(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 110 889 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
08.01.2025 Bulletin 2025/02

(21) Application number: **21706961.6**

(22) Date of filing: **25.02.2021**

(51) International Patent Classification (IPC):
C10M 173/02 $^{(2006.01)}$
C23C 22/46 $^{(2006.01)}$
C23G 1/00 $^{(2006.01)}$
C10N 40/20 $^{(2006.01)}$
C10N 80/00 $^{(2006.01)}$
C10N 50/02 $^{(2006.01)}$
C10M 177/00 $^{(2006.01)}$
C23C 22/83 $^{(2006.01)}$
C23G 1/08 $^{(2006.01)}$
C10N 70/00 $^{(2006.01)}$
C10N 30/12 $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
(C-Sets available)
C10M 173/02; C10M 177/00; C23C 22/46;
C23C 22/83; C23G 1/00; C23G 1/086;
C10M 2201/02; C10M 2201/081; C10M 2201/084;
C10M 2205/14; C10M 2205/16; C10M 2205/18;
C10M 2207/123; C10M 2209/04; C10M 2209/062;
(Cont.)

(86) International application number:
PCT/EP2021/054657

(87) International publication number:
WO 2021/170707 (02.09.2021 Gazette 2021/35)

(54) **ONE-STEP PRETREATMENT METHOD OF METALLIC SUBSTRATES FOR METAL COLD FORMING**

EINSTUFIGES VORBEHANDLUNGSVERFAHREN FÜR METALLISCHE SUBSTRATE ZUR KALTUMFORMUNG VON METALLEN

PROCÉDÉ DE PRÉTRAITEMENT EN UNE ÉTAPE DE SUBSTRATS MÉTALLIQUES POUR LE FORMAGE DE MÉTAL À FROID

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **25.02.2020 EP 20159323**

(43) Date of publication of application:
04.01.2023 Bulletin 2023/01

(73) Proprietor: **Chemetall GmbH**
60487 Frankfurt (DE)

(72) Inventors:
- **SHI, Yinfeng**
  60487 Frankfurt am Main (DE)
- **ORBEN, Martin**
  60487 Frankfurt am Main (DE)

(74) Representative: **BASF IP Association**
BASF SE
GBI - Z078
67056 Ludwigshafen (DE)

(56) References cited:
DE-B- 1 153 961
JP-A- S 545 847
US-B1- 6 695 931

EP 4 110 889 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

(Cont. next page)

(52) Cooperative Patent Classification (CPC): (Cont.)
C10M 2217/023; C10M 2217/024; C10M 2217/028;
C10N 2030/12; C10N 2040/243; C10N 2040/247;
C10N 2050/02; C10N 2070/02; C10N 2080/00

C-Sets
C10M 2209/04, C10M 2217/028

Description

[0001] The present invention relates to method for pretreatment of a metallic substrate for a subsequent metal cold forming process, said method comprising at least steps (1) and (2) and optionally step (3), namely providing at least one substrate having at least one surface at least partially made of at least one metal (1), contacting the at least one surface of the substrate provided in step (1) with an aqueous lubricant composition (A) having a pH value below 2.0 and comprising besides water oxalate anions (a1), thiosulfate anions (a2), chloride anions (a3), at least one film-forming polymer (a4), which is a homopolymer and/or copolymer being prepared by polymerization of at least one ethylenically unsaturated monomer, at least one wax (a5), and fluoride anions and/or bifluoride anions (a6), and optionally drying the coating film obtained after having performed step (2), a pretreated metallic substrate obtainable by the aforementioned inventive method, a method of cold forming of a metallic substrate including a step of subjecting the inventive pretreated metallic substrate to a cold forming process, an aqueous lubricant composition (A) as defined above and a master batch for preparing the aqueous composition (A).

Background of the invention

[0002] Cold forming of metallic workpieces is conventionally achieved by rolling such as thread rolling, drawing, in particular sliding drawing or deep-drawing, pressing, stretch forming and/or cold upsetting of the workpieces in order to transform them into articles having a desired shape. Cold forming usually takes place at temperatures below the recrystallization temperature of the metallic material of the workpiece subjected to cold forming, such as at temperatures below and up to 450°C. No external heating source is used in the method of cold forming. Instead, any heat development or temperature increase in general is caused solely by frictional forces between the metallic workpiece and the work tools used during forming and due to internal friction forces generated by material flow in the workpiece. Cold forming usually results in an increased pressure, e.g. for steel, for example in the range of from 200 MPa to 1 GPa and sometimes even up to 2 GPa. The temperature of the workpieces to be cold formed is initially at ambient temperature, i.e. at approximately 10 to 32 °C. In case the workpieces are pre-heated prior to forming, for example to a temperature in the range from 650 to 1250 °C, the forming process is no longer a "cold forming" process, but rather a "semi-hot" forming, a hot forming or a forging process.

[0003] If the metallic workpieces are cold formed to shaped articles with a comparably only low degree of deformation rather low forces for the cold forming process to take place are needed. For this purpose, conventionally non-reactive forming oils are applied to the workpieces. At higher degrees of deformation, however, usually at least one coating film such as a conversion coating film is applied onto the workpieces prior to the cold forming process, which functions as separating layer between the workpiece and the tools used in order to prevent a cold welding during the cold forming. The conversion coating film used as separating layer in this case can also function as lubricant film if no additional coating film is applied on top of it. Such processes are, e.g., disclosed in DE 1 179 437, DE 1 196 467 and EP 0 233 503 A1:
DE 1 179 437 relates to a pretreatment of wires of iron or steel for a subsequent cold forming. An oxalate coating is applied for this purpose onto the wires. The coating is obtained by making use of a solution containing inter alia oxalic acid and an alkenyl phosphonic acid such as vinyl phosphonic acid in monomeric form.

[0004] DE 1 196 467 also relates to a pretreatment of metal substrates for a subsequent cold forming. An oxalate coating is applied for this purpose onto the wires. The coating is obtained my making use of a solution containing inter alia oxalic acid and polyvinyl phosphonic acid and/or a copolymer comprising vinyl phosphonic acid in the form of monomeric units.

