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(54) **Metal Working Fluid**

Metallbearbeitungsfluid

Fluide de travail de métal

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Description

[0001] The present invention relates to the field of water-based metalworking compositions.

5 TECHNICAL FIELD

[0002] The invention relates especially to aqueous, environmentally friendly, recyclable, synthetic, amine-free, petroleum oil-free and VOC-free metalworking compositions which are to a high extent free of hazardous materials and which are compatible with a wide range of metal alloys.

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BACKGROUND OF THE INVENTION

[0003] Metalworking compositions are employed in many metal treatment operations such as cutting, grinding, forming, lapping, drawing, forming, pressing, punching, rolling, stamping and others to lubricate and to cool the metalworking tool, to flush off the metallic chips and impurities if there should be some from the workpiece and to protect the tool and parts of a machine from damage, wear and corrosion as far as possible. Such treatments comprise cutting operations showing a metal removal like grinding, turning, milling, tapping, broaching and hobbing as well as forming operations showing mostly no metal removal like bending, hot and cold rolling, drawing, forging, stamping and blanking. The metalworking compositions may assist to flush away oil and debris from these metallic components. And they shall provide to these components corrosion protection.

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[0004] The main classes of metalworking compositions are the straight oil type and the water-based type.

[0005] The water-based types may be further differentiated into the following types:

A) Soluble oils contain typically at least 70 % by weight of petroleum oil, emulsifiers, any lubricity additive, alkanolamine and less than 2 % by weight of water.

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B) Semi-synthetic fluids contain typically 5 to 60 % by weight of petroleum oil, a high content of emulsifiers, any lubricity additive, alkanolamine and 10 to 60 % by weight of water. The disadvantages of the semi-synthetic fluids are the low heat capacity so that they have a low cooling effect, the poor emulsion stability, the often occurring bacterial growth and the problems of cleanability of petroleum oil residues.

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C) Synthetic fluids are petroleum oil-free and contain typically any water-soluble lubricity additive like a mixture of water-soluble short-chain carboxylic acids, water-soluble polyalkylene glycols and water-soluble EO/PO block copolymers, further on any water-soluble corrosion inhibitor, alkanolamine for corrosion inhibition and for pH buffering capability and a very high content of water. The synthetic metalworking compositions C) have the advantage of not having the cleaning issues of petroleum oils, having good hard water stability and microbial control, and a long sump life. But the drawbacks of the existing synthetic metalworking compositions are typically problems in the cleaning of residues caused by lubricity additives added, in the reduced lubricity when compared to petroleum oil-containing products on an equal cost basis, in the increased sump and machine maintenance corrosion issues, and in the potential for skin irritation to the workers.

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D) Neo-synthetic fluids use vegetable oil and/or animal oil instead of petroleum oil and contain typically additionally any emulsifiers, corrosion inhibitors, alkanolamine and a content of water. But they typically have only a medium high lubricity and have the disadvantages that the emulsions are often very unstable and that there is very often bacterial growth.

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[0006] In the state of the art, many metalworking compositions are petroleum oil-based dispersions or emulsions of water and oil. Today, more than 80 % of metalworking operations are performed with petroleum oil rich metal working compositions. But a content of petroleum oil in any metalworking composition causes several problems like the following: 1.) poor heat conductivity so that there is a lower cooling effect, 2.) it enables microbial growth and may harm workers, 3.) petroleum oil causes misting and residues that are difficult to be cleaned off, 4.) disposal problems and not environmentally friendly and 5.) water hardness may impact the emulsion stability. Therefore, there is the need to further develop petroleum oil-free metalworking compositions. Therefore, industry is turning toward the use of water-based metalworking compositions.

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[0007] Alkanolamines have the disadvantages that some of these are very hazardous compounds and environmentally unfriendly, that some of these cause a high volatile organic content VOC and that some of these cause irritations and illness of the skin and body. Further on, these compounds may lead to strong smelling.

[0008] The lubricity and stability of synthetic petroleum oil-free metalworking compositions in the market is still quite limited. Industry is still searching for better products that are better lubricating, that are better and longer stable and have a less amount of hazardous compounds.

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[0009] In addition, a metalworking composition should be capable of sequestering and removing debris, contaminants

and oils from the metallic components and should provide good corrosion protection to all metallic components. But further on, such compositions are often micro-emulsions or macro-emulsions, which need to be stable not to split the emulsion as far as possible, at the same time as a concentrate and as a dilution which has been gained by diluting the concentrate with a low or a high amount of water. The more severe a metalworking operation is, the higher should be the concentration of the metalworking composition applied. For metalworking operations of low requirements like a grinding, a dilution to 5 % by weight of the metalworking composition may be sufficient. For metalworking operations of medium severe requirements, a dilution to 10 to 15 % by weight of the metalworking composition should be used. Further on, these compositions need to be non-foaming or low foaming compositions, when used for any metalworking operation. And these compositions should be more and more environmentally friendly. In the last years, several amine-containing metalworking compositions were used, as the amines and especially the alkanolamines help in bio-resistance, corrosion protection and emulsion stability, but several amines are very toxic and participate in volatile organic compounds VOC too. The formulation of aqueous metalworking compositions without using any amine is much more difficult. For universal application of one metalworking composition, the coverage of the whole range of properties and chances is expected.

[0010] As will be described in the following, the present invention is directed to an aqueous metalworking composition which provides very good lubricity without the aid of any petroleum oil for all kinds of metallic materials and very good stability. As the different metalworking compositions have been tested for an aluminum based metallic material and for a steel, it is believed that these tested materials represent a vast majority of different metallic materials, if not even all kinds of metallic materials, so as to fulfil multi-metal purposes. The metalworking compositions of the present invention are therefore compatible with, and non-corrosive toward, a wide variety of metals and alloys. They remove petroleum oils, dirt and debris well from the metallic components. They are environmentally friendly, low foaming, corrosion protecting, recyclable, long time usable and may be resistant to biological growth.

[0011] Further on, such compositions may be used for cold forming operations, wherein cold forming includes: slide drawing (forming under a combination of tensile and compressive conditions), e.g. of welded or seamless tubes, hollow profiles, rods, solid profiles or wires, ironing and/or deep drawing, e.g. of strips, sheets or hollow parts to form hollow parts, cold extrusion (forming under compressive conditions), e.g. of hollow or solid parts and/or cold heading, e.g. of wire sections to form joining elements such as e.g. nut or screw blanks.

[0012] US 7,018,959 B2 discloses a water-based, recyclable metalworking fluid which comprises an aqueous solution of a polyalkylene glycol, an alkanolamine, a polyglycol surfactant, a polyol surfactant, a biocide package and a corrosion inhibitor.

[0013] US 2009/0149359 A1 concerns compositions and constituents for aqueous metalworking compositions, but any details are only described to a certain extent in the examples. The pH of these compositions shall be at least 3, but acidic pH values are only acceptable for aluminum based metallic materials and not for steels. The use of aqueous metalworking compositions for steels is much more complicated than for aluminum based metallic materials and often requires high pH values. The best properties gained are disclosed for sample C, which will be compared in this application in Table 4 too. This publication indicates the use of amines and even of alkanolamines as well as of many other compounds.

[0014] An object of the present application is to propose an environmentally friendly metalworking composition which shows high lubricity, a high stability and a good corrosion protection.

[0015] Another object of the present application is to propose a composition that is well usable for multi-metal metalworking operations. Further on, there is an object to propose a method to prepare a stable metalworking emulsion.

[0016] It has been found that the properties of aqueous metalworking compositions based on the teaching of US 2009/0149359 A1 need to be further modified and optimized, as these compositions seem to be only good on aluminum based materials and as is disclosed in detail in present Table 4.

SUMMARY OF THE INVENTION

[0017] The aqueous metalworking composition of the present invention is an aqueous metalworking composition according to claim 1.

[0018] The present invention relates further to a method to prepare an aqueous metalworking composition by first adding to water any compounds (b) and (d), then adding any compounds (a) and afterwards then (c), during which mixing procedure until here a heating to temperatures in the range of from 30 to 50 °C and an agitation is used, and optionally then all other compounds are added.

[0019] The present invention relates further to a method of use of an aqueous metalworking composition of the present invention as a coolant, as a lubricant and/or for bending, for blanking, for boring, for broaching, for cooling, for cutting, for drawing, for drilling, for forging, for grinding, for hobbing, for honing, for hydroforming, for lapping, for lubricating, for forming, for milling, for pressing, for punching, for reaming, for cold rolling, for hot rolling, for sawing, for stamping, for tapping, for threading, for turning or for any combination thereof.

[0020] The present invention relates finally to a metalworking process characterized in that the metalworking operation is performed by flushing, spraying, high pressure spraying, brushing, flowing, fluting, roll coating, immersion or any

combination thereof with the aqueous metalworking composition of the invention.

DETAILED DESCRIPTION

5 [0021] Preferably, the aqueous metalworking composition of the invention is of low VOC, which typically means a content of volatile organic compounds of less than 1 % by weight. More preferred, the aqueous metalworking composition of the invention is of zero-VOC or is preferably petroleum oil-free or is preferably alkanolamine-free or is amine-free or is preferably free of any combination thereof, at least until start of its application in a metalworking operation.

10 [0022] "VOC" means "volatile organic compounds" and comprises in praxis petroleum oil and specifically low-molecular weight petroleum oil, organic solvents and alkanolamines. Most preferred, the metalworking composition is in many embodiments even amine-free or there is not added any amine intentionally during formulation and preparation of the metalworking composition, at least until start of its application in a metalworking operation. In seldom embodiments, the metalworking composition of the present application may comprise an alkanolamine or an alkyl amine or an oil content or any combination thereof in a total content in the range of from 0.01 to less than 5 % by weight or in such a content
15 that the test method of Environmental Protection Agent of US government EPA24 does not allow to detect a content of VOC. But in reality, minor traces of amines could sometimes not be avoided in case that they are contained in traces in any raw materials that are mixtures or if there is an impurity in the process or if a metalworking composition is used for longer time or is recycled or any combination thereof. Even if there should be a small content of an amine like an alkanolamine or alkyl amine or of any other amine based substance or of an oil or of any combination thereof, it has
20 been found that the VOC tested according to EPA24 does nevertheless often not allow to detect a content of VOC. Then, there is sometimes no need to be amine-free, alkanolamine-free, petroleum oil-free or oil-free or free of any such combination. Further on, it is preferred that the aqueous metalworking composition is free from any ammonium content and of ammonia, at least until start of its application. Preferably, the compositions are substantially free or totally free of organic solvents, of strongly acidic compounds, of waxes, of chlorinated fatty acids and their esters with chain lengths
25 $\leq C_{12}$ and/or of heavy metals like chromium and nickel.

[0023] Preferably, the composition has a pH in the range of from 5 to 14, more preferred of from 7 to 13.5 or of from 8 to 13 or of 9 to 12 or of 10 to 11 in general, for a concentrate as well as for a diluted composition. But even at a pH > 13, no technical problem occurs with a metalworking composition. Most compositions are therefore slightly or strongly
30 alkaline. The alkalinity may be necessary for corrosion protection, for emulsification and emulsion stability and for biostability. The pH value respectively the degree of alkalinity does often not influence the stability or lubricity of the aqueous metalworking composition. If there is a low pH, this may result in corrosion and rusts on the parts and on machines and in the growth of bacteria. The alkalinity of the composition is mostly caused by the addition of at least one compound of an alkalinity agent (d). A low alkalinity corresponds to a low pH. At a pH of 5 to 6, the composition may have a good lubricity especially on aluminum based metallic parts, but a very bad corrosion protection. Any pH value significantly
35 lower than optimum may increase the danger of phase separation in a metalworking emulsion, and therefore of inconsistent lubricating action. At a pH of 13 to 14, the composition may have a good corrosion protection and a good lubricity on metallic materials that do not show alkaline attack, but aluminum, zinc and their alloys may be dissolved at a pH greater than 12. The best results are often gained with a pH in the range of from 7 to 10.

[0024] The chemical compounds may be applied in the aqueous metalworking composition independently one to the other in ionic, unstable or stable, hypothetical, unreacted and/or any reacted form of any other chemical species defined
40 by number and type of atoms present, as well as in compounds with well defined molecules.

[0025] The present invention relates to an aqueous metalworking composition comprising in a concentrate or after dilution of a concentrate with water in a diluent at least one compound of each class of compounds from the components (a), (b), (c), (d) and (e): A first necessary ingredient of the composition according to this invention is its primary lubricity
45 imparting **component (a)**, which contains the primarily lubricity imparting compounds. The compounds (a) are water-insoluble. Mostly, the compounds (a) spend additionally good corrosion resistance and good emulsification.

[0026] There are several different ways how to add or how to prepare a lubricity imparting mixture: Preferably, However, a vegetable oil respectively an animal oil contains a mixture of quite different carboxylic acids and their derivatives. Such oil(s) may be independently one to the other be purified, refined, conditioned, chemically modified, synthesized or
50 prepared by any combination thereof. Additionally, there is added to the metalworking composition at least one specific compound (a) or at least one chemical product having a compound (a) as main compound and optionally any other compound (a). The metalworking composition comprises at least two or at least three or at least four different specific compounds (a). This enables chances for synergistic property effects.

[0027] Component (a) is contained in a range of from 6 to 40 % by weight. Preferably, component (a) is contained in a range of from 6 to 36 % by weight or of from 6 to 32 % by weight or of from 6 to 28 % by weight or of from 6 to 24 %
55 by weight or of from 6 to 20 % by weight or of from 6 to 17 % by weight or of from 6 to 14 % by weight or of from 6 to 12 % by weight or of from 6 to 10 % by weight or of from 6 to 8 % by weight, independently if it is a concentrate or a dilution. If there would be a lower content of component (a), the metalworking composition would not be effective, but if

it would have a higher content, it would often not be a stable composition.

[0028] The compounds of component (a) are selected from the group of compounds consisting of compounds (a1), (a2) and/or (a3). Compounds (a1), (a2) and/or (a3) may optionally be assisted by an addition of an optional compound A.

[0029] The metalworking composition contains at least one compound (a1) as defined in claim 1.

[0030] Compounds (a1) are fatty acids and are selected from the group consisting of lauric/dodecanoic acid, myristic/tetradecanoic/myristoleic acid, pentadecanoic acid, palmitic/hexadecanoic/palmitoleic/hexadecapolyenoic acid, margaric/margaroleic acid, ricinoleic acid, stearic/octadecanoic acid, linoleic/eicosanoic acid, oleic acid, linoleic/linolenic/octadecatetraenoic acid, arachidic/gadoleic/eicosadienoic/arachidonic/eicosapentaenoic acid, heneicosanoic acid, behenic/docosanoic/erucic/docosapolyenoic acid, docosahexaenoic acid and lignoceric acid. The respective derivatives of carboxylic acids (a1) belonging to the compounds (a3) preferably have 12 to 26 or 16 to 22 carbon atoms per chain.

