; wiping; air-atomized spraying; air-assisted spraying; airless spraying; high-volume low-pressure spraying; and, air-assisted airless spraying.

[0099] At the conclusion of the application step, the article is dried using, for instance, ambient air drying, circulating warm air, forced air drying or infrared heating. The surface temperature of the substrate is controlled during drying: the peak metal temperature (PMT) need not exceed 150°C and should, more particularly, be in the range from 100 to 125°C, for example 100 to 120°C.

[0100] The above-described treatment should yield a protective film over the metal substrate, said film preferably having a film weight of from 1 to 50 g/m^2, preferably from 1 to 40 g/m^2 or from 5 to 40 g/m^2. The type of metal working to be performed, the degree of working and the substrate surface roughness will be determinative of the optimal thickness of the dried coating. Generally, however, when the dried film is too thin, contact can occur between the working tools and the substrate itself and seizure will then be prone to occur. When the dried film is too thick, a fraction of the film may not be drawn into the interface between the working tool and the substrate: this fraction would thus constitute a waste of the waterborne lubricant.

[0101] There is no intention to limit the base substrate to which the aqueous lubricating composition may be applied. As such, suitable base metal substrates may include but not be limited to: iron; titanium; nickel; zinc; copper; aluminium; tin; cobalt; and, alloys thereof. Substrates comprising or consisting of steel may be mentioned in particular, of which examples include: galvanized and galvanneal steel meeting the requirements of ASTM Designation A653; GALVALUME®, a 55% Al / 43.4% Zn / 1.6% Si alloy coated sheet steel available from Bethlehem Steel Corporation; and, GALFAN®, a 5% Al/ 95% Zn alloy coated sheet steel available from Weirton Steel Corporation.

[0102] The initial form of the substrate to which the aqueous lubricating composition is applied also need not be limited, save to say that the form must be appropriate for tools to be utilized and the target shape or form to be attained after cold-working. Whilst more complex shapes are certainly not precluded, conventional stock forms in which the metal and alloy substrates may be provided include: sheets; plates; cuboids; spheres; annuli; solid cylinders; tubes; and, wires.

[0103] As noted above, the present disclosure also provides for the use of the aqueous waterborne lubricant composition or the dried film obtained therefrom in the plastic cold working of metallic substrates.

[0104] The present disclosure further provides a process for the plastic cold working of a solid metallic substrate by mechanically forcing said solid metallic substrate through an aperture bounded by at least one solid surface of at least one metal working tool, said process comprising the steps of:

i) applying the aqueous lubricating composition as defined herein above to at least one solid surface of said metallic substrate, which surface or surfaces would, if not coated, directly contact a solid metal working tool surface during the process;
ii) drying the applied aqueous lubricating composition to form a film on said at least one solid surface of said metallic substrate; and
iii) mechanically forcing the metallic substrate formed in step ii) through said aperture bounded by at least one metal working tool surface, so that the metallic substrate is cold worked.

[0105] It is acknowledged that the plastic cold working of metals is conventionally an iterative process. As such, the above-described method may include the following further steps:

iv) removing the residual film from said at least one solid surface of the cold worked metallic substrate formed in step iii);
v) annealing said metallic substrate obtained in step iv); and,
vi) repeating steps i) to iii).

[0106] In an embodiment, step iv) comprises the treatment of the residual film with an alkaline degreaser. It is particularly preferred that step iv) does not comprise the treatment of the residual film with an acidic pickling liquor.

[0107] In the event that the residual lubricating film attained after step iii) is not removed prior to annealing, carbon, sulphur, phosphorus and other components of the lubricant film may infiltrate into the metallic substrate, thereby impairing the corrosion resistance and mechanical strength of that substrate. Further, the residual lubricating film would not present a surface to which the aqueous lubricating composition would adhere in the second (and further) iterations of step i) above.

[0108] Various features and embodiments of the disclosure are described in the following example, which is intended to be representative and not limiting.

EXAMPLE

[0109] The following commercial products are used in Example 1 which represents a composition in accordance with the present invention: the remaining ingredients mentioned hereinbelow are obtainable from Sigma Aldrich.

Chemipearl™ W900:	Low molecular weight polyethylene (PE) available from Mitsui Chemicals.
Laponite RD:	Highly-purified, synthetic colloidal clay available from BYK Chemie.
Triton DF16:	Capped ethoxylated alcohol surfactant, available from Dow Chemical.

Plurafac LF1430:	Alkoxylated fatty alcohol surfactant, available from BASF.
Surfynol 440:	Non-ionic surfactant, available from Evonik Industries.

[0110] An aqueous lubricating composition was prepared by mixing the ingredients given in Table 1 herein below. A solution of the inorganic salts (a) in water was prepared to which was added the rheological control agents (c), base (d) and surfactants and, subsequently, the solid lubricants (b). The solid lubricants (b) were added as pre-prepared dispersions in water.

[0111] In view of the foregoing description and examples, it will be apparent to those skilled in the art that equivalent modifications thereof can be made without departing from the scope of the claims.