[0005] EP 0 233 503 A1 relates to a pretreatment method for facilitating a subsequent cold forming of stainless steel substrates. An oxalate coating is applied for this purpose to the substrate. The coating is obtained by making use of an aqueous solution containing inter alia oxalic acid, fluoride and nitrate anions as well as a water-soluble polymer. The solution used is essentially free of any chloride anions and preferably is free of thiosulfate anions as well as the presence of these anions is undesired according to EP 0 233 503 A1.

[0006] Alternatively, it is also possible and known in the prior art that not only the conversion coating film applied onto the metallic substrates can be solely used at the same time as lubricant film, but that rather an additional lubricant composition is further applied onto the conversion coating film to form a lubricant film on top of this film in order to (further) reduce the frictional resistance between the surface of the workpiece and the tools and to avoid the occurrence of cold welding. Different kinds of conversion coating films can be used for this purpose, in particular phosphate or oxalate coating films, which are applied from corresponding phosphate or oxalate containing aqueous acidic compositions. In addition, different kinds of lubricant compositions are known in the prior art. For example, aqueous lubricant compositions such as soaps or soap solutions, e.g. based on alkali or earth alkali stearate, polymer dispersions, solid lubricants such as MoS_2 and/or graphite, and/or oil-based lubricants can be used for forming corresponding lubricant films. Processes of this kind are, e.g., disclosed in EP 0 232 929 A1, WO 94/16119 A1, WO 2009/095373 A1, WO 2009/095375 A1, WO 2009/095374 A1 and JP S56 72090 A.

[0007] EP 0 232 929 A1 relates to a two-step pretreatment method for facilitating a subsequent cold forming of stainless steel substrates. In a first step an oxalate coating is applied onto the substrate by making use of a solution containing inter alia oxalic acid, hydroxyl ammonium sulfate as well as a water-soluble polymer. EP 0 232 929 A1 teaches that the use of chloride and fluoride anions in the oxalating solutions should be avoided. Afterwards, in a second step a lubricant is applied onto the oxalate coating. Metal soaps are named as suitable lubricants in EP 0 232 929 A1.

[0008] WO 94/16119 A1 discloses a liquid aqueous composition for forming a conversion coating on metal surfaces in a first step for a subsequent cold forming process. The composition comprises an organic cationic polymer and may further comprise oxalate anions. In a second step a lubricating film can be applied onto the conversion film by making use of inter alia oil-based lubricants and/or soaps.

[0009] WO 2009/095373 A1 discloses a two-step pretreatment method for facilitating a subsequent cold forming of metal substrates. In a first step a phosphate layer on the surface of the workpiece is formed by using an aqueous acidic phosphatizing solution containing Ca, Mg and/or K cations. In a second step, an aqueous alkaline lubricant composition containing organic polymers is applied.

[0010] WO 2009/095375 A1 and WO 2009/095374 A1 both disclose a method for the preparation of metallic workpieces for cold forming. A lubricant coating layer is applied onto the metallic surface of the workpieces optionally bearing a conversion coating layer as separating layer by contacting the surface with an aqueous lubricant composition comprising at least one water-soluble, water-containing or water-binding oxide and/or silicate and an organic polymer in case of WO 2009/095375 A1 or by contacting the surface with an aqueous lubricant composition comprising at least two waxes and an organic polymer in case of WO 2009/095374 A1.

[0011] JP S56 72090 A relates to a two-step pretreatment method for facilitating a subsequent cold forming of steel substrates. An oxalate coating is applied for this purpose onto the substrates in a first step. The oxalate coating is obtained by making use of a solution containing inter alia oxalic acid and a water-soluble organic titanium compound as well as a polyvinyl pyrrolidone. In a second step, a lubricant is applied onto the oxalate coating. Metal soaps and solid lubricants are named as suitable lubricants in JP S56 72090 A.

[0012] There are, however, several drawbacks as far as the processes known in the prior art are concerned. First of all, both for ecologic reasons and in order to avoid the formation of undesired phosphorous-induced delta ferrite on the substrate, it is desired to not use phosphate coating films as conversion coating films such as the conversion coating films applied in the process disclosed in WO 2009/095373 A1, but to rather only use phosphate-free systems. As far as the lubricant compositions known from the prior art are concerned, oil-based lubricant compositions in general lead to a higher VOC-content, since considerable amounts of oil can evaporate during their use. In addition, oil-based lubricant systems may cause safety issues, as they are flammable and must be stored at flash points >150 °C as hazardous materials. For these reasons, the use of oil-based lubricant formulations is undesired. Solid lubricants such as lubricants based on MoS_2 and/or graphite are only feasible for heavy cold forming with extensive degrees of deformation and thus, such lubricants are of limited use only. Furthermore, sulfide present in such lubricant films often has a detrimental effect in particular on stainless steel. The use of aqueous lubricant compositions is thus more desirable both for ecologic and economic reasons than using solid and/or oil-based lubricants.

[0013] The conventional aqueous lubricant compositions of the prior art are, however, usually alkaline compositions such as the (metal) soaps and soap solutions disclosed in EP 0 232 929 A1, WO 2009/095373 A1, WO 2009/095375 A1, WO 2009/095374 A1 and JP S56 72090 A, which are for example based on alkali or earth alkali stearate. Such alkaline lubricant composition baths often have only comparably short lifetimes and thus have to be renewed rather frequently. This, of course, is disadvantageous both from an ecological view (higher amounts of water and of the constituents present in the compositions have to be used) and an economic view (higher energy costs and changeover time). In contrast to these aqueous alkaline lubricant compositions used for providing a lubricant layer on the prior to be applied conversion coating layer, the compositions used for generating said aforementioned conversion coating layer are acidic compositions - as already mentioned hereinbefore. For performing such a two-steps pretreatment process usually two different open treatment baths are employed, into which the metallic workpieces are dipped, namely a first bath containing the aqueous acidic conversion coating composition and a second bath containing the aqueous alkaline lubricant composition. It is essential, however, to include a rinsing and/or neutralization step between these two dipping steps in order to remove any excessive acid present onto the workpiece after having it removed from the first acidic bath and before having dipped it into the second alkaline bath in order to preserve the life of the two baths and in particular of the second bath as long as possible. It is, however, disadvantageous for economic and ecological reasons to have to necessarily carry out such a rinsing and/or neutralization step. Simple mixing or combining the conventional aqueous acidic compositions such as phosphate and/or oxalate compositions for providing the conversion coating layer with the conventional aqueous alkaline compositions for providing the lubricant layer is not possible as these compositions are not miscible with each other and consequently an undesired phase separation would be observed. Moreover, most of the known organic polymer dispersions used for preparing conventional aqueous alkaline lubricant compositions are unstable in an acidic environment. Therefore, it is not always possible to simply use acidic versions of the known aqueous alkaline lubricant compositions.