[0031] A more preferred base spend e.g. oleic acid or similar compounds (a1) as contained with an essential content e.g. in rapeseed oil, castor oil, coconut oil, soybean oil, sunflower oil, lard oil or any combination thereof. If the number of carbon atoms of such oil or compound would be lower than 12 per chain, it may occur that these compounds are not effectively in lubricity, but if the number of carbon atoms would be higher than 24 per chain, it may occur that the metalworking composition is no stable composition.

[0032] For example, oleic acid has 18 carbon atoms. For example, castor oil contains in about 85 to 95 % by weight of ricinoleic acid, which has 18 carbon atoms too. Since castor oil exists as a triglyceride, which ester may be based on one glycerol unit with three ricinoleic acid units, the total number of carbon atoms in castor oil is often of about 57. Another common vegetable oil which may be used as lubricity additive is rapeseed oil. Often in about 41 % by weight of rapeseed oil is erucic acid. The total number of carbon atoms of the triglyceride of erucic acid is 69.

[0033] The aqueous metalworking composition of the invention comprises preferably at least one triglyceride (a2) as defined in claim 1.

[0034] Especially preferred derivatives (a3) of (a2) are esters.

[0035] The triglycerides show side-chains that are identical or different independently one to the other and the fatty acids of the triglycerides have independently one to the other a "medium chain length" or a "long chain length". Such chains are called to be of "medium chain length" or of "long chain length" if they contain 6 to 12 carbon atoms respectively 14 to 24 carbon atoms independently one to the other. A triglyceride is an ester derived from glycerol and three fatty acids. It is the main constituent of vegetable oil and animal fats. A specific example of an unsaturated fat triglyceride is based on glycerol and on the other side of palmitic acid, oleic acid and alpha-linolenic acid, C₅₅H₉₈O₆. Triglycerides are triesters of glycerin. The water-insoluble triglycerides (a2) as defined in claim 1 are triglycerides of three identical or two or three different carboxylic acids and especially triesters based on oleic acid, stearic acid, ricinoleic acid, erucic acid, lignoceric acid and/or lauric acid.

[0036] The metalworking composition contains at least one compound (a3) as defined in claim 1, which is a derivative of compound (a1) or (a2) or both and has independently one to the other 12 to 5.000 carbon atoms.

[0037] Preferred derivatives (a3) are chlorinated or sulfurized derivatives - which may optionally be used as extreme pressure additives too -, esters, ethers, ethoxylates, ethoxylate-propoxylates, propoxylates, alkali metal salts, alkaline earth metal salts and/or compounds having been condensed with at least one carboxylic acid like ricinoleic acid. More preferred derivatives are esters, ethoxylates, ethoxylate-propoxylates and/or propoxylates. Preferably, the derivatives have of from 14 to 170 or of from 16 to 130 or of from 18 to 100 or of from 20 to 70 or of from 22 to 52 or of from 24 to 42 carbon atoms. Specific examples of such derivatives are ricinoleic acid ester and polymerized ricinoleic acid ester, which last one may be a condensation product of about four molecules. As examples for triglycerides ethoxylated castor oil, castor oil each having 12 to 120 carbon atoms, may be used.

[0038] Preferably, the lubricity imparting compound(s) (a) has/have a water-solubility at 20 °C of less than 0.05 g/liter or of less than 0.001 g/liter. As the particular cations present in a salt of the compounds (a) is not believed to have any significant effect on the performance obtained, the concentration of the cation is not further specified. Preferably, these cations are selected from alkali metals and alkaline earth metals. As cations, sodium and potassium are most preferred, but others may be used too. The degree of neutralization or of ionization of the acid or of the salt may change in the process of preparation, dilution or application in the actual metalworking composition. All these different conditions are included within the general measures of the invention.

[0039] Another necessary ingredient of the composition according to this invention is a **component (b)** comprising at least one water-soluble corrosion inhibiting compound (b) as defined in claim 1. Preferably, the metalworking composition contains 0.002 to 30 % by weight of component (b) comprising at least one water-soluble corrosion inhibiting compound (b) which has a water-solubility at 20 °C of more than 0.1 g/liter. More preferred, the water-soluble corrosion inhibiting compound(s) (b) has/have a water-solubility at 20 °C of more than 0.5 g/liter or of more than 1 g/liter or of more than 5 g/liter. The water-soluble compounds (b) contribute to the bio-stability of the aqueous metalworking compositions. The water-soluble compounds (b1) and (b3) to (b5) may aid in the metalworking composition to improve stability of the emulsion.

[0040] Preferably, component (b) or the at least one compound (b) is contained in a range of from 0.1 to 36 % by

weight or of from 0.3 to 32 % by weight or of from 0.7 to 28 % by weight or of from 1 to 24 % by weight or of from 1.5 to 20 % by weight or of from 2 to 17 % by weight or of from 3 to 14 % by weight or of from 4 to 12 % by weight or of from 5 to 10 % by weight or of from 6 to 8 % by weight, independently if it is a concentrate or a dilution. If the content of the metalworking composition of the at least one corrosion inhibiting compound (b) would be lower, it may occur that the component (b) is not effective, but if it would have a higher content, it may occur that the metalworking composition is no stable composition. In many cases, it will be preferred to add to the metalworking composition two, three or four different specific compounds (b) or two, three or four different chemical products having each a compound (b) as their main compound. Preferably, the corrosion inhibiting component (b) contains at least two or at least three or at least four different compounds (b), especially to optimize corrosion protection. As such mixture of corrosion inhibiting compounds may enhance the corrosion protection effect strongly without adding a too high amount of such compounds. Such mixtures enable chances for synergistic property effects.

[0041] The metalworking composition contains at least one corrosion inhibiting compound (b) which is selected from the group consisting of more or less well water-soluble compounds (b1).

[0042] The metalworking composition contains at least one compound (b1), which is a straight and/or branched, a saturated and/or unsaturated water-soluble compound and which has in total 6 to 40 carbon atoms and having chain lengths of 4 to 12 carbon atoms. More preferred, the compounds (b1) have independently one to the other 6 to 10 or 6 to 8 carbon atoms per aliphatic chain. The compounds (b1) are selected from the group of compounds consisting of monocarboxylic acids, dicarboxylic acids, tricarboxylic acids and polycarboxylic acids and their alkali metal salts and alkaline earth metal salts. Preferably, there are monocarboxylic acids, dicarboxylic acids and/or their derivatives used. For example, the water solubility of C8-monocarboxylic acid (caprylic acid) in water at 20 °C is 0.7 g/liter.

[0043] The following compounds (b2)-(b5) may optionally be present in the composition but are not counted as (b) compounds with respect to the type and amount of (b) required by claim 1.

[0044] Preferred compounds (b2) are boric acid, its salts like its alkali metal salts and its alkaline earth metal salts and boric acid esters. A boric compound (b2) may in addition assist in bio-stability.

[0045] Preferred compounds (b3) are imidazoles, imidazolines and their derivatives like their esters and salts, especially like their alkali metal salts and alkaline earth metal salts, for example benzimidazoles and their salts.

[0046] The preferred thiazoles and their derivatives (b4) comprise especially their alkali metal salts, alkaline earth metal salts and esters, for example benzothiazoles, mercaptobenzothiazoles and their salts and esters.

[0047] The preferred triazoles and their derivatives (b5) comprise especially their salts and esters and as examples benzotriazoles, tolyltriazole $C_7H_7N_3$, and their derivatives as well as alkali metal salts, alkaline earth metal salts and esters of triazoles.

[0048] Another necessary ingredient of the composition according to this invention is a **component (c)** containing at least one emulsifying and/or dispersing compound (c) as defined in claim 1. The metalworking composition contains 0.002 to 45 % by weight of **at least one emulsifying and dispersing agent (c)** which contains at least one emulsifying and/or dispersing compound (c) which is water-soluble, water-miscible or water-dispersable and which is selected from the group consisting of non-ionic, anionic and zwitterionic surfactants and which may be in some instances even corrosion inhibiting. As the compounds (a) and (b) often are hydrophobic, the composition would separate into droplets or even bigger drops or layers or any combination thereof, if no emulsifying and dispersing agent is added.

[0049] If there would be used a lower content of component (c), then the metalworking composition would not be effective, but if it would have a higher content, then it would often not be a stable composition. Preferably, the emulsifying agent and dispersing agent (c) is contained in the metalworking composition of the invention in a range of from 0.01 to 40 % by weight or of from 0.05 to 35 % by weight or of from 0.1 to 32 % by weight or of from 0.5 to 25 % by weight or of from 1 to 20 % by weight or of from 3 to 15 % by weight or of from 5 to 12 % by weight, independently if it is a concentrate or a dilution.

[0050] Preferably, the emulsifying agent and dispersing agent (c) has a HLB in the range of from 1 to 40 or of from 6 to 24 or of from 8 to 16 or of from 10 to 12. Preferably, the emulsifying agent and dispersing agent (c) is selected from surfactants that all have a HLB value in the range of from 1 to 40 or of from 6 to 24 or of from 8 to 16 or of from 10 to 12. Preferably, the individual emulsifying and/or dispersing compounds (c) have a HLB value in the range of from 1 to 40 or of from 6 to 24 or of from 8 to 16 or of from 10 to 12. Preferably, the emulsifying and dispersing agent (c) contains at least two or at least three or at least four different compounds (c), especially to gain a broad distribution of HLB within one composition. Such combination of different compounds (c) offers chances to synergistic effects.

[0051] If the aqueous metalworking composition has an insufficient emulsifying effect, the emulsion may easily split into two or more layers one above the other. If the aqueous metalworking composition has an inadequate emulsifying effect because of wrong HLB range e.g. despite of adding a high amount of compound(s) (c), the emulsion may easily split into two or more layers one above the other. If the aqueous metalworking composition has a too high emulsifying effect, the emulsion may have a significantly lowered lubricity, may be high foaming and may have an insufficient corrosion protection effect.

[0052] The at least one emulsifying and/or dispersing compound (c) is selected from the group of non-ionic, anionic

and zwitterionic surfactants consisting of:

- (c1) alkyl alcohols,
- (c2) alkyl phenols,
- 5 • (c3) alkanolic acids, fatty acids, ether carboxylates and/or other organic acids,
- (c4) block and random copolymers,
- (c5) alkyl polyglucosides,
- (c6) anionic surfactants having at least one sulfate or sulfonate group,
- (c7) ether sulfates,
- 10 • (c8) ether phosphates,
- (c9) phosphate esters,
- (c10) monoglycerides,
- (c12) fatty amines,
- (c13) sorbitan and its derivatives, and
- 15 • (c14) succinic acid and its derivatives

as defined in claim 1.

[0053] Preferably, these surfactants are selected one to the other independently to be ethoxylated or ethoxylated-propoxylated and without or with end-group capping.

20 **[0054]** The at least one emulsifying and/or dispersing compound (c) is selected from the group of non-ionic, anionic and zwitterionic surfactants consisting of:

(c1) ethoxylated alkyl alcohols, ethoxylated-propoxylated alkyl alcohols, ethoxylated alkyl alcohols with end-group capping and ethoxylated-propoxylated alkyl alcohols with end-group capping, and especially, the alkyl group of the
25 alkyl alcohols is saturated or unsaturated and has an average number of carbon atoms ranging from 4 to 24 and has either a linear or a branched chain structure;

(c2) ethoxylated alkyl phenols, ethoxylated-propoxylated alkyl phenols, ethoxylated alkyl phenols with end-group capping and ethoxylated-propoxylated alkyl phenols with end-group capping, and especially, the alkyl group of the
30 alkyl phenols - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 18 and has either a linear or a branched chain structure;

(c3) ethoxylated or ethoxylated-propoxylated alkanolic acids, ethoxylated or ethoxylated-propoxylated fatty acids and/or other ethoxylated or ethoxylated-propoxylated organic acids such as terpene acids, e.g. abietic acid, and especially, the alkyl acids have an alkyl radical - saturated, unsaturated and/or cyclic - which has an average number
35 of carbon atoms ranging from 4 to 24 and which has a linear or branched chain structure;

(c4) block copolymers containing at least one polyethylene oxide block and at least one polypropylene oxide block as well as random copolymers, and especially, the block copolymers have a polyethylene oxide block which comprises an average number of 2 to 100 ethylene oxide units and a polypropylene oxide block which comprises an
40 average number of 2 to 100 propylene oxide units, and optionally, the molecule contains one or more polyethylene oxide blocks or polypropylene oxide blocks independently of one another, wherein some of these block copolymers may contribute to lubricity of the composition too, wherein these block copolymers may sometimes have antifoaming and defoaming properties too;

(c5) alkyl polyglucosides whose alkyl group - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 18 and either a linear or a branched chain structure, and has an average of 1 to 5 units of at least one sugar, and optionally, the units of the sugar(s) are glucosidically linked to the alkyl group, wherein the term
"sugar" is understood to include all saccharides and all other sugar-like compounds;

(c6) anionic surfactants whose alkyl group - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 24 and either a linear or a branched chain structure, and optionally, the alkyl moiety has one or more aromatic groups, and especially, there is at least one sulfate or sulfonate group present in the molecule, wherein the alkyl alcohol chain preferably has an average number of 10 to 14 carbon atoms and wherein benzene
55 is preferably incorporated as the aromatic group;

(c7) ether sulfates whose ethoxylated alkyl alcohols or ethoxylated-propoxylated alkyl alcohols have a sulfate group, and especially, the alkyl group of the alkyl alcohols - saturated or unsaturated - ha an average number of carbon

atoms ranging from 4 to 24 and either a linear or a branched chain structure, wherein optionally, the ethylene oxide chain has an average number of 2 to 30 ethylene oxide units and further on optionally, the propylene oxide chain has an average number of 1 to 25 propylene oxide units and wherein the alkyl moiety has optionally one or more aromatic and/or phenolic groups;

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(c8) ether phosphates whose ethoxylated alkyl alcohols or ethoxylated-propoxylated alkyl alcohols have a phosphate group, and especially, the alkyl group of the alkyl alcohols - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 24 and either a linear or a branched chain structure, and optionally, the ethylene oxide chain has an average number of 2 to 30 ethylene oxide units and optionally, the propylene oxide chain has an average number of 1 to 25 propylene oxide units, wherein the alkyl moiety has optionally one or more aromatic and/or phenolic groups;

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(c9) phosphate esters whose one or two alkyl groups - saturated or unsaturated - have independently of one another an average number of carbon atoms ranging from 4 to 24 and either a linear or a branched chain structure, and optionally, the alkyl moiety has one or more aromatic and/or phenolic groups, wherein there is one phosphate group present in the molecule;

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(c10) monoglycerides ethoxylated, propoxylated, ethoxylated-propoxylated or ethoxylated especially with closed end-groups, wherein these monoglycerides may sometimes have antifoaming and defoaming properties too;

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(c12) fatty amines as well as fatty amines ethoxylated, propoxylated, ethoxylated-propoxylated or ethoxylated especially with closed end-groups;

(c13) sorbitan and sorbitan derivatives comprise sorbitans ethoxylated, propoxylated, ethoxylated-propoxylated or ethoxylated with closed end-groups as well as for example polysorbates, sorbitan oleates as well as their derivatives;

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(c14) succinic acid and derivatives of succinic acid comprise their esters and salts as well as for example alkyl-succinates, hydrogensuccinates, sulfosuccinates, succinamates, sulfosuccinamates as well as their derivatives.