Table 1

Material	**Component**	**Function**	**Example 1 (wt.%, based on weight of composition)**
Deionized Water			70.02
Potassium Sulphate	a)	Dissolved Inorganic Salt	2.50
Sodium tripolyphosphate ($Na_5O_{10}P_3$)	a)	Dissolved Inorganic Salt	4.99
Potassium tripolyphosphate ($K_5O_{10}P_3$)	a)	Dissolved Inorganic Salt	9.98
Chemipearl W900	b)	Solid Lubricant	7.00
Zinc orthophosphate tetrahydrate	b)	Solid Lubricant	3.20
Metallic Soap	b)	Solid Lubricant	0.48
Laponite RD	c)	Thixotrope	0.50
Xanthan Gum	c)	Thixotrope	0.12
Carboxymethyl cellulose	c)	Thixotrope	0.85
Bis(2-dimethylaminoethyl) ether	d)	Amine Base	0.20
Acrylic acid homopolymer	e)	Surfactant	0.04
Triton DF16	e)	Surfactant	0.03
Plurafac LF 1430	e)	Surfactant	0.03
Surfynol 440	e)	Surfactant	0.06

Claims

1. An aqueous lubricating composition comprising, based on the weight of the composition:

from 1 to 20 wt.% of a) at least one water-soluble inorganic salt, said inorganic salt or salts being in a dissolved state;
b) at least one particulate solid lubricant;
from 0.1 to 5 wt.% of c) at least one rheological control agent;
from 0.1 to 5 wt.% of d) at least one base; and,
from 0.1 to 5 wt.% of e) at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants and
zwitterionic surfactants,
wherein said composition is free from boron and boron compounds and is further **characterized in that** the ratio by weight of b) said at least one solid lubricant to a) said at least one water-soluble inorganic salt [(b):(a)] is from 0.1:1 to 1:1.

2. The aqueous lubricating composition according to claim 1 comprising, based on the weight of the composition

from 2 to 20 wt.%, preferably from 5 to 20 wt.% of a) said at least one water-soluble inorganic salt;
b) said least one particulate solid lubricant;
from 0.1 to 2.5 wt.%, preferably from 0.1 to 2 wt.% of c) said least one rheological control agent;
from 0.1 to 2.5 wt.%, preferably from 0.1 to 2 wt.% of d) said least one base; and,
from 0.1 to 2.5 wt.%, preferably from 0.1 to 2 wt.% of e) said at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants and zwitterionic surfactants,
wherein said composition is free from boron and boron compounds and is further **characterized in that** the ratio by weight of b) said at least one solid lubricant to a) said at least one water-soluble inorganic salt [(b):(a)] is from 0.1:1 to 1:1, preferably from 0.2:1 to 1:1.

3. The aqueous lubricating composition according to claim 1 or claim 2 comprising from 60 to 90 wt.%, preferably from 65 to 85 wt.%, more preferably from 65 to 80 wt.% of water, based on the weight of the composition.

4. The aqueous lubricating composition according to any one of claims 1 to 3, wherein the composition is **characterized by** a viscosity of from 0.005 to 1 Pa·s, as measured using a Brookfield viscometer at 25°C.

5. The aqueous lubricating composition according to any one of claims 1 to 4, wherein the total amount of rheological control agent(s) c) included in the composition is from 1 to 10 wt.%, preferably from 2 to 8 wt.% of the total amount by weight of components a) and b).

6. The aqueous lubricating composition according to any one of claims 1 to 5 having a pH of from 7 to 10, preferably from 7 to 9.

7. The aqueous lubricating composition according to any one of claims 1 to 6, wherein component a) comprises a mixture of sodium sulphate, potassium tripolyphosphate and sodium tripolyphosphate.

8. The aqueous lubricating composition according to any one of claims 1 to 7, wherein the or each solid particulate lubricant included in the composition is **characterized by** a d_{50} particle size of less than 5 microns, as measured by laser diffraction.

9. The aqueous lubricating composition according to any one of claims 1 to 8, wherein said component b) comprises:

at least one phosphate salt selected from the group consisting of zinc phosphate, zinc calcium phosphate and manganese phosphate; and,
at least one wax selected from the group consisting of: polyethylene waxes; oxidized polyethylene waxes; polypropylene waxes; oxidized polypropylene waxes; and, co-polymeric waxes based on ethylene or propylene as the majority monomers,
further wherein said at least one wax is **characterized by** a number average molecular weight (Mn) of from 400 to 30,000 g/mol, preferably from 1000 to 25,000 g/mol.

10. The aqueous lubricating composition according to any one of claims 1 to 9, wherein c) said at least one rheological control agent is selected from the groups consisting of: cellulose derivatives; and, polysaccharides.

11. The aqueous lubricating composition according to claim 10, wherein component c) comprises carboxymethycellulose (CMC) and xanthan gum.

12. The aqueous lubricating composition according to any one of claims 1 to 11, wherein d) said at least one base is selected from the group consisting of: bis(2-(N,N'-dimethylamino)ethyl)ether; bis-(t-butylaminoethyl)ether, 1,2-bis-(t-butylaminoethoxy)ethane; 1,2-bis-(t-butylaminoethoxyethoxy)ethane; bis[2-(isopropylamino)propyl]ether; 1,2-[2-isopropylamino)-propoxy]ethane.

13. The aqueous lubricating composition according to claim 12, wherein component d) comprises or consists of bis(2-(N,N'-dimethylamino)ethyl)ether.

14. The use of the aqueous waterborne lubricating composition as defined in any one of claims 1 to 13 or of a dried film obtained therefrom in the plastic cold working of metallic substrates.

15. A process for the plastic cold working of a solid metallic substrate by mechanically forcing said solid metallic substrate through an aperture bounded by at least one solid surface of at least one metal working tool, said process comprising the steps of:

i) applying the aqueous lubricating composition as defined in any one of claims 1 to 13 to at least one solid surface of said metallic substrate, which surface or surfaces would, if not coated, directly contact a solid metal working tool surface during the process;
ii) drying the applied aqueous lubricating composition to form a film on said at least one solid surface of said metallic substrate; and
iii) mechanically forcing the metallic substrate formed in step ii) through said aperture bounded by at least one metal working tool surface, so that the metallic substrate is cold worked.

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EUROPEAN SEARCH REPORT

Application Number
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Place of search	Date of completion of the search	Examiner
Munich	20 April 2022	Pöllmann, Klaus

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