[0014] EP 3 290 544 A1 relates to an acidic water-based lubricating coating agent having a pH value of 2.0 to 6.5, which inter alia contains a chemical conversion component such as oxalic acid and a lubricating component such as a lipophilic lubricating component including an oil or a soap. The coating agent may further comprise a water-based resin as a binder component. EP 3 290 544 A1 further discloses a one-step pretreatment method of metal substrates for a subsequent cold forming.

[0015] JP S54 5847 A relates to a lubricant composition for facilitating the cold forming of metals. The lubricant contains oxalic acid and at least one constituent selected from water-soluble organic titanium compounds, vinyl pyrrolidone homopolymers and vinyl pyrrolidone copolymers. The lubricant composition may further contain a lubricating aid.

[0016] In addition, the conventional pretreatment processes for cold forming known in the prior art not always result in a sufficiently high coating weight of the lubricant layer formed on the workpiece or - if a separating layer such as a conversion coating layer is also present underneath the lubricant layer - in a sufficiently high coating weight of the lubricant layer and said separating layer combined. This may result in only insufficient adhesion properties of the layer(s) to the metallic substrate. Further, this can result in an ineffective separation of the tool from the workpiece after and during cold forming and in an only ineffective reduction of the coefficient of friction or even in an undesired cold welding, as an only insufficiently high amount of the coating layer(s) as measured by their coating weight remains present on the workpieces during the cold forming process.

[0017] Thus, there is a need for simplifying the conventional surface pretreatment processes for metal cold forming that make use of aqueous lubricant compositions both for economic reasons and for ecological reasons, in particular to provide an improved technology for the water-based pretreatment of metallic substrates for the cold forming process that requires fewer treatment steps and makes use of aqueous acidic lubricant compositions. At the same time such a simplified pretreatment must still lead to sufficiently high coating weights of the coating layer(s) formed on the metallic substrates in order to both ensure a good adhesion to the substrate and an effective reduction of the coefficient of friction during cold forming and to prevent cold welding.

Problem

[0018] It has been therefore an object underlying the present invention to provide a simplified surface pretreatment method for metal cold forming that make use of an aqueous lubricant composition both for economic reasons and for ecological reasons, in particular to provide an improved technology for the water-based pretreatment of metallic substrates for the cold forming process that requires fewer treatment steps and makes use of aqueous acidic lubricant compositions. At the same time, however, such a simplified pretreatment must still lead to sufficiently high coating weights of the coating layer(s) formed on the metallic substrates in order to both ensure a good adhesion to the substrate and an effective reduction of the coefficient of friction during cold forming and to prevent any cold welding.

Solution

[0019] This object has been solved by the subject-matter of the claims of the present application as well as by the preferred embodiments thereof disclosed in this specification, i.e. by the subject matter described herein.

[0020] A first subject-matter of the present invention is a method for pretreatment of a metallic substrate for a subsequent metal cold forming process, said method comprising at least steps (1) and (2) and optionally step (3), namely

(1) providing at least one substrate having at least one surface at least partially made of at least one metal,

(2) contacting the at least one surface of the substrate provided in step (1) with an aqueous lubricant composition (A) having a pH value below 2.0, wherein the aqueous lubricant composition (A) comprises besides water

(a1) oxalate anions,
(a2) thiosulfate anions,
(a3) chloride anions,
(a4) at least one film-forming polymer, which is a homopolymer and/or copolymer being prepared by polymerization of at least one ethylenically unsaturated monomer,
(a5) at least one wax, which is different from constituent (a4), and
(a6) fluoride anions and/or bifluoride anions,

and

(3) optionally drying the coating film obtained after having performed step (2).

[0021] A further subject-matter of the present invention is a pretreated metallic substrate obtainable by the inventive method.

[0022] A further subject-matter of the present invention is a method of cold forming a metallic substrate, characterized in that it comprises a step of subjecting the inventive pretreated metallic substrate to a cold forming process.

[0023] A further subject-matter of the present invention is an aqueous lubricant composition (A) as defined hereinbefore in connection with the inventive pretreatment method.

[0024] A further subject-matter of the present invention is a master batch to produce the inventive aqueous composition (A) by diluting the master batch with water and if applicable by adjusting the pH value.

[0025] It has been surprisingly found that all constituents present in aqueous lubricant composition (A) can be formulated as and into an acidic composition at a pH value below 2.0. It has been in particular surprisingly found that composition (A) is stable under such acidic conditions and that in particular the at least one film-forming polymer present in composition (A) is stable in such an acidic environment. This surprisingly has the advantage that composition (A) can be used in the inventive method both as lubricant composition and as a conversion coating composition in a single step only and that, consequently, it is not necessary to either apply any conversion coating composition or any lubricant coating composition in an additional step and that it is also no longer necessary to perform a rinsing step after step (2). Thus, the method can be simplified which has economic and ecologic advantages.

[0026] It has been further surprisingly found that baths containing the acidic aqueous lubricant composition (A) have comparably long lifetimes, in particular longer lifetimes that bath containing conventional alkaline aqueous lubricant compositions. This, of course, has economic and ecologic advantages.

[0027] In addition, it has been surprisingly found that the coating layer obtained from applying composition (A) adhered firmly on the substrate and showed good lubricant properties. Thus, the substrate pretreated by the inventive method can be subsequently subjected to a metal cold forming process, in particular with high speed drawing. In the cold forming of substrates such as stainless steel it has been found that a coating layer obtained from application of composition (A) to the substrate can be efficiently subjected to a drawing step for the purpose of metal cold forming.