[0055] Preferably, the emulsifying compound or dispersing compound or both (c) is selected from non-ionic surfactants having 1 to 20 units of the sum of EO groups or from non-ionic surfactants having 2 to 40 units of the sum of EO and PO groups. The higher the number of EO groups is, the more it is an emulsifying agent, the smaller it is, the more it is a dispersing agent.

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[0056] The at least one emulsifying and/or dispersing compound (c) shall aid in dispersing a second phase in an aqueous phase, in distributing solid particles, in stabilizing the dispersions and shall aid - if needed - in forming an emulsion. The term dispersion shall include here emulsions and solutions. Most preferred, such compound (c) is used as emulsifier or dispersant or both. Therefore, it may in many embodiments helpful to add at least two or at least three different surfactants, of which the first one acts primarily as an emulsifier and at least one other primarily as dispersant respectively as a defoamer. This enables chances for synergistic property effects.

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[0057] Further on, there is a need to add an **alkalinity agent (d)** containing at least one alkaline water-soluble compound (d) as defined in claim 1. The alkalinity agent contributes to a higher stability of the emulsion and in the corrosion resistance and often in the bio-stability too. The alkalinity assists that e.g. anionic surfactants may become be more stable.

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[0058] If the metalworking composition would not be sufficient alkaline, then the emulsion would not be stable enough, so that lubricity will be lowered or even go lost, the corrosion resistance may then be low too and microbial resistance will be lowered too. and that a metalworking composition gains a better corrosion protection and it may occur that an emulsifying agent does not work. If the alkalinity would be too high, the human skin of a worker may become irritated. It is in some embodiments preferred that the aqueous metalworking composition shall not have a pH higher than 12, but the concentrate may be much more alkaline. In some embodiments, a pH of about 14 does not disturb.

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[0059] The metalworking composition contains 0.002 to 30 % by weight of an alkalinity agent (d) comprising at least one alkaline water-soluble compound (d1) selected from the group consisting of hydroxides and carbonates. But nevertheless in seldom embodiments, there may be even added a small amount of an alkanolamine or of an alkyl amine or of both, which may be selected from the group consisting of primary alkanolamines like amino-methyl propanol AMP, diglycolamine DGA, methanolamine MEA and monoisopropylamine MIPA, of secondary alkanolamines like diethanolamine DEA und diisopropanolamine DIPA and N-butylethanol amine nBEA, of tertiary alkanolamines like triethanol amine TEA and n-butyl-diethanolamine nBDEA and of alkyl amines having an alkyl chain of 1 to 10 carbon atoms and 1 to 3 OH groups like dicyclic hexylamine DCHA. Such content of an alkanolamine or of an alkyl amine or of both is preferably in the range of from 0.01 to less than 5 % by weight or of from 0.1 to less than 2 % by weight or of from 0.2 to 0.8 % by weight. Preferably, the alkalinity agent (d) is contained in a range of from 0.01 to 25 % by weight or of from

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0.1 to 20 % by weight or of from 1 to 15 % by weight or of from 3 to 12 % by weight.

[0060] If there would be a lower content of the alkalinity agent (d), the corrosion protection may be insufficient, but if higher content, the lubricity may be too low and the alkaline sensitive metallic materials may be chemically attacked and dissolved. Preferably, the at least one alkalinity compound (d) is added in an amount as to reach a predetermined pH value.

[0061] More preferred, the alkalinity agent (d) is selected from hydroxides and carbonates of alkali metals and of alkaline earth metals (d1), for example potassium hydroxide, sodium hydroxide, a potassium carbonate, a sodium carbonate or any mixture of these. Sodium and potassium compounds are the most preferred alkalinity agents. It will be apparent to those skilled in the art that many other alkalinity agents could be used in alternative thereto. But amounts for example of alkanolamines and/or often of all kinds of amines may lead to high VOC, to the irritation of human skin coming in contact with such composition and may generate strong smelling. Therefore the alkanolamines and/or often of all kinds of amines are therefore undesirable.

[0062] Finally, a **transport component (e)** has to be added to the mixture, which contains at least water. At least 0.004 % or at least 0.01 % by weight of a transport component (e) contains at least 98 % by weight of water. Primarily, predominantly, nearly totally or only water is the liquid compound contained in the metal working composition as the transport component (e) or as water. Normally, a metalworking composition has a content of much more than 5 and until about 60 % by weight of a petroleum oil. For the present invention, there is preferably no addition of a petroleum oil or only of a content of up to 1 or up to 3 % by weight to the metalworking composition, as a content until start of its application for metalworking. A petroleum oil-free metalworking composition, which composition may be only polluted with any petroleum oil by its use in any metalworking operation, is especially preferred. In such a situation, the metalworking composition would be often only petroleum oil-free until a first application. If there is no content of a petroleum oil, the composition is in many embodiments of zero VOC; typically in most conventional metalworking compositions, they have a content of any of the compounds based on alkanolamines such as triethanolamine, on organic solvents, on petroleum oils and on low molecular weight petroleum oils, all causing a medium or often high value of volatile organic compounds VOC.

[0063] The transport component (e) may comprise in seldom embodiments even a small content of an organic solvent like an alcohol. The aqueous metalworking composition may then contain seldom more than 1 % by weight of an alcohol. But mostly, such solvents are not added intentionally, but may be contained in raw materials or are impurities in the process. It has been found that if any amounts of petroleum oil or of organic solvent are added, most compositions become unstable so that different types of emulsifiers are needed. On the other hand, it is preferred to work VOC-free and to a high extent environmentally friendly, so that it is preferred - depending on the use of the metalworking compositions and requirements - to avoid any content, any addition or an amount of petroleum oil or any organic solvent of more than 5 or 3 or 1 % by weight. Further on, for its use as synthetic coolant, the metalworking composition should not contain any petroleum oil or any organic solvent.

[0064] The aqueous metalworking composition of the invention, wherein at least 98 % by weight of the transport component (e) is water, wherein this is calculated such that the whole transport component (e) sums up to 100 % by weight. In embodiments, the water content of the transport agent (e) is higher like e.g. at least 99 % by weight. It is generally desirable to avoid the use of any organic solvents, especially of flammable solvents and solvents classified as volatile organic compounds.

[0065] For a composition that is a concentrate, the content of the transport agent (e) in the metalworking composition is preferably in a range of from 0.1 to 90 % by weight or in a range of from 1 to 80 % and especially preferred of from 10 to 70 or of from 20 to 60 % by weight. Often, its content in a concentrate is in a range of from 30 to 50 or of from 35 to 45 % by weight. Such compositions show typically a pH in the range of from 6 to 13 or of from 7 to 12. Of course, a concentrate does not need to be diluted before its use.

[0066] The diluted compositions are prepared by adding water. These "dilutions" preferably have a water content in a range of from 20 to 99.5 % by weight or of from 30 to 99 % by weight or more preferred of from 40 to 98 % by weight, of from 50 to 96 % by weight, of from 60 to 94 % by weight, of from 70 to 92 % by weight or of from 80 to 90 % by weight. They often show a pH in the range of from 6.5 to 11.

[0067] The weight ratio of compounds of component (a) to such of component (b) or of compounds of component (a) to such of component (c) or of compounds of component (a) to such of component (d) is preferably in a range of from 1 : (0.5 to 2) or in a range of from 1 : (0.8 to 1.5) or in a range of from 1 : (0.8 to 1.3) or in a range of from 1 : (0.9 to 1) or nearby to 1 : 1. The same weight ratios are preferably applied for the compounds of component (b) to such of component (c) or of compounds of component (b) to such of component (d). The same weight ratios are preferably applied for the compounds of component (c) to such of component (d).

[0068] The aqueous metalworking composition of the invention has a weight ratio of compounds of component (a) to such of component (b) to such of component (c) in a range of from 1 : (0.5 to 2) : (0.2 to 3).

[0069] Preferably, the weight ratio of compounds of component (a) to such of component (b) to such of component (c) is in a range of from 1 : (0.8 to 1.5) : (0.3 to 1.8) or in a range of from 1 : (0.8 to 1.3) : (0.8 to 1.3) or in a range of from 1 : (0.9 to 1) : (0.9 to 1) or nearby to 1 : 1 : 1. Preferably, the weight ratio of compounds of component (a) to such

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of component (b) to such of component (c) and to such component (d) is in a range of from 1 : (0.5 to 2) : (0.2 to 3) : (0.2 to 1.5) or in a range of from 1 : (0.8 to 1.5) : (0.3 to 1.8) : (0.2.5 to 1) or of from 1 : (0.8 to 1.3) : (0.8 to 1.3) : (0.3 to 1.1) or nearby to a range of from 1 : (0.9 to 1) : (0.9 to 1) : (0.4 to 1).

[0070] In preferred embodiments of the invention, the components of the composition are selected and their relative proportions and concentrations adjusted so as to provide a single phase formulation or a two phase formulation.

[0071] It is preferred that diluted compositions have a total content of compounds (a) to (d) in a range of from 80 to 0.5 % by weight of from 70 to 1 % by weight, of from 60 to 2 % by weight, of from 50 to 4 % by weight, of from 40 to 6 % by weight, of from 30 to 8 % by weight or more preferred of from 20 to 10 % by weight.

[0072] Table 1 discloses some examples which indicate the more preferred variation of contents in concentrates and dilutions.

Table 1: Examples of content of the different components in some concentrates and dilutions according to the invention, wherein (e) is only water

Components in % by weight	(a)	(b)	(c)	(d)	(e)
Concentrate 1	30	30	30	5	5
Concentrate 2	30	20	20	10	20
Concentrate 3	15	15	15	15	40
Concentrate 4	10	10	10	10	60
Concentrate 5	8	4	6	2	80

[0073] More preferred, the metalworking composition contains or consists essentially of or consists of the following contents of components in a concentrate:

- (a), which is the sum of (a1), (a2) and/or (a3), in a content in a range of from 10 to 20 % by weight,
- (b), which is the sum of (b1) in a content of 5 to 10 % by weight,
- (c), which is the sum of (c1), (c2), (c3), (c4), (c5), (c6), (c7), (c8), (c9), (c10), (c12), (c13) and/or (c14), in a content in a range of from 10 to 20 % by weight,
- (d), which is the sum of (d1) in a content in a range of from 5 to 15 % by weight,
- (e) in a content in a range of from 70 to 25 % by weight and

optionally components like any component selected from the group consisting of A to D in a total content of zero or in a range of from 0.01 to 10 % by weight.

[0074] The aqueous metalworking composition of the invention may show different features, depending on its specific application and composition. Preferably, it is especially useful for multi-metal purposes and/or it is an emulsion with an average hydrophobic droplet size of hydrophobic droplets in a range of from 10 to 200 nm especially for the concentrates and which is an emulsion with an average droplet size of hydrophobic droplets in the range of from 10 nm to 30 μ m especially for dilutions.

[0075] The average droplet size of the metalworking emulsion may be adjusted to a wanted droplet size 1.) in an early stage by variation of the amount and type of emulsifying compound(s) (c) especially by their HLB values and 2.) before application for a metalworking operation by the degree of dilution with more or less water and by using pure or more or less hard water for the dilution. Then it is preferred to adapt the average droplet size to such size of about the average roughness R_a of a metallic surface to be metalworked. On the other hand by the control of the average droplet size, the degree of lubricity, the stability of the emulsion, the foaming degree, the corrosion resistance and/or the bio-stability are often influenced to better or worse quality. Therefore typically during a metalworking operation, any emulsifying and/or dispersing compound(s) (c) are replenished to the recycled metalworking composition to adjust the emulsification degree and other properties, e.g. as tank side addition.

[0076] Preferably, the composition of the invention is a dispersion, emulsion and/or solution at 25 °C. Most often, the concentrates as well as the diluents prepared from it are emulsions. Preferably at least 95 % by weight of the composition are in a liquid state at 25 °C.

[0077] For individual compounds of (a) to (d), these compounds can be at room temperature and at effective working temperature in a range for example of from 10 to 40 °C in the form of a liquid e.g. dissolved in water or a solid, typically at room temperature, although most of them are liquid at room temperature. Of course, a compound like KOH can be solid too, but will dissolve easily in water.

[0078] If a composition should contain particles like of a wax, these particles or more than 90 % of these are preferably

less than 100 nm.

[0079] If a composition contains a hydrophobic liquid in the form of drops, the average droplet size may vary between about 5 nm and about 80 μm . It has been found that droplets of an average droplet size bigger than 50 μm may lead to instability of the metalworking composition, so that the composition may easily split into two immiscible layers of liquids. It has been found that even average droplet sizes of more than 30 μm may lead to such instability. On the other hand, there may be a precipitation of any substance added, which may settle down and which precipitation should be avoided as far as possible.

[0080] In many cases, the metalworking composition according to the invention is an emulsion. There are generally two types of emulsions:

1.) There may be emulsions that are micro-emulsions or macro-emulsions, which show an average droplet size preferably from about 100 nm up to about 50 μm . The emulsion looks usually almost clear or translucent for an average droplet size in the range of from about 0.1 μm or about 0.15 μm to about 0.3 μm . If it is looking nearly translucent to light milky, it may be called to look hazy. It looks usually light milky for an average droplet size in the range of from about 0.3 μm to 1 μm . It looks usually milky for an average droplet size in the range of more than 1 μm . However, for stable emulsions, the average droplet size is often smaller than 30 μm .

2.) Micro-emulsions show often an average droplet size in a range of from 5 nm to 150 nm or in a range of from 20 nm to 100 nm. Nevertheless, the concentrates are micro-emulsions that look usually clear like a clear solution or are translucent. As concentrates that are not clear micro-emulsions are often not very stable, it is preferred that the concentrates are even clear micro-emulsions.

[0081] It has been found that if a concentrate is clear or translucent, it is a micro-emulsion and it is stable. If a concentrate looks hazy or very hazy or milky, the concentrate can be stable or can be unstable. For dilutions, it is not a problem if they do not look clear or translucent, but hazy or very hazy or milky. They may look clear or translucent, but they need not. They do not need to be clear or translucent micro- or macro-emulsions.

[0082] Mostly the aqueous metalworking compositions of the present invention are emulsions, which are as concentrates mostly micro-emulsions and which are as dilutions mostly micro- or macro-emulsions. The dilutions show often a stability such that there is no separation of any phase visible with the naked eye and that there is a clear or translucent micro-emulsion or a transparent, hazy or more or less milky macro-emulsion in a composition diluted with pure water or with hard water of up to 1200 ppm Ca content.

[0083] If the amount of component (a) is increased and/or if the amount of component (c) is decreased, there may sometimes be a change in the consistency of the metalworking composition from micro-emulsions to macro-emulsions; and vice-versa normally too. If the amount of any component (a), (b) and/or (c) is increased or is decreased, there may sometimes be a change in the consistency of the metalworking composition from micro-emulsions to macro-emulsions, too.