[0028] Furthermore, it has been surprisingly found that the coated metallic substrates obtained by the inventive method bear a sufficiently high coating weight of the coating layer(s) formed on the metallic substrates obtained from applying composition (A). The resulting coating layer(s) is/are homogenous, thick and adhered firmly on the surface of the substrate. It has been found that such a high coating weight not only ensures a good adhesion to the substrate, but also an effective reduction of the coefficient of friction during cold forming and to prevent any cold welding. It has been surprisingly found that inter alia selecting a pH value of composition (A) below 2.0 results in formation of a comparably thick conversion coating layer, which in turn is advantageous for the subsequent metal cold forming process. This in particular applies to metal substrates, which are at least partially made of stainless steel. In case of higher pH values, the formed conversion coating layers are not sufficiently thick.

[0029] It has been further surprisingly found that the conversion coating layers formed are homogeneous, in particular when using metal substrates, which are at least partially made of stainless steel. It has been found that inter alia the presence of fluoride and/or bifluoride and chloride and thiosulfate anions have been found as being advantageous in this regard.

[0030] Moreover, it has been surprisingly found that coated metal workpieces obtained from the inventive method have a good corrosion resistance. Further, it has been found that no stable foams have been formed during the inventive surface treatment process.

[0031] In addition, it has been further found that the coating film obtained after step (2) or optionally after step (3) is a combined conversion and lubricant coating film. Thus the coating film obtained combines the properties of a conversion layer and a lubricant layer. The lubricant coating film can be present on top of the conversion coating film. Surprisingly, the combined layers can be separated and adjusted in part. For example, a longer treatment time in step (2) results in a thicker conversion layer, i.e. in a higher layer thickness of the conversion layer, calculated as coating weight, whereas a higher concentration of the at least one wax (a5) and optionally of the at least one constituent (a4) leads to a thicker lubricant layer, i.e. a higher layer thickness of the lubricant layer, calculated as coating weight. In this way, a combined conversion and lubricant layer tailored to the respective conditions of cold forming can be produced.

Detailed description of the invention

[0032] The term "comprising" in the sense of the present invention, in particular in connection with the inventive method, the inventive composition (A) and the master batch used to prepare the composition (A), preferably has the meaning "consisting of". In this case, for example, with regard to the inventive composition (A), in addition to the mandatory constituents therein (constituents (a1) to (a6) and water) one or more of the further optional components mentioned hereinafter may be contained in the composition. The same principle applies with respect to the composition (A) used in the inventive method and the master batch. All components/constituents can be present in each case in their preferred embodiments mentioned hereinafter. The same applies to the further subject-matters of the present invention.

Inventive pretreatment method

[0033] The inventive method is a method for pretreatment of a metallic substrate for a subsequent metal cold forming process. The inventive method comprises at least steps (1) and (2) and optionally additionally step (3). The inventive method may further comprise one or more additional steps.

Step (1)

[0034] In step (1) of the inventive method at least one substrate having at least one surface at least partially made of at least one metal is provided.

[0035] The surface of the substrate used is at least partially made of at least one metal, i.e. at least one region of said surface is made of at least one metal. The surface can consist of different regions comprising different metals. Preferably, the overall surface of the substrate is made of at least one metal. More preferably, the substrate consists of at least one metal.

[0036] Preferably, the at least one metal is selected from the group consisting of aluminum, aluminum alloys, zinc, steel including cold rolled steel, hot rolled steel, galvanized steel (zinc plated steel) including hot-dip galvanized steel (hot zinc dipped steel) or electrolytically galvanized steel, stainless steel, steel alloys including stainless steel alloys, magnesium and/or zinc-magnesium alloys and/or zinc-iron alloys and mixtures thereof. In particular, the metal is ferrous and most preferably is steel. Most preferred is stainless steel and/or alloys thereof.

[0037] Preferably, the at least one surface of the substrate is at least partially made of stainless steel, more preferably the substrate as such is made of stainless steel.

[0038] As substrates e.g. strips, sheets, slugs, wires, wire coils, more complicated shaped parts, sleeves, profiles such as hollow or solid profiles, tubes, discs, discs, rods, bars or cylinders can be used.

Optional steps (1a) and (1b)

[0039] The surfaces to be substrates provided in step (1) may be cleaned by means of an acidic, alkaline or pH-neutral cleaning composition and/or etched before treatment with the acidic aqueous composition (A) in step (2) as it will be outlined hereinafter: Prior to step (2) of the inventive method one or more of the following optional steps can be performed, preferably in this order:

Step (1a): cleaning, preferably by making use of an alkaline aqueous cleaning composition, and optionally subsequently rinsing the surface of the substrate provided in step (1), and

Step (1b): subjecting the surface of the substrate to acidic pickling, i.e., etching, and subsequently rinsing the surface of the substrate.

[0040] Preferably, both steps (1a) and (1b) are performed. Rinsing included in step (1a) is preferably performed with deionized water or tap water. Preferably, the acidic pickling is performed by making use of hydrochloric acid, hydrofluoric acid, sulphuric acid, nitric acid and/or phosphoric acid.

[0041] Most preferably, at least step (1b) is performed, in particular by making use of hydrofluoric acid and/or nitric acid for pickling, in particular when the substrate is at least partially made of stainless steel.

Step (2)

[0042] In step (2) of the inventive method the at least one surface of the substrate provided in step (1) is contacted with, preferably dipped into, an aqueous lubricant composition (A) having a pH value below 2.0, wherein the aqueous lubricant composition (A) comprises besides water oxalate anions as constituent (a1), thiosulfate anions as constituent (a2), chloride anions as constituent (a3), at least one film-forming polymer as constituent (a4), which is a homopolymer and/or copolymer being prepared by polymerization of at least one ethylenically unsaturated monomer, at least one wax as constituent (a5) and fluoride anions and/or bifluoride anions as constituent (a6).

[0043] The treatment procedure according to step (2), i.e. the "contacting", can, for example, include a spray coating and/or a dip coating procedure. The composition (A) can also be applied by flooding the surface or by roll coating or even manually by wiping or brushing. However, dipping is preferred. In this case, the substrate used is dipped into a bath containing the composition (A).

[0044] Preferably, contacting step (2) is performed by at least partially dipping the substrate into a bath containing the aqueous lubricant composition (A) having a bath temperature in the range of from 20 to 95 °C, preferably of from 30 to 90 °C, in particular of from 45 to 85 °C, most preferably of from 50 to 75 °C.

[0045] The treatment time, i.e. the period of time the surface is contacted with the aqueous composition (A) used in step (2) is preferably from 15 seconds to 20 minutes, more preferably from 30 seconds to 10 minutes, and most preferably 45 seconds to 5 minutes, as for example 1 to 4 minutes.

[0046] Preferably, no rinsing step is performed after having carried out step (2).

Composition (A)

[0047] The term "aqueous" with respect to composition (A) in the sense of the present invention preferably means that the composition (A) is a composition containing at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-% in particular at least 80 wt.-%, most preferably at least 90 wt.-% or 95 wt.-% or 98 wt.-% or 99 wt.-% or even 100 wt.-% of water, based on its total content of organic and inorganic solvents including water. Thus, the composition (A) may contain at least one organic solvent besides water - however, in an amount significantly lower than the amount of water present. Preferably, composition (A) is free of organic solvents. Thus, preferably water is the only solvent/diluent present.

[0048] Preferably, composition (A) contains water in an amount of at least 50 wt.-%, more preferably of at least 60 wt.-%, even more preferably of at least 70 wt.-% and still more preferably of at least 80 wt.-%, in each case based on the total weight of composition (A).

[0049] Preferably, composition (A) has a pH value below 1.9, preferably below 1.7, in particular a pH value in a range of from 0.1 to 1.5, most preferably in a range of from 0.5 to 1.5.

[0050] Preferably, composition (A) is present in the form of a solution or dispersion, in particular in the form of a solution, preferably at a temperature of at least 40°C, in particular at least 50°C.

[0051] Preferably, composition (A) is free of phosphate anions. This means that at least on purpose no phosphate is added to composition (A). In case of subsequent heat treatment of sensitive components such as the hardening and tempering of screws otherwise phosphorus-induced delta-ferrite may be formed, which may lead to disadvantageous material properties.

[0052] Preferably, composition (A) is free of silicone, i.e. free of siloxanes and/or polysiloxanes. This means that at least on purpose no silicone is added to composition (A). The presence of silicones may be disadvantageous when applying coating materials such as paint to the substrate after having performed a subsequent cold forming.

[0053] Preferably, composition (A) has a solid content in the range of from 0.1 to 25 wt.-%, more preferably in the range of from 0.2 to 20 wt.-%, even more preferably in the range of from 0.3 to 15 wt.-%, still more preferably in the range of from 0.4 to 12 wt.-%, in each case based on the total weight of composition (A).

[0054] The sum of all components/constituents present in composition (A) adds up to 100 wt. -%.

[0055] Since composition (A) comprises (a1) oxalate anions it represents an oxalating composition, which is suitable of forming a conversion coating on the surface of a substrate. Since composition (A) also comprises (a5) at least one wax and at least one film-forming polymer (a4) it also represents a lubricant composition, which is suitable of forming a lubricating coating on the surface of a substrate.

Constituents (a 1), (a2) and (a3)

[0056] Preferably,

> the oxalate anions (a1) are present in the composition (A) in an amount in the range of from 2 to 500 g/l, more preferably of from 5 to 100 g/l, in particular of from 10 to 50 g/l of oxalic acid, calculated in each case as oxalic acid dihydrate, and/or
>
> the thiosulfate anions (a2) are present in the composition (A) in an amount in the range of from 0.01 to 25 g/l, more preferably of from 0.5 to 10 g/l, in particular of from 1.0 to 5.0 g/l, calculated in each case as sodium thiosulfate.

[0057] The chloride anions (a3) are present in the composition (A) in an amount in the range of from 0.1 to 25 g/l, preferably of from 0.5 to 10 g/l, in particular of from 1.0 to 5.0 g/l, calculated in each case as sodium chloride.

[0058] In the sense of the present invention, "oxalic acid" also means the single and double deprotonated form of oxalic acid. Likewise, in the sense of the present invention, "oxalate" also means the single and double protonated form thereof, the double protonated from being oxalic acid. Preferably, oxalic acid dihydrate is used, as is it cheap and less hygroscopic.

[0059] If, in connection with weight concentrations (e.g., g/l), the term "calculated as X" is used, where X is a specific, specified chemical compound, this is to be understood as follows: If an alternative chemical compound (not X) it should be used in such a molar concentration as calculated for X, taking into account its molar mass, from the specific weight concentration (e.g. g/l) indicated in each case.

[0060] The content of cations and anions mentioned herein with respect to composition (A) can be monitored and determined by the means of ICP-OES (optical emission spectroscopy with inductively coupled plasma). Said method is described hereinafter in detail. The content of free fluoride anions is, however, determined by means of a fluoride electrode.

Constituent (a4)

[0061] Composition (A) comprises at least one film-forming polymer, which is a homopolymer and/or copolymer being prepared by polymerization of at least one ethylenically unsaturated monomer as constituent (a4), which is different from constituent (a5).

[0062] Preferably, the at least one film-forming polymer is water-soluble or water-dispersible, more preferably water-soluble. Preferably, the at least one film-forming polymer is soluble or dispersible, more preferably soluble, in composition (A).

[0063] Preferably, the at least one film-forming polymer (a4) is a homopolymer and/or copolymer, said homopolymer and/or copolymer being prepared at least from at least one monomer bearing at least one vinyl group, preferably selected from the group consisting of vinyl amine, vinyl alcohol, vinyl formamide, vinyl pyrrolidone, vinyl caprolactam, vinyl acetate and vinyl imidazole, preferably from at least one monomer selected from the group consisting of vinyl pyrrolidone and vinyl acetate, in particular from at least vinyl pyrrolidone. Exemplary polymers are Sokalan® K 17P, from BASF SE, Germany and Lupamin® 9030 from BASF SE, Germany.

[0064] Most preferred are polyvinyl pyrrolidone homopolymers and copolymers of vinyl pyrrolidone and vinyl acetate.