[0084] Most preferred, the metalworking compositions of the present invention comprise or consist essentially of or consist of the following combination of components: [(a1) and/or (a3)] and (b1) and (c3) and (d1) and (e), which are as concentrates preferably micro-emulsions or even clear micro-emulsions and which are as dilutions preferably micro- or macro-emulsions. Each component is herein represented by at least one substance added or contained or both. Most preferred, these components are contained in the following contents in a concentrate: [(a1) and/or (a3)] in a total content in a range of from 10 to 20 % by weight, (b1) in a content of 5 to 10 % by weight, (c3) in a content in a range of from 10 to 20 % by weight, (d1) in a total content in a range of from 5 to 15 % by weight, (e) in a content in a range of from 70 to 25 % by weight and optionally components like any component selected from the group consisting of A to D in a total content of zero or in a range of from 0.01 to 10 % by weight.

[0085] Preferably, an emulsion of a concentrate or of a dilution shows an average droplet size predominantly in a range of from 10 nm to 50 μm or more preferred in a range of from 50 nm to 10 μm . Reasonable ranges for the average droplet size are often in a range of from 0.15 to 50 microns or of from 0.15 micron to 30 microns. When a metalworking composition like a concentrate is diluted, a true solution, a clear micro-emulsion especially with an average droplet size in a range of from 5 to 150 nm or an emulsion (= macro-emulsion) especially with an average droplet size in a range of from 150 nm to 50 microns can be formed.

[0086] In the case that solid particles are contained in a metalworking composition, a dispersion (concentrate or dilution) shows preferably average particle sizes predominantly in a range of from 10 nm to 10 μm or more preferred in a range of from 50 nm to 1 μm . As solid compounds that may be present in a metalworking composition as particles a wax, grinding particles and/or lapping particles may be contained. But such solid particulate compounds are used very seldom and typically only in low amount.

[0087] The term "multi-metal purposes" means that the metalworking composition usually has good lubricity on at least two different metallic materials, which may preferably be selected from aluminum, magnesium, titanium, zinc, any

of their alloys, brass and steel. In the examples of the present application, a test for the lubricity is only performed on aluminum alloy(s) and steel(s), respectively. This test indicates the usability for different metallic materials well, if the lubricity test on aluminum and on steel gives good results.

[0088] Preferably, the aqueous metalworking composition often has a viscosity at 25 °C in a range of from 0.05 to 10 Pa·s or more preferred in a range of from 0.2 to 3 Pa·s.

[0089] The composition of the present invention may additionally include, if desired in seldom embodiments, one or more of **additives** selected from the group consisting of the **optional components A to D**.

[0090] The aqueous metalworking composition of the invention may preferably comprise additionally in total 0.002 to 60 % by weight of at least one optional compound selected from the group of optional components A to D. Component A may be contained in a content of 0 % by weight or in a range of from 0.002 to 30 % by weight or preferably in a range of from 1 to 20 % by weight. Component B may be contained in a content of 0 % by weight or in a range of from 0.002 to 5 % by weight in a range of from 0.1 to 2 % by weight. Component C may be contained in a content of 0 % by weight or in a range of from 0.002 to 3 % by weight in a range of from 0.1 to 1.5 % by weight. Component D may be contained in a content of 0 % by weight or in a range of from 0.002 to 30 % by weight or preferably in a range of from 1 to 20 % by weight.

[0091] Preferably, the aqueous metalworking composition comprises at least one optional **lubricity imparting component A** or lubricity imparting compound A, which is a vegetable oil, an animal oil, an ethoxylated, propoxylated or ethoxylated-propoxylated derivative or any combination or any part of any of these, but its content is only contained in the metalworking composition of the present invention in a range of from 1 to 200 % by weight of its content of the component (a), preferably in a range of from 20 to 180 % by weight or of from 40 to 160 % by weight or of from 60 to 140 % by weight. The at least one optional lubricity imparting component A or lubricity imparting compound A may be a water-soluble, a water-dispersible, a water-miscible or a water-insoluble compound. Especially preferred compounds A are the ethoxylated derivatives, which optionally may be compounds contained in any vegetable oil or animal oil or both which is purified, refined, conditioned, chemically modified, synthesized or prepared by any combination thereof.

[0092] Preferably, the aqueous metalworking composition comprises at least one **biocide B**, at least one **fungicide B** or both.

[0093] Preferably, the aqueous metalworking composition of the invention comprises at least one **antifoaming agent C** and/or at least one **defoamer C**. The optional component C is preferably selected from polyglycols, siloxanes, polysiloxanes and waxes.

[0094] Finally, a content of organic polymeric material may be added to or contained in the aqueous metalworking composition of the invention as **optional component D**. Such organic polymeric material D may predominantly contain or consist of monomers, oligomers, cooligomers, polymers and/or copolymers based on ionomers, acrylamide, acrylic acid/methacrylic acid, butane, epoxide, ethylene, isobutylene, poly- α -olefine, polyamide, polyglycerols, polyisobutene, propylene, styrene, polysulfonic acid, urethane, their ester(s) and/or their salt(s). Preferably, the aqueous metalworking composition comprises at least one optional component D, which is based on monomers, oligomers, cooligomers, polymers and/or copolymers of acrylamide, acrylic acid/methacrylic acid, butane, epoxide, ethylene, ionomers, isobutylene, poly- α -olefine, polyamide, polyglycerols, polyisobutene, propylene, styrene, polysulfonic acid, urethane, their ester(s) and/or their salt(s). Preferred organic materials comprise for example: Acrylamide-(meth)acrylate copolymer, ethylene-(meth)acrylate copolymer, styrene-(meth)acrylate copolymer, urethane-carbonate copolymer, urethane-carbonate-... copolymer, urethane-ester-carbonate copolymer, isobutylene-butene copolymer, polysulfonic acid. These organic materials may be sometimes added either as solids, as emulsions or as liquids. Such organic polymeric material D may be helpful for further enhancing the lubricity and at the same time enhancing the bio-stability of the composition. It may be added to and used for many types of cutting, forming and cold forming operations, which require high degrees of lubricity. The content of such organic polymeric material D in the aqueous metalworking composition may be chosen in a range of from 0.1 to 50 % by weight or in a range of from 1 to 30 % by weight or in a range of from 3 to 15 % by weight or in a range of from 5 to 10 % by weight.

[0095] The method to prepare an aqueous metalworking composition of the invention is characterized by first adding to water any compounds (b) and (d), then adding any compounds (a) and afterwards then (c), during which mixing procedure until here a heating to temperatures in the range of from 30 to 50 °C and an agitation is used - wherein this mixing succession, heating and agitation are used to get a stable emulsion - and optionally then all other compounds are added. On demand, the concentrate prepared may be diluted with water to a wanted dilution degree.

[0096] The application of the aqueous metalworking composition of the invention may be performed by spraying, high pressure spraying, brushing, roll coating, immersion or other such methods like flowing water. The coated metal substrate may then be metalworked, e.g. cut, ground or machined in the manner desired, wherein the liquid flowing metalworking composition provides a favourable lubricating effect.

[0097] The method of use of an aqueous metalworking composition of the invention is characterized that the aqueous metalworking composition may be used as a coolant and/or as a lubricant and/or for bending, for blanking, for boring, for broaching, for cooling, for cold forming, for warm forming, for cutting, for drawing, for drilling, for forging, for grinding, for hobbing, for honing, for hydroforming, for lapping, for lubricating, for forming, for milling, for pressing, for punching,

for reaming, for cold rolling, for hot rolling, for sawing, for stamping, for tapping, for threading, for turning or for any combination thereof.

[0098] It was surprising that the aqueous metalworking compositions of the present invention show such a high lubricity for very different metallic materials so that they may be excellently used in multi-metal purposes.

[0099] It was further on surprising that the aqueous metalworking compositions of the present invention show an excellent corrosion protection for very different metallic materials.

[0100] It was further on surprising that the aqueous metalworking compositions of the present invention show an excellent emulsion stability for the concentrates as well as for the dilutions.

[0101] It was further on surprising that the aqueous metalworking compositions of the present invention result in clean, shiny and smooth metal surfaces of the finished metallic parts that have been metalworked with this composition.

[0102] It was finally surprising that the aqueous metalworking compositions of the present invention show nearly all properties to be expected from industry requirements, even typically low-foaming and high bio-stability as well as despite high environmentally friendly compositions like zero-VOC, freedom from alkanolamines and/or freedom from petroleum oils.

EXAMPLES AND COMPARISON EXAMPLES

[0103] This invention may be further appreciated in detail by consideration of the following examples, including preferred embodiments, which are not intended to limit the invention in any way.

[0104] Properties and their measurement:

The aqueous metalworking composition of the invention has preferably a **lubricity** as measured as average torque number of not more than 300 N·cm, when measured in a Microtap test with a tapping torque instrument Microtap Megatap II-G8 of Microtap GmbH in Germany.

[0105] Such tapping torque instrument is often called Microtap instrument. The test may be performed according to ASTM D5619 by drilling into a metal or alloy bar especially into a bar of aluminium 6061 or steel 1018 or both. The Microtap test is not performed exactly according to this standard, but it is used according to the test procedures recommended by the instrument producer for dilutions of 10 % by weight or seldom of down to 5 % by weight. The metal bar usually has pre-drilled holes. The sample of the metalworking composition is added to the hole. Then, a tap will drill through the hole, and the instrument will measure the torque number, using a depth of 14.4 mm, a speed of 660 rpm, a torque of 700 N·cm and a force of 5 N·cm for aluminum 6061 bars and using a depth of 14.4 mm, a speed of 500 rpm, a torque of 700 N·cm and a force of 5 N·cm for steel 1018 bars. In the Microtap test, a tap drills through a hole filled with the aqueous metalworking composition, and the instrument output data show an average torque number in N·cm. Very good data for aluminium and its alloys show ≤ 200 N·cm and very good data for steel show ≤ 230 N·cm.

[0106] The aqueous metalworking composition of the invention has preferably a **stability** such that there is no separation of any phase visible with the naked eye, but a clear or transparent or more or less milky emulsion or any combination thereof in a composition diluted only with pure water or with hard water having a Ca content of up to 1200 ppm Ca. If there is an unstable emulsion, it will split with time and the split will be seen with the eyes. There are two types of stability tests:

A) To measure the stability of a concentrate:

1.) Oven test at 50 °C for 3 cycles and each cycle is 24 hours.

2.) Freeze/thaw test. Freeze a concentrate sample at about -16 °C, and then thaw at room temperature, which is also used in 3 cycles.

B) To measure the stability of a diluted emulsion:

Prepare the dilution with pure water and another dilution with hard water of at least 300 ppm Ca, each at a desired concentration, usually at 5 or 10 % by weight, and then observe the stability by eyes at least after one week (emulsion stability test).

[0107] That there is no separation of the emulsion means that the composition is not split and that there is no settled part of the emulsion. A stable concentrate can have a clear, transparent or hazy appearance. It does not matter, if it is clear, transparent or hazy, as long as the metalworking composition does not split: Then it is stable. An emulsion can even be more or less milky, but as long as it is stable, it does not matter which appearance a diluted emulsion has.

[0108] For the determination of stability of a metalworking composition, the following stability test methods have been used for concentrates and dilutions, wherein the check of the stability of concentrates or dilutions only by the eyes is still the most common way:

For concentrate samples:

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In the 50 °C oven test, leave a concentrate sample in the oven at 50 °C for 24 hours, then take the sample out and leave it on a bench until the temperature of the concentrate sample decreases to room temperature. If there is no separation observed, which may be visualized by the eyes, the sample is stable. The test is repeated two more times at 50 °C. The concentrate sample should be stable, which means, it must be clear, transparent or hazy, but there should not be any separation which is seen by the eye.

[0109] In the freezing/thaw test, put a concentrate sample into a freezer for 24 hours to freeze the sample, then take the sample out of the freezer and leave it on the bench until it defreezes back to liquid state. Repeat the freezing and defreezing two more times. No separation should be observed by our eyes.

[0110] For diluted samples:

Prepare a 5 % dilution in hard water containing 600 ppm of calcium acetate. Leave the solution at 50 °C in an oven for three days. No separation should be observed, so that the dilution samples appear clear, hazy or milky.

[0111] Preferably, the aqueous metalworking composition of the invention has a **corrosion protecting effect**. The corrosion protecting effect is preferably checked with a cast iron chip test CIC resulting in a corrosion rating of 2 or less if a cast iron bar or more preferred and here used small clean chips are used and tested in contact with a diluted composition of 2 % by weight in deionized water over 24 hours. The test procedure of the cast iron chip test (CIC) is similar, but few measures are not identical with the data in the standard test methods ASTM D4627 and DIN 51360-2: The chip size is smaller and is of 2 to 3 mm, wherein 2 g of chips and 2 g of aqueous metalworking 5 % dilution in DI-water and 24 hours are used in a petro-dish with cover. The smaller the rating value, the better. The worst results show a rating of 5, the best of zero. Starting with a rating value of 3, such aqueous metalworking compositions do not seem to be acceptable for industry.

[0112] It is expected that the metalworking composition should not have any corrosive effect on the tool and on parts of the machine in many instances, if the metalworking composition has been tested successfully in a CIC test over 24 hours.

[0113] Preferably, the aqueous metalworking composition of the invention is **stable against foaming**, especially under the specific operating conditions of a metalworking. In several metalworking operations it is wanted that even high pressure spraying cannot cause trouble with foam generation. Further on, foam generated during a metalworking operation should break down after the metalworking operation within 1 minute or less than 1 minute to be a low foaming composition.

[0114] Preferably, the metalworking composition is stable against foaming such that there is no longer foam in a foam test as performed in a mixer method in a 1000 ml beaker with 200 ml of a metalworking composition which has 5 % by weight of the concentrate having a concentration of active substances of 5 % by weight in water with a Black and Decker 12-speed mixer at speed 10 for 5 minutes and such that there is then a foam break time of less than 30 seconds for the foam to dissipate. Foam break means total foam dissipation, that is, zero foam on the surface of a solution.

[0115] The foam test method TM# 2142 is an internal test method. There is no standard method for foam testing. A 5 % dilution means 5 % by weight of a concentrate sample in 95 % DI water. The purpose of this test is to determine the amount of foam generated in a highly agitated system and the time required for that foam to dissipate. Use a 1000 ml Kimax beaker so that the height of the beaker is defined, a 100 ml graduated cylinder, a Black and Decker 12-speed mixer with timer and a stop watch.

[0116] Foam Testing Procedure:

1. Measure 190 ml of plant water into the 1000 ml Kimax beaker.
2. Add 10 ml of product to be tested into the beaker.
3. Place the beaker under the beaters of the mixer.
4. Blend at speed 10 for 5 minutes.
5. When mixing stops, begin timing and measure total milliliters of foam.
6. Measure time for foam to dissipate.
7. Record results as height of foam and time to dissipate.

[0117] VOC Test according to EPA24 method:

VOC content of a composition is tested according to ASTM D 2369-81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings. A sample of a metalworking fluid concentrate is placed at 110 °C for at least 60 minutes or until the weight becomes constant to drive out all the water and volatile organic materials. Then VOC content can be calculated by the weight loss in grams/Liter.