[0065] In case the at least one film-forming polymer (a4) is a copolymer at least one further monomer bearing at least one ethylenically unsaturated group and being different from the above defined monomers can be used for preparing constituent (a4). Preferably, such further monomers bears at least one (meth)acrylic group. (Meth)acrylic groups include e.g. (meth)acrylate groups and (meth)acrylic acid groups. The further monomer can be an ionomer. The further monomer can also be ethylene, propylene, butylene, styrene etc. The term "(meth)acryl" means "acryl" and/or "methacryl". Similarly, "(meth)acrylate" means acrylate and/or methacrylate.

[0066] Preferably, the at least one film-forming polymer (a4) has a weight average molecular weight (M_w) in the range of from 1 000 to 100 000 g/mol, more preferably of from 3 000 to 75 000 g/mol, even more preferably of from 5 000 to 50 000. Determination of M_w is performed by gel permeation chromatography (GPC).

[0067] Preferably, the at least one film-forming polymer (a4) is present in the composition (A) in an amount in the range of from 0.05 to 20 wt.-%, more preferably in the range of from 0.10 to 15 wt.-%, even more preferably in the range of from 0.15 to 10 wt.-%, still more preferably in the range of from 0.20 to 7.5 wt.-%, in particular of from 0.25 to 5.0 wt.-%, in each case based on the total weight of the composition (A).

Constituent (a5)

[0068] Composition (A) comprises at least one wax as constituent (a5), which is different from constituent (a4).

[0069] As the term "wax "already implies, the at least one wax is a solid substance at room temperature (23 °C). A person skilled in the art is familiar with the term "wax". Said term is e.g. defined in by the German Society for Fat Science (DGF) within DGF standard method M-I 1 (75) (2015). Preferably, the at least one wax used as constituent (a5) satisfies this definition of a wax. Waxes according to this definition can be kneaded at 20 °C, have a firm (solid) to brittle hardness, have a coarse to fine crystalline structure, are translucent to opaque in color but not glassy or glass-like, melt without decomposition at temperatures above 40 °C, are slightly liquid above their melting point and have a low viscosity above their melting point, have a highly temperature-dependent consistency and solubility, and can be polished under light pressure. Preferably and according to the definition of the DGF (DGF standard method M-I 1 (75)), a substance is not a wax if it does not meet more than one of the above properties.

[0070] Preferably, the at least one wax (a5) is water-soluble or water-dispersible, more preferably water-dispersible. Preferably, the at least one wax (a5) is soluble or dispersible in composition (A).

[0071] Preferably, composition (A) is obtainable by using an aqueous dispersion or solution of the at least one wax (a5) for its preparation.

[0072] Preferably, the at least one wax (a5) has a melting point in the range of from 40 °C to 170 °C, more preferably in the range of from 50°C to 160°C, especially preferred in the range of from 50 °C to 140 °C.

[0073] Composition (A) preferably comprises more than one wax as constituent (a5). Preferably, composition (A) comprises at least two, more preferably at least three different waxes as constituents (a5). Preferably, the at least two or at least three different waxes differ from each other at least in their melting temperature (melting point). Preferably, the difference between melting points of at least two of the waxes is at least 20 °C.

[0074] Preferably, the at least one wax (a5) is present in the composition (A) in an amount in the range of from 0.1 to 20 wt.-%, more preferably in the range of from 0.5 to 15 wt.-%, even more preferably in the range of from 0.75 to 12.5 wt.-%, still more preferably in the range of from 1.0 to 10.0 wt.-%, in particular of from 1.5 to 9.0 wt.-%, most preferably in the range of from 2.0 to 7.5 wt.-%, in each case based on the total weight of the composition (A).

[0075] Preferably, the at least one wax (a5) is selected from the group consisting of cationic waxes, cationically stabilized waxes and non-ionic waxes. A "cationically stabilized wax" is preferably a wax that is stabilized by cationic groups in acidic medium such as in the composition (A) or is stabilized by at least one cationic surfactant.

[0076] Preferably, the at least one wax (a5) is stabilized by at least one emulsifier. For example, the at least one wax (a5) can be stabilized by a cationic emulsifier (cationically stabilized) or can be stabilized by a non-ionic emulsifier (non-ionically stabilized). Examples of cationic emulsifiers are alkoxylated such as ethoxylated stearyl amine and/or polyalkoxylated such as polyethoxylated tallow amine. Examples of non-ionic emulsifiers are alcohols including for example diethylaminoethanol.

[0077] Preferably, the at least one wax (a5) is selected from the group consisting of polyolefin waxes (including polyethylene waxes, in particular HDPE (high density polyethylene) and/or polypropylene waxes, natural waxes including plant and animal waxes such as montan waxes, bees waxes and/or carnauba waxes, paraffin waxes (petroleum derived waxes) and mixtures thereof.

[0078] In this context, the term "olefin" mainly refers to alkenes typical of polyolefins, preferably alkenes with 2 to 8, especially alkenes with 2 to 6 and especially alkenes with 2 to 4 carbon atoms, especially those with a terminal double bond. In the context of this invention, preferred representatives are ethylene, propylene, 1-butene and isobutene. Ethylene and propylene are particularly preferred olefin monomers in the context of this invention. The term "polyolefin" is generally understood to mean homopolymers of a single type of olefin monomer (e.g. ethylene homopolymers) or copolymers of at least two olefin monomers (e.g. polymers of mixtures comprising or consisting of ethylene, propylene, 1-butene and/or isobutene). Polyolefins thus contain one or more types of olefin monomers and are therefore homopolymers or copolymers. However, they may also additionally contain one or more ethylenically unsaturated monomers other than olefin monomers, in particular ethylenically unsaturated monomers bearing carboxylic acid groups, polymerized or grafted. If different ethylenically unsaturated monomers with carboxyl groups or carboxylic acid anhydride groups are used for the purpose of polymerization or grafting of the olefin monomers, this is done in an amount such that the polyolefin wax as constituent (a5) containing carboxyl groups has an acid number in the range from 3 to 50, preferably from 5 to 40, particularly preferably from 8 to 35, very particularly preferably from 10 to 25 and particularly preferably from 13 to 20 mg KOH/g. Polyolefin waxes are preferably selected from the group consisting of oxidized polyethylene waxes, oxidized polypropylene waxes, oxidized poly(ethylene-co-propylene) waxes and oxidized ethylene-olefin copolymers, ethylene-(meth)acrylic acid copolymers and polymers of ethylene and/or propylene other than the abovementioned copolymers, which have been grafted, for example, with maleic anhydride (converted into the hydrolyzed form, and carrying free COOH groups). Of course, other ethylenically unsaturated acids such as acrylic acid can also be used for grafting.

[0079] The paraffin waxes used are preferably microcrystalline.

[0080] Exemplary waxes that are commercially available and that can be used are, e.g. Aquacer® 1041 from BYK Chemie, Germany, Aquacer® 561 from BYK Chemie, Aquacer® 517 from BYK Chemie, Wükonil® O-33a from Münzing Chemie and Licowax® KST from Clariant, Germany,

Constituent (a6)

[0081] Composition (A) further comprises at least one of fluoride anions and bifluoride anions as constituent (a6). Preferably, composition (A) comprises fluoride anions as constituent (a6), more preferably in combination with bifluoride anions.

[0082] Fluoride anions and/or bifluoride anions are present in the composition (A) in each case independently of one another in an amount in the range of from 0.01 to 25 g/l, preferably of from 0.5 to 10 g/l, in particular of from 1.0 to 5.0 g/l calculated as sodium fluoride in case of fluoride anions and as sodium bifluoride in case of bifluoride anions.

Optional further constituents

[0083] Optionally, composition (A) may comprise at least one furthers constituent (a7). Said at least one further constituent (a7) is preferably selected from the group consisting of thickeners, pigments, fillers, corrosion inhibitors, defoamers, surfactants and mixtures thereof. Constituent(s) (a7) may be present in amount of from 0.01 to 10 wt.-% in composition (A), based on the total weight of composition (A).

[0084] Examples of defoamers are polymer-based, silicone-free defoamers. If a defoamer is present, which is preferred, the amount of the at least one defoamer in composition (A) is preferably in a range of from 0.01 to 3 wt.-%, based on the total weight of composition (A).

[0085] Examples of corrosion inhibitors are morpholine, benzylamine, butindiol, diisopropylamine nitrite, morpholine nitrite, 2-(2-heptadec-8-enyl-2-imidazolin-1-yl)ethanol, dicyclohexylamine nitrite, cyclohexylamine benzoate, dicyclohexylamine caprylate, guanadine chromate, hexamethyleneimine benzoate, dicyclohexylamine benzoate, ethylaniline, mercaptobenzotriazole, pyridine, rosin amine, phenylacridine, hexamethylentetramin, nonylphenoxyacetic acid, succinic acid semi-ester and butindiol. If a corrosion inhibitor is present the amount of the at least one corrosion inhibitor in composition (A) is preferably in a range of from 0.01 to 3 wt.-%, based on the total weight of composition (A).

[0086] Examples of thickeners are polysaccharide, polysiloxane, polyvinlyamide, polyacrylamide and polyglycol.

[0087] Examples of pigments and fillers are boron nitride, graphite and molybdenum sulfide. However, as in particular graphite and molybdenum sulfide are solid lubricants and their use is related to disadvantages as outlined in the introductory part, preferably no such pigments, in particular neither graphite nor molybdenum sulfide, is present in composition (A).

[0088] Examples of surfactants are fatty alcohol alkoxylates and especially fatty alcohol ethoxylates.

Optional step (3)

[0089] Optional step (3) of the inventive method is a step, wherein the coating film obtained after step (2) is optionally dried.

[0090] The drying step (3) may be preferably performed, e.g. at a temperature in the range of 15°C to 100°C, more preferably at a temperature in the range of 18°C to 95°C, in particular at a temperature in the range of 20°C to 90°C.

Inventive pretreated substrate

[0091] A further subject-matter of the present invention is a pretreated metallic substrate obtainable by the inventive method.

[0092] All preferred embodiments described above herein in connection with the inventive method of pretreatment are also preferred embodiments of pretreated substrate. The same applies, of course, to the embodiments of the substrate as such as outlined hereinbefore in connection with step (1) of the inventive method.

[0093] The coating film obtained after step (2) or optionally after step (3) is a combined conversion and lubricant coating film. Thus, the coating film obtained combines the properties of a conversion layer and a lubricant layer.

[0094] Preferably, the pretreated metallic substrate obtainable by the inventive method contains a conversion coating film obtained by performing step (2) and further contains a lubricant coating film on top of said conversion coating film also obtained by performing step (2). However, it is also possible that the coating film obtained after step (2) or optionally after step (3) is chemically heterogeneous.

[0095] Preferably, the coating film present on the surface of the substrate after having performed step (2) and optionally step (3) has a coating weight in a range of from 1.0 to 40.0 g/m^2, preferably in a range of from 5.0 to 35.0 g/m^2, more preferably in a range of from 10.0 to 30.0 g/m^2. The method for determining the coating weight is disclosed in the example section.

Inventive cold forming method

[0096] A further subject-matter of the present invention is a method of cold forming a metallic substrate, characterized in that it comprises a step of subjecting the inventive pretreated metallic substrate according to a cold forming process, preferably by drawing.

[0097] All possible cold forming processes known in the prior art can be carried out, in particular rolling such as thread rolling or beating, e.g. for nut or bolt blanks, drawing, in particular sliding drawing (tensile compression forming), e.g. of welded or seamless tubes, hollow sections, solid sections, wires or rods, e.g. during wire drawing or tube drawing, or deep-drawing, e.g. of strips or sheet metal, pressing such as cold extrusion (pressure forming), e.g. of hollow or solid bodies, stretch forming (forming to gauge block/final size) and/or cold upsetting, e.g. from wire sections to fasteners such as nuts.

[0098] The most common shaped bodies to be formed from the inventive pretreated metallic substrates are strips, sheets, slugs, wires, wire coils, more complicated shaped parts, sleeves, profiles such as hollow or solid profiles, tubes, discs, discs, rods, bars or cylinders.

[0099] Preferably, the cold-formed substrate obtained after the cold forming process still bears at least part of the coating film obtained after having performed step (2) and optionally step (3): Due to the amount of the coating weight of the coating film obtained after step (2) or optionally step (3) present on the pretreated substrate, said coating film "survives" conventional cold forming processes. For example, this leaves at least 10 %, preferably at least 15 %, particularly preferred at least 20 % of the coating weight on a pretreated and cold formed substrate after cold forming, in particular if the substrate has undergone a drawing.