[0118] Test of the average droplet size of an emulsion:

Test of the average droplet size of an emulsion is measured with an instrument equipped with light scattering technology like Marvern Mastersizer. A light beam or laser beam passes through an emulsion and hits emulsion particles or oil droplets, which scatter the light and change the light intensity. From the light intensity and angle changes, the average droplet size can be calculated.

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[0119] As the different metalworking compositions have been tested for an aluminium based metallic material and for a steel, it is believed that these tested materials represent a vast majority of different metallic materials, if not even all kinds of metallic materials, so as to fulfil multi-metal purposes.

[0120] The materials identified by other than standard chemical names in the "Ingredient" column of Table 3 as well as further ingredients for such examples and testings have the following characteristics as mentioned in the following Table 2. They are the more preferred compounds to be used in a metalworking composition.

Table 2: Selection of some of the ingredients used for the examples and comparison examples and chemical information to these ingredients

Type	Name	Chemical Characterization
(a1)	Erucic acid C22	high content erucic rapeseed acid, C22
(a1)	Dicarboxylic acid C22	diacid acid, C22
(a2)	Triglyceride with three oleic acids	trimer with glycerin and three oleic acids of C57
(a3)	Polyester of C12	polyester of lauric acid, C12
(a3)	Polyester of C18	polyester of trimethylpolyol oleate, C18
(a3)	Polyester of C18	polyester of trimer, C18
(a3)	Chlorinated polyester of C18-24	chlorinated polyester of C18-24
(a3)	Polyester of C36 4EO	polyethylene glycol dioleate, higher grade of estering, C36
(a3)	Dibasic acid diester of C \geq 44 nEO	dibasic acid diester of C \geq 44 nEO
(a3)	Polyester of C \geq 61	polyester of succinic acid and aliphatic alcohol, C \geq 61
(a3)	Polyester of C72	polyester of ricinoleic acid, n-C18, MW 1192
(a3)	Polyester of C \geq 86	polyester of natural and synthetic fatty acids and a polyfunctional alcohol, C \geq 86
(a3)	Polyester of C108	polymerized branched chain vegetable ester
(a3)	Polyester of C $>$ 2.000	polyester of pentaerythritol and fatty acids, MW \geq 35.000, C $>$ 2.000
(a4)	Oleyl alcohol (cis-9-octadecen-1-ol)	primary aliphatic straight chain alcohol of C18
(b1)	Dibasic acid C11+C12	undecanedioic acid+dodecanedioic acid C11+C12
(b1)	Neo-decanoic acid C12	C12
(b1)	Isononanoic acid C9	C9
(b1)	Octanoic/carpylic acid C8	C8
(b2)	Boric acid	
(b5)	Benzotriazole salt	
(b5)	Benzotriazole	
(c1)	5-9EO alcohol C12-18	5-9EO alcohol C12-18
(c2)	7-11EO alkyl phenol C23-43	7-11EO alkyl phenol C23-43
(c3)	3-5EO oleate C18	3-5EO oleate C18
(c3)	5-9EO fatty acid C18	5-9EO fatty acid C18
(c3)	2-10EO ether carboxylate C18-44	2-10EO ether carboxylate C18-44
(c4)	EO/PO random copolymer 1	EO/PO random copolymer
(c4)	EO/PO block copolymer 1	EO/PO block copolymer, MW 2.150. less PO
(c4)	EO/PO block copolymer 2	EO/PO block copolymer, MW 2.650, more PO

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(continued)

Type	Name	Chemical Characterization
(c4)	EO/PO block copolymer 3	EO/PO block copolymer, MW 2.000-4.000
(c4)	EO/PO random copolymer 3	EO/PO random copolymer, MW 15.000, C _≈ 300
(c4)	EO/PO random copolymer 2	EO/PO random copolymer, MW 18.000, C _≈ 400
(c5)	Alkyl polyglucoside, fatty ester type	sodium lauryl glucose carboxylate of C18
(c6)	Anionic sulfonate surfactant	sodium stearic sulfonate, C18
(c7)	Ether sulfate	sodium lauryl ether sulfate
(c8)	Ether phosphate	phosphated decyl alcohol ethoxylated
(c9)	Phosphate ester	mono-phosphate ester of C12-18
(c10)	Fatty ester, monoglyceride	glycerol mono-tallate, C21
(c11)	Ethoxylated triglyceride	
(c12)	Ethoxylated fatty amine	C12-18 alkyl amine with 3-7EO
(c13)	Sorbitan derivative	20EO sorbitan monolaurate
(c14)	Succinic acid derivative	polyisobutylene succinic anhydride, MW around 1.000
(d1)	Potassium hydroxide	KOH
A	Ethoxylated soybean oil	ethoxylated soybean oil, ester
A	Ethoxylated castor oil 1	ethoxylated castor oil, ester
A	Ethoxylated castor oil 2	ethoxylated castor oil, ester
A	Ethoxylated castor oil 3	ethoxylated castor oil, ester
A	Ethoxylated coconut oil	ethoxylated coconut oil, ester
B	Carbamate	fungicide
B	Oxazole	biocide
C	Siloxane 1	siloxane
C	Siloxane 2	siloxane
D	Polyglycerol	polyglycerol, MW 3.000-25.000
D	Ethylene-acrylate copolymer	ethylene-acrylate copolymer

[0121] To learn from the tests which are the better and the best aqueous metalworking compositions, the compounds of the components (b) and (c) added to the composition were in many examples maintained to observe the influence of different compounds (a) and of other compounds on the chemical system.

[0122] The aqueous metalworking compositions for these examples and for further testing these were prepared by first adding to water the selected compounds (b) and (d), then adding the selected compounds (a) and afterwards then the selected compounds (c). During this mixing procedure a heating to temperatures in the range of from 30 to 50 °C and an agitation was used to get an emulsion - and optionally then all other selected compounds were added. On demand, the concentrates prepared were diluted with water to the wanted dilution degree.

[0123] Table 3 shows a selection for 20 compositions and their properties out of nearly 400 different compositions tested for their lubricity and stability. It was astonishing to identify the different lubricity degrees of the different lubricity imparting compounds tested and to identify the different emulsification degrees of the different emulsifying compounds (c) tested. Further on, it was astonishing that it is not self-understanding that a stable metalworking composition does work well for lubricity on aluminum based metallic materials and on steels at the same time. Therefore, it was necessary to learn how to compose and stabilize a metalworking composition for multi-metal purposes. It was astonishing that it is possible to have a stable, well-lubricating metalworking composition for multi-metal purposes that is still insufficient in corrosion protection. Therefore, it is not easy to gain a metalworking composition fulfilling all the above mentioned

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requirements well and including low foaming at the same time. Examples E3, E5, E6 and E17 are inventive examples. Examples E1, E2, E4, E7 to E16, E18 to E20, E26 and E27 as well as CE1 to CE3 are non-inventive examples.

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Table 3: Selection of compositions and test results for lubricity and stability

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Example No.	Compon.	E1 (1)	E2 (123)	E3 (3)	E4 (106)	E5 (5)	E6 (64)	E7 (1p)	E8 (50)
Stability and appearance of concentrate		stable	hazy stable	stable	stable	stable	stable	stable	stable
Stability and appearance of dilution to 10 % with DI water		stable	stable	stable	stable	stable	stable	stable	stable
Lubricity: Torque number on steel 1018 (diluent to 10 %)		224	196	225	253	197	177	202	180
Lubricity: Torque number on Al 6061 (diluent to 10 %)		223	164	203	197	194	167	198	166
(a) water-insoluble lubricity agents									
Erucic acid C22	(a1)	3.50	1.70	3.00		3.50		3.50	
Dicarboxylic acid C22	(a1)		1.60						
Polyester of C≥61	(a3)				2.00				
Polyester of C72	(a3)	6.00	1.70	5.50	3.00	4.00	5.00	6.00	5.00
Polyester of C≥86	(a3)	6.00		5.50		4.00		6.00	4.00
Polyester of C108	(a3)								4.00
Polyester of C36 4EO	(a3)						7.00		7.00
(b) corrosion inhibiting compounds									
Dibasic acid C11+C12	(b1)	2.00	2.38	2.00	2.38	2.00	2.50	2.00	2.50
Neo-decanoic acid C12	(b1)	3.00	6.67	3.50	6.67	3.00	7.00	3.00	3.00
Isononanoic acid C9	(b1)	1.00	2.86	1.50	2.86	1.00	3.00	1.00	1.00
Boric acid H ₃ BO ₃	(b2)	3.00	0.86	1.50	0.86	3.00	1.00	3.00	1.00
Benzotriazole salt	(b5)	0.50	0.48	0.50	0.48	0.50	0.50	0.50	0.50

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Example No.	Compon.	E1 (1)	E2 (123)	E3 (3)	E4 (106)	E5 (5)	E6 (64)	E7 (1p)	E8 (50)
(c) emulsifying and dispersing agents									
5-9EO alcohol C12-C18	(c1)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
3-5EO oleate C18	(c3)	4.00		5.00		4.00	7.00	4.00	7.00
5-9EO fatty acid C18	(c3)				10.00				
EO/PO block copolymer 1	(c4)	15.00	19.05	15.00	10.00	15.00	10.00	15.00	10.00
EO/PO block copolymer 3	(c4)	4.80	4.76	4.80	4.76	4.80	4.80	4.80	4.80
(d) amine-free alkalinity agent									
Potassium hydroxide	(d1)	9.30	11.90	8.90	10.30	9.25	14.00	9.30	9.10
(e) transport agent									
deionized water	(e)	39.50	45.69	40.90	46.34	45.55	32.80	29.50	36.70
Optional Compounds A									
Ethoxylated soybean oil	A						5.00		4.00
Optional Compounds C									
Carbamate	B	1.00		1.00				1.00	
Oxasole	B	1.00		1.00				1.00	
Optional Compounds C									
Siloxane 1	C	0.20	0.15	0.20	0.15	0.20	0.20	0.20	0.20
Optional Compounds D									
Polyglycerol	D						10.00		
Ethylene-acrylate copolymer	D		10.00						

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Example No.	Compon.	E9 (57)	E10 (75)	E11 (73)	E12 (72)	E13 (66)	E14 (68)	E15 (27)	E16 (54)
Stability and appearance of concentrate		stable	stable	hazy stable	milky stable	stable	stable	stable	stable
Stability and appearance of dilution to 10 % with DI water		stable	stable	hazy stable	milky stable	stable	stable	stable	stable
Lubricity: Torque number on steel 1018 (diluent to 10 %)		181	236	239	254	304	236	175	175
Lubricity: Torque number on Al 6061 (diluent to 10 %)		184	226	221	256	249	188	194	194
(a) water-insoluble lubricity agents									
Erucic acid C22	(a1)	5.00						4.00	4.00
Polyester of C36 4EO	(a3)	7.00	3.00	3.00				5.00	5.00
Polyester of C72	(a3)	5.00						5.00	5.00
Polyester of C≥86	(a3)	5.00							
Polyester of C108	(a3)							3.00	3.00
Polyester of C18	(a3)				5.00				
Polyester of C12	(a3)					5.00			
Chlorinated polyester of C18-C24	(a3)						5.00		
(b) corrosion inhibiting compounds									
Dibasic acid C11+C12	(b1)	2.50	2.50	2.50	2.50	2.50	2.50	2.00	2.00
Neo-decanoic acid C12	(b1)	3.50	7.00	7.00	7.00	7.00	7.00	3.00	3.00
Isononanoic acid C9	(b1)	1.50	3.00	3.00	3.00	3.00	3.00	1.00	1.00
Boric acid H ₃ BO ₃	(b2)	1.00	1.00	1.00	1.00	1.00	1.00	3.00	3.00

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Example No.	Compon.	E9 (57)	E10 (75)	E11 (73)	E12 (72)	E13 (66)	E14 (68)	E15 (27)	E16 (54)
Benzotriazole salt	(b5)	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
(c) emulsifying and dispersing agents									
5-9EO alcohol C12-C18	(c1)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
3-5EO oleate C18	(c3)	7.00							
5-9EO fatty acid C18	(c3)		10.00	10.00	10.00	10.00	10.00		
EO/PO random polymer	(c3)		5.00	5.00	5.00	5.00	5.00		
EO/PO block copolymer 1	(c4)	10.00	10.00	10.00	10.00	10.00	10.00	15.00	15.00
EO/PO block copolymer 3	(c4)	4.80	4.80	4.80	4.80	4.80	4.80	4.80	4.80
(d) amine-free alkalinity agent									
Potassium hydroxide	(d1)	10.90	14.00	14.00	14.00	13.50	13.50	9.10	9.10
(e) transport agent									
deionized water	(e)	35.90	36.80	36.80	36.80	37.30	37.30	44.20	44.20
Optional Compounds A									
Ethoxylated castor oil 1	A		5.00						
Ethoxylated castor oil 3	A			5.00					
Optional Compounds C									
Siloxane 1	C	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20

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Example No.	Compon.	E17 (4)	E18 (1a)	E19 (1b)	E20 (1c)	CE1(112)	CE2 (94)	CE3 (89)
Stability and appearance of concentrate		stable	stable	stable	stable	Split, very unstable	unstable	unstable
Stability and appearance of dilution to 10 % with DI water		stable	stable	stable	stable	hazy stable	slightly hazy, stable	hazy stable
Lubricity: Torque number on steel 1018 (diluent to 10 %)		229	230	228	227	225	288	207
Lubricity: Torque number on Al 6061 (diluent to 10 %)		198	197	199	200	159	210	204
(a) water-insoluble lubricity agents								
Erucic acid C22	(a1)	3.00	3.50	3.50	3.50			
Polyester of C≥61	(a3)					2.00		
Polyester of C72	(a3)	5.00	6.00	6.00	6.00	3.00		
Polyester of C≥86	(a3)	5.00	6.00	6.00	6.00			5.00
(b) corrosion inhibiting compounds								
Isononanoic acid C9	(b1)	2.00	1.00	1.00	1.00	2.86	2.86	3.00
Dibasic acid C11+C12	(b1)	2.00	2.00	2.00	2.00	2.38	2.38	2.50
Neo-decanoic acid C12	(b1)	4.00	3.00	3.00	3.00	6.67	6.67	7.00
Boric acid H ₃ BO ₃	(b2)	1.50	3.00	3.00	3.00	0.86	0.86	1.00
Benzotriazole salt	(b5)	0.50	0.50	0.50	0.50	0.48	0.48	0.50
(c) emulsifying and dispersing agents								
5-9EO alcohol C12-C18	(c1)	0.20	0.20	0.20	0.20	0.20	0.20	0.20

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Example No.	Compon.	E17 (4)	E18 (1a)	E19 (1b)	E20 (1c)	CE1(112)	CE2 (94)	CE3 (89)
3-5EO oleate C18	(c3)	5.00	4.00	4.00	4.00			
5-9EO fatty acid C18	(c3)						10.00	5.00
EO/PO random polymer	(c3)							10.00
EO/PO block copolymer 1	(c4)	15.00	15.00	15.00	15.00	20.00	10.00	10.00
EO/PO block copolymer 3	(c4)	4.80	4.80	4.80	4.80	4.76	4.76	4.80
(d) amine-free alkalinity agent								
Potassium hydroxide	(d1)	9.30	9.30	9.30	9.30	10.30	11.70	13.50
(e) transport agent								
deionized water	(e)	40.50	39.50	39.50	39.50	46.34	44.94	37.30
Optional Compounds A								
Ethoxylated castor oil 1	A						5.00	
Optional Compounds B								
Carbamate	B	1.00	1.00		1.00			
Oxasole	B	1.00		1.00	1.00			
Optional Compounds C								
Siloxane 1	C	0.20	0.20	0.20	0.20	0.15	0.15	0.20
Siloxane 2	C				0.10			

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Example No.	Compon.	E1 (1)	E26	E27
Stability and appearance of concentrate		stable	stable	hazy stable
Stability and appearance of dilution to 10 % with DI water		stable	stable	stable
Lubricity: Torque number on steel 1018 (diluent to 10 %)		224	n.d.	n.d.
Lubricity: Torque number on Al 6061 (diluent to 10 %)		223	n.d.	n.d.
VOC test with EPA24 method in g/l		3.85	0	0
(a) water-insoluble lubricity agents				
Erucic acid C22	(a1)	3.00	3.00	3.00
Polyester of C72	(a3)	6.00	6.00	6.00
Polyester of C≥86	(a3)	6.00	6.00	6.00
(b) corrosion inhibiting compounds				
Isononanoic acid C9	(b1)	1.00	1.00	1.00
Dibasic acid C11+C12	(b1)	2.00	2.00	2.00
Neo-decanoic acid C12	(b1)	3.00	3.00	3.00
Boric acid H ₃ BO ₃	(b2)	3.00	3.00	3.00
Benzotriazole salt	(b5)	0.50	0.48	0.50
(c) emulsifying and dispersing agents				
5-9EO alcohol C12-C18	(c1)	0.20	0.20	0.20

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Example No.	Compon.	E1 (1)	E26 (44)	E27 (45)
3-5EO oleate C18	(c3)	4.00	4.00	4.00
EO/PO block copolymer 1	(c4)	15.00	15.00	15.00
EO/PO block copolymer 3	(c4)	4.80	4.80	4.80
(d) amine-free alkalinity agent				
Potassium hydroxide	(d1)	9.30	9.30	9.30
Amino-methyl propanol	(d2)		0.25	2.40
Tri-ethanol amine	(d2)		0.25	2.40
(e) transport agent				
deionized water	(e)	39.50	39.20	34.70
Optional Compounds B				
Carbamate	B	1.00	1.00	1.00
Oxasole	B	1.00	1.00	1.00
Optional Compounds C				
Siloxane 1	C	0.20	0.20	0.20

40 **[0124]** Table 3 shows that even hazy and milky metalworking concentrates may show excellent properties, if the emulsion is stable. The visual appearance is not mentioned, if the concentrate or dilution shows clear or translucent appearance. The stability of the concentrate is more important than its visual appearance. All comparison examples show hazy or milky concentrates and all of them are unstable or split, even CE4.

45 **[0125]** There is a strong variation of the lubricity data, even for good to excellent examples. The lower the lubricity data are, the better is the lubricity of the composition. Very good torque data for aluminium and its alloys show ≤ 200 N·cm and very good torque data for steel show ≤ 230 N·cm. Many of the compositions showing the lowest torque data enable their use in severe metalworking operations.

50 **[0126]** The composition of CE1 failed, as it does not have enough emulsifying compounds (c). The composition of CE2 failed, as it does have adequate emulsifying compounds (c), although the compounds (c) have already been increased. The composition of CE3 failed, as it does not have enough adequate emulsifying compounds (c), although even further increased amounts. It is assumed that HLB values of a combination of different emulsifying compounds (c) influence the emulsifying effect, so that not only the amount of any emulsifying compounds (c) is important, but even the chemical characteristics of such compounds are to be selected in a way to stabilize the emulsion. Therefore, specific care has to be taken in an adequate selection of emulsifying compounds (c).

55 **[0127]** Table 4 shows the results of composition C of US 2009/0149359 A1 as indicated in its examples 1 and 2 in comparison to the results of compositions according to the present application. Examples CE4 and E21 to E25 are non-inventive examples.

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Table 4: Compositions and test results for selected compositions and their properties of the present invention and for the best sample C of US 2009/0149359 A1

Examples/ Content in weight%	*C=CE4	E21 (2)	E22 (28)	E23 (40)	E24 (42)	E25 (44)
Compounds (a)	0*	15	17	18	14.5	18
(a1)		3	4	3	1.5	2
(a3)		12	13	15	13	16
Compounds (b)	14*	9.5	9.5	8	8	8
(b1)		7	6	6.5	6.5	6.5
(b2)		2	3	1	1	1
(b5)		0.5	0.5	0.5	0.5	0.5
Compounds (c)	25*	24	20	20	24	19
(c1)		0.2	0.2	0.2	0.2	0.2
(c3)		4	0	0	4	4
(c4)		19.8	19.8	19.8	19.8	14.8
Compounds (d)	0*	9.4	9.1	9	8.7	9
Water (e)	remainder*	39.9	44.2	44.8	43.1	43.8
Zero-VOC, petroleum oil-free, alkanolamine-free	yes	yes	yes	yes	yes	yes
Opt. compound A	0*	0	0	0	1.5	2
Opt.: Biocides B	0*	2	0	0	0	0
Opt: Defoamer C	0*	0.2	0.2	0.2	0.2	0.2
Weight sum	100	100	100	100	100	100
pH of concentrate	7-8	9.8	9.1	9.8	about 10	about 9.9
pH of dilution 5 %	6.7 - 7.2	8.9	8.9	9.0	9.3	9.1
Tapping torque Al 6061 N/cm	3713*	-	-	-	-	-
Tapping torque Al 6061 N•cm	194	204	190	145	169	181
Tapping torque Steel 1018 N•cm	258	229	176	176	177	186
Appearance of dilutions to 5 to 10 %	milky macro-emulsion	clear micro-emulsions				
Diluent: Average droplet size nm	350*					
Diluent: Average droplet size nm	300 to 500	< 200	< 200	< 200	< 200	< 200
CIC corrosion rating cast iron	4 to 5	0	0	0	0	0
Foaming	low	low	low	low	low	low
Stability of concentrate until °C	50	50	50	50	50	50
Stability of dilutions to 5 to 10 % until °C	< 40	50	50	50	50	50

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(continued)

Examples/ Content in weight%	*C=CE4	E21 (2)	E22 (28)	E23 (40)	E24 (42)	E25 (44)
Stability of dilutions to 5 to 10 % in hard water at 50 °C	until 300 ppm Ca	until 600 ppm Ca	until 600 ppm Ca	until 600 ppm Ca	until 600 ppm Ca	until 600 ppm Ca

[0128] Data with * for CE4 are mentioned in the publication, but data without * for CE4 have been tested now with the original non-disclosed formulation in comparison to the results of compositions according to the present application. C = CE4 is the best example of US 2009/0149359 A1.

[0129] The table clearly shows that according to this publication, there are no compounds (a) and (d) added. The pH of CE4 is significantly lower than for E21 to E25. The lubricity measured by tapping torque data for steel of CE4 is in comparison with that of E21 to E25 bad. The corrosion resistance of CE4 too is clearly bad in comparison with that of E21 to E25 as measured in a CIC test. Even the stability of the diluted emulsion of CE4 too is lower in comparison with that of E21 to E25 as measured in an emulsion stability test for dilutions with pure water and/or with hard water.

[0130] Further on, long-term field trials were performed on very different metallic materials which confirmed the excellent behaviour and properties in industrial size metalworking operations of the metalworking compositions of the present invention, which were found before in the laboratory testing and which are partially shown above.

Claims

1. An aqueous metalworking composition comprising in a concentrate or after dilution of a concentrate with water in a diluent:

- 6 to 40 % by weight of **component (a)** which is a **lubricity agent** comprising at least one water-insoluble compound (a) having at least one hydrophobic aliphatic chain and at least one polar group and having a water solubility at 20 °C of less than 0.1 g/liter and which are selected from the group of compounds consisting of:

- (a1) fatty acids selected from the group consisting of lauric/dodecanoic acid, myristic/tetradecanoic/myristoleic acid, pentadecanoic acid, palmitic/hexadecanoic/palmitoleic/hexadecapolyenoic acid, margaric/margaroleic acid, ricinoleic acid, stearic/octadecanoic acid, linoleic/eicosanoic acid, oleic acid, linoleic/linolenic/octadecatetraenoic acid, arachidic/gadoleic/eicosadienoic/arachidonic/eicosapentaenoic acid, he-neicosanoic acid, behenic/docosanoic/erucic/docosapolyenoic acid, docosahexaenoic acid and lignoceric acid;
- (a2) triglycerides of three identical or two or three different carboxylic acids based on oleic acid, stearic acid, ricinoleic acid, erucic acid, lignoceric acid and/or lauric acid; and
- (a3) derivatives of compounds (a1) or (a2) or both having 12 to 5.000 carbon atoms selected from chlorinated or sulfurized derivatives, esters, ethers, ethoxylates, ethoxylate-propoxylates, propoxylates, alkali metal salts, alkaline earth metal salts and compounds having been condensed with at least one carboxylic acid;

- 0.002 to 40 % by weight of **component (b)** comprising at least one **water-soluble corrosion inhibiting compound (b)** having a water-solubility at 20 °C of more than 0.1 g/liter and which are selected from the group consisting of:

- (b1) straight and/or branched, saturated and/or unsaturated monocarboxylic acids, dicarboxylic acids, tricarboxylic acids and polycarboxylic acids having in total 6 to 40 carbon atoms and having chain lengths of 4 to 12 carbon atoms and their alkali metal salts and alkaline earth metal salts ;

- 0.002 to 45 % by weight of **at least one emulsifying and dispersing agent (c)** which contains at least one emulsifying and/or dispersing compound (c) which is water-soluble, water-miscible or water-dispersable and which is selected from the group consisting of non-ionic, anionic and zwitterionic surfactants consisting of

- (c1) ethoxylated alkyl alcohols, ethoxylated-propoxylated alkyl alcohols, ethoxylated alkyl alcohols with end-group capping and ethoxylated-propoxylated alkyl alcohols with end-group capping, and wherein the alkyl group of the alkyl alcohols is saturated or unsaturated and has an average number of carbon atoms

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ranging from 4 to 24 and has either a linear or a branched chain structure;

• (c2) ethoxylated alkyl phenols, ethoxylated-propoxylated alkyl phenols, ethoxylated alkyl phenols with end-group capping and ethoxylated-propoxylated alkyl phenols with end-group capping, wherein the alkyl group of the alkyl phenols - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 18 and has either a linear or a branched chain structure;

• (c3) ethoxylated or ethoxylated-propoxylated alkanolic acids, ethoxylated or ethoxylated-propoxylated fatty acids and/or other ethoxylated or ethoxylated-propoxylated organic acids, and wherein the alkyl acids have an alkyl radical - saturated, unsaturated and/or cyclic - which has an average number of carbon atoms ranging from 4 to 24 and which has a linear or branched chain structure;

• (c4) block copolymers containing at least one polyethylene oxide block and at least one polypropylene oxide block as well as random copolymers, and wherein the block copolymers have a polyethylene oxide block which comprises an average number of 2 to 100 ethylene oxide units and a polypropylene oxide block which comprises an average number of 2 to 100 propylene oxide units;

• (c5) alkyl polyglucosides whose alkyl group - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 18 and either a linear or a branched chain structure, and has an average of 1 to 5 units of at least one sugar, wherein the units of the sugar(s) are glucosidically linked to the alkyl group, wherein the term "sugar" is understood to include all saccharides and all other sugar-like compounds;

• (c6) anionic surfactants whose alkyl group - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 24 and either a linear or a branched chain structure, wherein there is at least one sulfate or sulfonate group present in the molecule;

• (c7) ether sulfates whose ethoxylated alkyl alcohols or ethoxylated-propoxylated alkyl alcohols have a sulfate group, wherein the alkyl group of the alkyl alcohols - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 24 and either a linear or a branched chain structure, wherein the ethylene oxide chain has an average number of 2 to 30 ethylene oxide units and wherein the propylene oxide chain has an average number of 1 to 25 propylene oxide units;

• (c8) ether phosphates whose ethoxylated alkyl alcohols or ethoxylated-propoxylated alkyl alcohols have a phosphate group, wherein the alkyl group of the alkyl alcohols - saturated or unsaturated - has an average number of carbon atoms ranging from 4 to 24 and either a linear or a branched chain structure, and wherein the ethylene oxide chain has an average number of 2 to 30 ethylene oxide units and wherein the propylene oxide chain has an average number of 1 to 25 propylene oxide units;

• (c9) phosphate esters whose one or two alkyl groups - saturated or unsaturated - have independently of one another an average number of carbon atoms ranging from 4 to 24 and either a linear or a branched chain structure, wherein there is one phosphate group present in the molecule;

• (c10) monoglycerides ethoxylated, propoxylated, ethoxylated-propoxylated or ethoxylated especially with closed end-groups;

• (c12) fatty amines as well as fatty amines ethoxylated, propoxylated, ethoxylated-propoxylated or ethoxylated with closed end groups;

• (c13) sorbitan and sorbitans that are ethoxylated, propoxylated, ethoxylated-propoxylated or ethoxylated with closed end-groups;

• (c14) succinic acid and their esters and salts;

- 0.002 to 30 % by weight of an **alkalinity agent (d)** containing at least one alkaline water-soluble compound (d) selected from the group consisting of hydroxides and carbonates; and

- at least 0.004 % by weight of a **transport component (e)**, wherein at least 98 % by weight of the transport component (e) is water,

wherein the lubricity agent (a) contains at least two or at least three or at least four different compounds (a), wherein the weight ratio of compounds of component (a) to such of component (b) to such of component (c) is in a range of from 1 : (0.5 to 2) : (0.2 to 3).

- The aqueous metalworking composition of claim 1, wherein the metalworking composition contains the following contents of components in a concentrate: (a) in a content in a range of from 10 to 20 % by weight, (b) in a content of 5 to 10 % by weight, (c) in a content in a range of from 10 to 20 % by weight, (d) in a content in a range of from 5 to 15 % by weight, (e) in a content in a range of from 70 to 25 % by weight and optionally components in a total content of zero or in a range of from 0.01 to 10 % by weight.
- The composition of claim 1 or 2, which is a dispersion, emulsion and/or solution at 25 °C and of which at least 95 % by weight of the composition are in a liquid state at 25 °C.

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4. The composition of any of claims 1 to 3, which pH is in the range of from 5 to 13.
5. The aqueous metalworking composition of any of claims 1 to 4, which is an emulsion with an average hydrophobic droplet size of hydrophobic droplets in a range of from 10 to 200 nm for the concentrates and which is an emulsion with an average droplet size of hydrophobic droplets in the range of from 10 nm to 30 μm for dilutions, wherein the average droplet size of the emulsion is measured with an instrument equipped with light scattering technology like Marvern Mastersizer.
6. The aqueous metalworking composition of any of claims 1 to 5, which has a lubricity as measured as average torque number of not more than 300 N \cdot cm, when measured in a Microtap test with a tapping torque instrument Microtap Megatap II-G8 of Microtap GmbH.
7. The aqueous metalworking composition of any of claims 1 to 6, which has a stability such that there is no separation of any phase visible with the naked eye and which is a clear or translucent micro-emulsion or a transparent, hazy or more or less milky macro-emulsion in a composition diluted with pure water or with hard water of up to 1200 ppm Ca content.
8. The aqueous metalworking composition of any of the claims 1 to 7, wherein the content of component (a) is contained in a range of from 6 to 28 % by weight.
9. The aqueous metalworking composition of any of the claims 1 to 8, wherein the corrosion inhibiting component (b) contains at least two or at least three or at least four different compounds (b), especially to optimize corrosion protection.
10. The aqueous metalworking composition of any of the claims 1 to 9, wherein component (b) is contained in a range of from 0.01 to 28 % by weight.
11. The aqueous metalworking composition of any of the claims 1 to 10, wherein the alkalinity agent (d) is selected from hydroxides and carbonates of alkali metals and of alkaline earth metals.
12. The aqueous metalworking composition of any of the claims 1 to 11, wherein the alkalinity agent (d) is contained in a range of from 0.01 to 15 % by weight or of from 0.1 to 12 % by weight or of from 1 to 10 % by weight or of from 3 to 12 % by weight.
13. A method to prepare an aqueous metalworking composition of any of claims 1 to 12 by first adding to water any compounds (b) and (d), then adding any compounds (a) and afterwards then (c), during which mixing procedure until here, a heating to temperatures in the range of from 30 to 50 °C and an agitation is used, and optionally then all other compounds are added.
14. Use of an aqueous metalworking composition of any of claims 1 to 12 as a coolant, as a lubricant and/or for bending, for blanking, for boring, for broaching, for cooling, for cutting, for drawing, for drilling, for cold forming, for warm forming, for forging, for grinding, for hobbing, for honing, for hydroforming, for lapping, for lubricating, for forming, for milling, for pressing, for punching, for reaming, for cold rolling, for hot rolling, for sawing, for stamping, for tapping, for threading, for turning or for any combination thereof.
15. A metalworking process **characterized in that** the metalworking operation is performed by flushing, spraying, high pressure spraying, brushing, flowing, fluting, roll coating, immersion or any combination thereof with the aqueous metalworking composition of any of the claims 1 to 12.

Patentansprüche

1. Wässrige Metallbearbeitungszusammensetzung, die in einem Konzentrat oder nach dem Verdünnen eines Konzentrats mit Wasser in einem Verdünnungsmittel Folgendes umfasst:
- 6 bis 40 Gew.-% Komponente (a), bei der es sich um ein Schmiermittel handelt, das mindestens eine wasserunlösliche Verbindung (a) mit mindestens einer hydrophoben aliphatischen Kette und mindestens einer polaren Gruppe aufweist und eine Wasserlöslichkeit bei 20 °C von weniger als 0,1 g/Liter aufweist und die ausgewählt

sind aus der Gruppe bestehend aus:

- (a1) Fettsäuren, die ausgewählt sind aus der Gruppe bestehend aus Laurin-/Dodecansäure, Myristin-/Tetradecan-/Myristoleinsäure, Pentadecansäure, Palmitin-/Hexadecan-/Palmitolein-/Hexadecapolyensäure, Margarin-/Margaroleinsäure, Ricinolsäure, Stearin-/Octadecansäure, Linol-/Eicosaensäure, Ölsäure, Linol-/Linolen-/Octadecatetraensäure, Arachidin-/Gadolein-/Eicasodien-/Arachidon-/Eicosapentaensäure, Heneicosansäure, Behen-/Docosan-/Eruca-/Docosapolyensäure, Docosahexaensäure und Lignocerinsäure;
- (a2) Triglyceriden von drei identischen oder zwei oder drei verschiedenen Carbonsäuren auf der Basis von Ölsäure, Stearinsäure, Ricinolsäure, Erucasäure, Lignocerinsäure und/oder Laurinsäure und
- (a3) Derivaten der Verbindungen (a1) oder (a2) oder beiden mit 12 bis 5000 Kohlenstoffatomen, die ausgewählt sind aus chlorierten oder sulfurierten Derivaten, Estern, Ethern, Ethoxylaten, Ethoxylat-Propoxylaten, Propoxylaten, Alkalimetallsalzen, Erdalkalimetallsalzen und Verbindungen, die mit mindestens einer Carbonsäure kondensiert worden sind;

- 0,002 bis 40 Gew.-% Komponente (b), die mindestens eine wasserlösliche korrosionshemmende Verbindung (b) mit einer Wasserlöslichkeit bei 20 °C von mehr als 0,1 g/Liter umfasst und die ausgewählt sind aus der Gruppe bestehend aus:

- (b1) geradkettigen und/oder verzweigten, gesättigten und/oder ungesättigten Monocarbonsäuren, Dicarbonsäuren, Tricarbonsäuren und Polycarbonsäuren mit insgesamt 6 bis 40 Kohlenstoffatomen und Kettenlängen von 4 bis 12 Kohlenstoffatomen und deren Alkalimetallsalzen und Erdalkalimetallsalzen;

- 0,002 bis 45 Gew.-% mindestens eines Emulgier- und Dispergiermittels (c), das mindestens eine emulgierende und/oder dispergierende Verbindung (c) enthält, die wasserlöslich, wassermischbar oder wasserdispergierbar ist und die ausgewählt ist aus der Gruppe bestehend aus nichtionischen, anionischen und zwitterionischen Tensiden, die aus Folgendem bestehen:

- (c1) ethoxylierten Alkylalkoholen, ethoxylierten-propoxylierten Alkylalkoholen, ethoxylierten Alkylalkoholen mit Endgruppenverkappung und ethoxylierten-propoxylierten Alkoholen mit Endgruppenverkappung und wobei die Alkylgruppe der Alkylalkohole gesättigt oder ungesättigt ist und eine von 4 bis 24 reichende mittlere Zahl von Kohlenstoffatomen aufweist und entweder eine lineare oder eine verzweigte Kettenstruktur aufweist;
- (c2) ethoxylierten Alkylphenolen, ethoxylierten-propoxylierten Alkylphenolen, ethoxylierten Alkylphenolen mit Endgruppenverkappung und ethoxylierten-propoxylierten Alkylphenolen mit Endgruppenverkappung, wobei die gesättigte oder ungesättigte Alkylgruppe der Alkylphenole eine von 4 bis 18 reichende mittlere Zahl von Kohlenstoffatomen aufweist und entweder eine lineare oder eine verzweigte Kettenstruktur aufweist;
- (c3) ethoxylierten oder ethoxylierten-propoxylierten Alkansäuren, ethoxylierten oder ethoxylierten-propoxylierten Fettsäuren und/oder anderen ethoxylierten oder ethoxylierten-propoxylierten organischen Säuren und wobei die Alkansäuren einen gesättigten, ungesättigten und/oder cyclischen Alkylrest aufweisen, der eine von 4 bis 24 reichende mittlere Zahl von Kohlenstoffatomen aufweist und der eine lineare oder verzweigte Kettenstruktur aufweist;
- (c4) Block-Copolymeren, die mindestens einen Polyethylenoxid-Block und mindestens einen Polypropylenoxid-Block enthalten, sowie statistischen Copolymeren und wobei die Block-Copolymere einen Polyethylenoxid-Block, der eine mittlere Zahl von 2 bis 100 Ethylenoxideinheiten umfasst, und einen Polypropylenoxid-Block aufweisen, der eine mittlere Zahl von 2 bis 100 Polypropylenoxideinheiten umfasst;
- (c5) Alkylpolyglucosiden, deren gesättigte oder ungesättigte Alkylgruppe eine von 4 bis 18 reichende mittlere Zahl von Kohlenstoffatomen und entweder eine lineare oder eine verzweigte Kettenstruktur aufweist und durchschnittlich 1 bis 5 Einheiten mindestens eines Zuckers aufweist, wobei die Zuckereinheiten glucosidisch mit der Alkylgruppe verbunden sind, wobei der Begriff "Zucker" dahingehend zu verstehen ist, als er alle Saccharide und alle anderen zuckerartigen Verbindungen einschließt;
- (c6) anionischen Tensiden, deren gesättigte oder ungesättigte Alkylgruppe eine von 4 bis 24 reichende mittlere Zahl von Kohlenstoffatomen und entweder eine lineare oder eine verzweigte Kettenstruktur aufweist, wobei mindestens eine Sulfat- oder Sulfonatgruppe im Molekül vorhanden ist;
- (c7) Ethersulfaten, deren ethoxylierte Alkylalkohole oder ethoxylierte-propoxylierte Alkylalkohole eine Sulfatgruppe aufweisen, wobei die gesättigte oder ungesättigte Alkylgruppe der Alkylalkohole eine von 4 bis 24 reichende mittlere Zahl von Kohlenstoffatomen und entweder eine lineare oder eine verzweigte

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Kettenstruktur aufweist, wobei die Ethylenoxidkette eine mittlere Zahl von 2 bis 30 Ethylenoxideinheiten aufweist und wobei die Propylenoxidkette eine mittlere Zahl von 1 bis 25 Propylenoxideinheiten aufweist;

- (c8) Etherphosphaten, deren ethoxylierte Alkylalkohole oder ethoxylierte-propoxylierte Alkylalkohole eine Phosphatgruppe aufweisen, wobei die gesättigte oder ungesättigte Alkylgruppe der Alkylalkohole eine von 4 bis 24 reichende mittlere Zahl von Kohlenstoffatomen und entweder eine lineare oder eine verzweigte Kettenstruktur aufweist und wobei die Ethylenoxidkette eine mittlere Zahl von 2 bis 30 Ethylenoxideinheiten aufweist;
- (c9) Phosphateestern, deren eine oder zwei gesättigte oder ungesättigte Alkylgruppen unabhängig voneinander eine von 4 bis 24 reichende mittlere Zahl von Kohlenstoffatomen und entweder eine lineare oder eine verzweigte Kettenstruktur aufweisen, wobei eine Phosphatgruppe im Molekül vorhanden ist;
- (c10) ethoxylierten, propoxylierten, ethoxylierten-propoxylierten Monoglyceriden oder die insbesondere ethoxyliert sind und geschlossene Endgruppen aufweisen;
- (c12) Fettaminen sowie ethoxylierten, propoxylierten, ethoxylierten-propoxylierten Fettaminen oder die ethoxyliert sind und geschlossene Endgruppen aufweisen;
- (c13) Sorbitan und Sorbitanen, die ethoxyliert, propoxyliert, ethoxyliert-propoxyliert sind oder die ethoxyliert sind und geschlossene Endgruppen aufweisen;
- (c14) Bernsteinsäure und deren Estern und Salzen;

- 0,002 bis 30 Gew.-% eines Alkalisierungsmittels (d), das mindestens eine alkalische wasserlösliche Verbindung (d) enthält, die ausgewählt ist aus der Gruppe bestehend aus Hydroxiden und Carbonaten; und

- mindestens 0,004 Gew.-% einer Transportkomponente (e), wobei mindestens 98 Gew.-% der Transportkomponente (e) Wasser sind,

wobei das Schmiermittel (a) mindestens zwei oder mindestens drei oder mindestens vier verschiedene Verbindungen (a) enthält, wobei das Gewichtsverhältnis von Verbindungen von Komponente (a) zu denen von Komponente (b) zu denen von Komponente (c) in einem Bereich von 1 : (0,5 zu 2) : (0,2 zu 3) liegt.

2. Wässrige Metallbearbeitungszusammensetzung nach Anspruch 1, wobei die Metallbearbeitungszusammensetzung die folgenden Komponentengehalte in einem Konzentrat enthält: (a) in einem Gehalt in einem Bereich von 10 bis 20 Gew.-%, (b) in einem Gehalt von 5 bis 10 Gew.-%, (c) in einem Gehalt in einem Bereich von 10 bis 20 Gew.-%, (d) in einem Gehalt in einem Bereich von 5 bis 15 Gew.-%, (e) in einem Gehalt in einem Bereich von 70 bis 25 Gew.-% und gegebenenfalls Komponenten in einem Gesamtgehalt von null oder in einem Bereich von 0,01 bis 10 Gew.-%.
3. Zusammensetzung nach Anspruch 1 oder 2, bei der es sich bei 25 °C um eine Dispersion, Emulsion und/oder Lösung handelt und wobei mindestens 95 Gew.-% der Zusammensetzung bei 25 °C in einem flüssigen Zustand vorliegen.
4. Zusammensetzung nach einem der Ansprüche 1 bis 3, wobei der pH-Wert im Bereich von 5 bis 13 liegt.
5. Wässrige Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 4, die für die Konzentrate eine Emulsion mit einer mittleren hydrophoben Tröpfchengröße von hydrophoben Tröpfchen in einem Bereich von 10 bis 200 nm ist und die für Verdünnungen eine Emulsion mit einer mittleren Tröpfchengröße von hydrophoben Tröpfchen im Bereich von 10 nm bis 30 µm ist, wobei die mittlere Tröpfchengröße der Emulsion mit einem Instrument gemessen wird, das mit einer Lichtstreuungstechnik ausgestattet ist, wie ein Malvern Mastersizer.
6. Wässrige Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 5, die eine als mittlere Drehmomentzahl gemessene Schmierfähigkeit von nicht mehr als 300 N·cm aufweist, wenn in einem Microtap-Test mit einem Tapping-Torque-Instrument Microtap Megatap II-G8 der Microtap GmbH gemessen wird.
7. Wässrige Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 6, die eine solche Stabilität aufweist, dass mit bloßem Auge keine Trennung einer beliebigen Phase sichtbar ist und die in einer Zusammensetzung, die mit reinem Wasser oder hartem Wasser mit einem Ca-Gehalt von bis zu 1200 ppm Ca eine klare oder halbdurchlässige Mikroemulsion oder eine transparente, trübe oder mehr oder weniger milchige Makroemulsion ist.
8. Wässrige Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 7, wobei der Gehalt von Komponente (a) in einem Bereich von 6 bis 28 Gew.-% enthalten ist.

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9. Wässrige Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 8, wobei die korrosionshemmende Komponente (b) mindestens zwei oder mindestens drei oder mindestens vier verschiedene Verbindungen (b) insbesondere zur Optimierung des Korrosionsschutzes enthält.
- 5 10. Wässrige Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 9, wobei Komponente (b) in einem Bereich von 0,01 bis 28 Gew.-% enthalten ist.
- 10 11. Wässrige Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 10, wobei das Alkalisierungsmittel (d) aus Hydroxiden und Carbonaten von Alkalimetallen und Erdalkalimetallen ausgewählt ist.
12. Wässrige Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 11, wobei das Alkalisierungsmittel (d) in einem Bereich von 0,01 bis 15 Gew.-% oder von 0,1 bis 12 Gew.-% oder von 1 bis 10 Gew.-% oder von 3 bis 12 Gew.-% enthalten ist.
- 15 13. Verfahren zur Herstellung einer wässrigen Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 12 zuerst durch das Zugeben von beliebigen Verbindungen (b) und (d) zu Wasser, dann das Zugeben von beliebigen Verbindungen (a) und danach dann (c), wobei bei diesem Mischverfahren bis hier ein Erwärmen auf Temperaturen im Bereich von 30 bis 50 °C und ein Rühren erfolgen und gegebenenfalls dann alle anderen Verbindungen zugegeben werden.
- 20 14. Verwendung einer wässrigen Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 12 als Kühlmittel, als Schmiermittel und/oder zum Biegen, zum Ausschneiden, zum Aufbohren, zum Räumen, zum Kühlen, zum Schneiden, zum Ziehen, zum Bohren, zum Kaltumformen, zum Warmumformen, zum Schmieden, zum Schleifen, zum Einsenken, zum Honen, zum hydrostatischen Ziehen, zum Läppen, zum Schmieren, zum Formdrehen, zum Walzen, zum Pressen, zum Stanzen, zum Reiben, zum Kaltwalzen, zum Warmwalzen, zum Sägen, zum Prägen, zum Gewindebohren, zum Aussengewindeschneiden, zum Drehen oder für eine beliebige Kombination davon.
- 25 15. Metallbearbeitungsverfahren, das **dadurch gekennzeichnet ist, dass** der Metallbearbeitungsvorgang durch Spülen, Sprühen, Hochdrucksprühen, Bürsten, Fließen, Kanellieren, Walzenbeschichten, Tauchen oder eine beliebige Kombination davon mit der wässrigen Metallbearbeitungszusammensetzung nach einem der Ansprüche 1 bis 12 durchgeführt wird.
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35 Revendications

1. Composition aqueuse de travail de métaux comprenant dans un concentré ou après dilution d'un concentré avec de l'eau dans un diluant :
- 40 • 6 à 40 % en poids de composant (a) qui est un agent lubrifiant comprenant au moins un composé insoluble dans l'eau (a) possédant au moins une chaîne aliphatique hydrophobe et au moins un groupe polaire et possédant une solubilité dans l'eau à 20 °C inférieure à 0,1 g/litre et qui sont choisis dans le groupe de composés constitués par :
- 45 • (a1) des acides gras choisis dans le groupe constitué par l'acide laurique/dodécanoïque, l'acide myristique/tétradécanoïque/myristoléique, l'acide pentadécanoïque, l'acide palmitique/hexadécanoïque/palmitoléique/hexadécapolyénoïque, l'acide margarique/margaroléique, l'acide ricinoléique, l'acide stéarique/octadécanoïque, l'acide linoléique/eicosanoïque, l'acide oléique, l'acide linoléique/linoléinique/octadécatétraénoïque, l'acide arachidique/gadoléique/eicosadiénoïque/arac hidonique/eicosapentaénoïque, l'acide hénicosanoïque, l'acide béhénique/docosanoïque/érucique/docosapolyénoïque, l'acide docosahexaénoïque et l'acide lignocérique ;
- 50 • (a2) des triglycérides de trois acides carboxyliques identiques ou deux ou trois acides carboxyliques différents à base d'acide oléique, d'acide stéarique, d'acide ricinoléique, d'acide érucique, d'acide lignocérique et/ou d'acide laurique ; et
- 55 • (a3) des dérivés de composés (a1) ou (a2) ou les deux possédant 12 à 5 000 atomes de carbone choisis parmi les dérivés chlorés ou sulfurés, les esters, les éthers, les éthoxylates, les éthoxylates-propoxylates, les propoxylates, les sels de métaux alcalins, les sels de métaux alcalino-terreux et les composés ayant été condensés avec au moins un acide carboxylique ;

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- 0,002 à 40 % en poids de composant (b) comprenant au moins un composé inhibant la corrosion soluble dans l'eau (b) possédant une solubilité dans l'eau à 20 °C de plus de 0,1 g/litre et qui sont choisis dans le groupe constitué par :

5 • (b1) des acides monocarboxyliques, des acides dicarboxyliques, des acides tricarboxyliques et des acides polycarboxyliques linéaires et/ou ramifiés, saturés et/ou insaturés possédant au total de 6 à 40 atomes de carbone et possédant des longueurs de chaînes de 4 à 12 atomes de carbone et leurs sels de métal alcalin et sels de métal alcalino-terreux ;

10 - 0,002 à 45 % en poids d'au moins un agent émulsifiant et dispersant (c) qui contient au moins un composé émulsifiant et/ou dispersant (c) qui est soluble dans l'eau, miscible à l'eau ou dispersible dans l'eau et qui est choisie dans le groupe constitué par des tensioactifs non ioniques, anioniques et zwitterioniques constitué par

15 • (c1) des alcools d'alkyle éthoxylés, des alcools d'alkyle éthoxylés-propoxylés, des alcools d'alkyle éthoxylés comportant un coiffage de groupe terminal et des alcools d'alkyle éthoxylés-propoxylés comportant un coiffage de groupe terminal, et le groupe alkyle des alcools d'alkyle étant saturé ou insaturé et possédant un nombre moyen d'atomes de carbone dans la plage de 4 à 24 et possédant soit une structure de chaîne linéaire, soit une structure de chaîne ramifiée ;

20 • (c2) des alkylphénols éthoxylés, des alkylphénols éthoxylés-propoxylés, des alkylphénols éthoxylés comportant un coiffage de groupe terminal et des alkylphénols éthoxylés-propoxylés comportant un coiffage de groupe terminal, le groupe alkyle des alkylphénols - saturé ou insaturé - possédant un nombre moyen d'atomes de carbone dans la plage de 4 à 18 et possédant soit une structure de chaîne linéaire, soit une structure de chaîne ramifiée ;

25 • (c3) des acides alcanoïques éthoxylés ou éthoxylés-propoxylés, des acides gras éthoxylés ou éthoxylés-propoxylés et/ou d'autres acides organiques éthoxylés ou éthoxylés-propoxylés, et les acides d'alkyle possédant un radical alkyle - saturé, insaturé et/ou cyclique - qui possède un nombre moyen d'atomes de carbone dans la plage de 4 à 24 et possédant soit une structure de chaîne linéaire, soit une structure de chaîne ramifiée ;

30 • (c4) des copolymères à bloc contenant au moins un bloc de poly(oxyde d'éthylène) et au moins un bloc de poly(oxyde de propylène) ainsi que des copolymères statistiques, et les copolymères à bloc possédant un bloc de poly(oxyde d'éthylène) qui comprend un nombre moyen de 2 à 100 motifs d'oxyde d'éthylène et un bloc de poly(oxyde de propylène) qui comprend un nombre moyen de 2 à 100 motifs d'oxyde de propylène ;

35 • (c5) des alkyl-polyglycosides dont le groupe alkyle - saturé ou insaturé - possède un nombre moyen d'atomes de carbone dans la plage de 4 à 18 et soit une structure de chaîne linéaire, soit une structure de chaîne ramifiée, et possède une moyenne de 1 à 5 motifs d'au moins un sucre, les motifs du ou des sucres étant liés de manière glycosidique au groupe alkyle, le terme « sucre » étant compris comme comprenant tous les saccharides et/ou les autres composés de type sucre ;

40 • (c6) des tensioactifs anioniques dont le groupe alkyle - saturé ou insaturé - possède un nombre moyen d'atomes de carbone dans la plage de 4 à 24 et soit une structure de chaîne linéaire, soit une structure de chaîne ramifiée, dans lesquels il y a au moins un groupe sulfate ou sulfonate présent dans la molécule ;

 • (c7) des sulfates d'éther dont les alcools d'alkyle éthoxylés ou les alcools d'alkyle éthoxylés-propoxylés possèdent un groupe sulfate, le groupe alkyle des alcools d'alkyle

45 - saturé ou insaturé - possédant un nombre moyen d'atomes de carbone dans la plage de 4 à 24 et soit une structure de chaîne linéaire, soit une structure de chaîne ramifiée, la chaîne d'oxyde d'éthylène possédant un nombre moyen de 2 à 30 motifs d'oxyde d'éthylène et la chaîne d'oxyde de propylène possédant un nombre moyen de 1 à 25 motifs d'oxyde de propylène ;

50 • (c8) des phosphates d'éther dont les alcools d'alkyle éthoxylés ou les alcools d'alkyle éthoxylés-propoxylés possèdent un groupe phosphates, le groupe alkyle des alcools d'alkyle - saturé ou insaturé - possédant un nombre moyen d'atomes de carbone dans la plage de 4 à 24 et soit une structure de chaîne linéaire, soit une structure de chaîne ramifiée, la chaîne d'oxyde d'éthylène possédant un nombre moyen de 2 à 30 motifs d'oxyde d'éthylène et la chaîne d'oxyde de propylène possédant un nombre moyen de 1 à 25 motifs d'oxyde de propylène ;

55 • (c9) des esters de phosphate dont un ou deux groupes alkyle - saturé ou insaturé - possèdent indépendamment l'un de l'autre un nombre moyen d'atomes de carbone dans la plage de 4 à 24 et soit une structure de chaîne linéaire, soit une structure de chaîne ramifiée, dans lesquels il y a un groupe phosphate présent

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dans la molécule ;

- (c10) des monoglycérides éthoxylés, propoxylés, éthoxylés-propoxylés ou éthoxylés notamment avec des groupes terminaux fermés ;
- (c12) des amines grasses ainsi que des amines grasses éthoxylées, propoxylées, éthoxylées-propoxylées ou éthoxylées avec des groupes terminaux fermés ;
- (c13) un sorbitane et des sorbitanes qui sont éthoxylés, propoxylés, éthoxylés-propoxylés ou éthoxylés avec des groupes terminaux fermés ;
- (c14) l'acide succinique et leurs esters et sels ;

- 0,002 à 30 % en poids d'un agent d'alcalinité (d) contenant au moins un composé soluble dans l'eau alcalin (d) choisi dans le groupe constitué par des hydroxydes et des carbonates ; et
- au moins 0,004 % en poids d'un composant de transport (e), au moins 98 % en poids du composant de transport (e) étant de l'eau,

l'agent lubrifiant (a) contenant au moins deux ou au moins trois ou au moins quatre composés (a) différents, le rapport en poids de composés du composant (a) sur ceux du composant (b) sur ceux du composant (c) étant dans une plage allant de 1 : (0,5 à 2) : (0,2 à 3).

2. Composition aqueuse de travail de métaux selon la revendication 1, la composition de travail de métaux contenant les teneurs suivantes de composants dans un concentré : (a) en une teneur dans une plage allant de 10 à 20 % en poids, (b) en une teneur de 5 à 10 % en poids, (c) en une teneur dans une plage allant de 10 à 20 % en poids, (d) en une teneur dans une plage allant de 5 à 15 % en poids, (e) en une teneur dans une plage allant de 70 à 25 % en poids et éventuellement des composants en une teneur totale de zéro ou dans une plage allant de 0,01 à 10 % en poids.

3. Composition selon la revendication 1 ou 2, qui est une dispersion, une émulsion et/ou une solution à 25 °C et dont au moins 95 % en poids de la composition sont dans un état liquide à 25 °C.

4. Composition selon l'une quelconque des revendications 1 à 3, dont le pH est dans la plage allant de 5 à 13.

5. Composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 4, qui est une émulsion dotée d'une taille moyenne de gouttelette hydrophobe de gouttelettes hydrophobes dans une plage allant de 10 à 200 nm pour les concentrés et qui est une émulsion dotée d'une taille moyenne de gouttelette hydrophobe de gouttelettes hydrophobes dans une plage allant de 10 nm à 30 µm pour des dilutions, la taille moyenne de gouttelette de l'émulsion étant mesurée avec un instrument muni d'une technologie de diffusion de lumière comme un Mastersizer de Malvern.

6. Composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 5, qui possède un pouvoir lubrifiant tel que mesuré comme un nombre moyen de couple non supérieur à 300 N.cm, lorsqu'il est mesuré dans un essai de Microtap avec un instrument à couple de taraudage Microtap Megatap II-G8 de Microtap GmbH.

7. Composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 6, qui possède une stabilité telle qu'il n'y a pas de séparation d'une quelconque phase visible à l'œil nu et qui est une micro-émulsion limpide ou translucide ou une macro-émulsion transparente, trouble ou plus ou moins laiteuse dans une composition diluée avec de l'eau pure ou avec de l'eau dure d'une teneur en Ca allant jusqu'à 1 200 ppm.

8. Composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 7, la teneur du composant (a) étant contenue en une plage allant de 6 à 28 % en poids.

9. Composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 8, le composant d'inhibition de la corrosion (b) contenant au moins deux ou au moins trois ou au moins quatre composés (b) différents, notamment pour optimiser la protection contre la corrosion.

10. Composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 9, le composant (b) étant contenu dans une plage allant de 0,01 à 28 % en poids.

11. Composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 10, l'agent d'alcalinité (d) étant choisi parmi des hydroxydes et des carbonates de métaux alcalins et de métaux alcalino-terreux.

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12. Composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 11, l'agent d'alcalinité (d) étant contenu en une plage allant de 0,01 à 15 % en poids ou allant de 0,1 à 12 % en poids ou allant de 1 à 10 % en poids ou allant de 3 à 12 % en poids.

5 13. Procédé de préparation d'une composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 12 en ajoutant d'abord à de l'eau de quelconques composés (b) et (d), puis en ajoutant de quelconques composés (a) et après alors (c), durant laquelle procédure de mélange jusqu'à présent, un chauffage à des températures dans la plage allant de 30 à 50 °C et une agitation sont utilisés, et éventuellement ensuite tous les autres composés sont ajoutés.

10 14. Utilisation d'une composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 12 en tant qu'agent de refroidissement, comme lubrifiant et/ou pour le cintrage, pour le découpage, pour l'alésage, pour le brochage, pour le refroidissement, pour la coupe, pour l'étirage, pour le perçage, pour le formage à froid, pour le formage à chaud, pour le forgeage, pour le meulage, pour le taillage, pour le rodage, pour l'hydroformage, pour le rodage, pour la lubrification, pour le formage, pour le fraisage, pour l'emboutissage, pour le poinçonnage, pour l'alésage, pour le laminage à froid, pour le laminage à chaud, pour le sciage, pour l'estampage, pour le taraudage, pour le filetage, pour le tournage ou pour une quelconque combinaison correspondante.

15 15. Processus de travail de métaux **caractérisé en ce que** l'opération de travail de métaux est réalisée par rinçage, pulvérisation, pulvérisation à haute pression, brossage, écoulement, cannelure, revêtement au rouleau, immersion ou une quelconque combinaison correspondante avec la composition aqueuse de travail de métaux selon l'une quelconque des revendications 1 à 12.

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REFERENCES CITED IN THE DESCRIPTION

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