[0100] However, the coating film may be removed from the cold formed substrate, e.g., by using an aqueous cleaning composition. Thus, after the cold forming process, the obtained substrate is preferably cleaned, in order to remove the conversion and lubricant coating film from the substrate, e.g. by means of alkaline cleaners, acids or pickling agents.

Inventive composition (A)

[0101] A further subject-matter of the present invention is an aqueous lubricant composition (A) as defined hereinbefore in connection with the inventive pretreatment method.

[0102] All preferred embodiments described above herein in connection with the inventive method and the composition (A) used in step (2) thereof and the constituents contained therein are also preferred embodiments of the inventive composition (A).

Inventive master batch

[0103] A further subject-matter of the present invention is a master batch to produce the inventive aqueous composition (A) by diluting the master batch with water and if applicable by adjusting the pH value.

[0104] All preferred embodiments described above herein in connection with the inventive methods and the inventive composition (A) and the constituents contained therein are also preferred embodiments of inventive master batch.

[0105] If a master batch is used to produce the aqueous composition (A) according to the present invention, the master batch typically contains the constituents of the aqueous composition (A) to be produced in the desired proportions, but at a higher concentration. Such master batch is preferably diluted with water to the concentrations of constituents as disclosed above to form the aqueous composition (A). If necessary, the pH value of the aqueous composition (A) may be adjusted after dilution of the master batch.

[0106] Of course, it is also possible to further add any of the optional components to the water, wherein the master batch is diluted or to add any of the optional components after diluting the master batch with water. It is however preferred that the master batch already contains all necessary components.

[0107] Preferably, the master batch is diluted with water and/or an aqueous solution in the ratio of 1:5,000 to 1:5, more preferred 1:1,000 to 1:10, most preferred in the ratio of 1:300 to 1:10 and even more preferred 1:150 to 1:50 to produce composition (A).

METHODS

1. Total acid (TA)

[0108] The total acid (TA) is the sum of the divalent cations present as well as free and bound oxalic acids (the latter being oxalates). It is determined by the consumption of 0.1 M NaOH using 10 to 15 drops of phenolphthalein water solution as test indicator. For this, 10 ml of the composition are pipetted into a suitable vessel, for example a 300 ml Erlenmeyer flask and diluted with 50 ml of deionized water. It is then titrated with 0.1 M NaOH until a color change to red has taken place. The consumption in ml per 10 ml of the diluted composition corresponds to the total acid score (TA).

2. Solid content

[0109] The non-volatile fraction (solids or solid content) is determined in accordance with DIN EN ISO 3251 (date: June 2019). This involves weighing out 1 g of sample into an aluminum dish which has been dried beforehand and drying the dish with sample in a drying cabinet at 130°C for 60 minutes, cooling it in a desiccator, and then reweighing. The residue, relative to the total amount of sample employed, corresponds to the nonvolatile fraction.

3. ICP-OES

[0110] The amounts of certain elements in a sample under analysis is determined using inductively coupled plasma atomic emission spectrometry (ICP-OES) according to DIN EN ISO 11885 (date: September 1, 2009).

EXAMPLES

[0111] The following examples further illustrate the invention, but are not to be construed as limiting its scope.

1. Inventive lubricant composition

Inventive example 11

[0112] An acid stable aqueous polymeric lubricant composition I1 was prepared in a highspeed mixer with stirring. The composition of this lubricant is given in Table 1.

Table 1: Composition of lubricant example I1

Constituent	*Amount [wt.-%]*
Polymer 1	0.73
Aqueous wax dispersion 1 (40 wt.-% solids)	6.63
Aqueous wax dispersion 2 (40 wt.-% solids)	1.60
Wax 3	0.55
Defoamer	0.18
Oxalic acid dihydrate	4.93
Sodium chloride	1.95
Sodium hydrogen fluoride	0.84
Titanium dioxide	0.14
Sodium thiosulfate	0.07
Sodium fluoride	0.01
Deionized water	82.37
	Σ 100.0

[0113] Polymer 1 is a polyvinyl pyrrolidone homopolymer. A commercial product available from BASF SE has been used.

[0114] Aqueous wax dispersion 1 contains a polypropylene wax, which is commercially available from BYK Chemie. Aqueous wax dispersion 2 contains a microcrystalline wax, which is commercially available from Michelman. Wax 3 is a montan wax, which is dispersible in aqueous medium.

[0115] The composition has a pH value below 2.0.

Comparative example C1

[0116] The commercially available product Gardobond® AS 4200, which is an oxalating treatment solution containing oxalic acid, chloride and/or fluoride anions, and sodium thiosulfate, has been used as comparative composition C1.

Comparative examples C2, C3, C4 and C5

[0117] A number of further comparative compositions, namely compositions C2, C3, C4 and C5, were prepared. Composition C2 was identical to lubricant example I1, but no sodium chloride was used for its preparation. Composition C3 was identical to lubricant example I1, but no sodium thiosulfate was used for its preparation. Composition C4 was identical to lubricant example I1, but no sodium chloride and no sodium thiosulfate were used for its preparation. Composition C5 was identical to lubricant example I1, but its pH was adjusted to be >3.

2. Inventive method

2.1 *Oxalating treatment and lubricating treatment in a single step by making use of inventive composition 11*

[0118] As metal workpiece the following substrate S1 was used:
Sheet made of 1.0 mm stainless steel (material-No.: 1.4571).

[0119] The workpiece was dipped in a cleaning bath with a 50 g/L aqueous cleaning solution of Gardoclean® 351 available from Chemetall GmbH at 90°C for 10 min. and then rinsed by cold tap water for 1 min. Afterwards, the surface purified workpiece was then pickled by using an aqueous solution containing 20 wt.-% nitric acid and 4 wt.-% hydrofluoric acid at room temperature (23°C) for 1 min. and subsequently rinsed by cold tap water for 1 min.

[0120] Then, in a single step, the workpiece was dipped into a bath containing lubricant example I1 at 65°C for 10 min.

[0121] Finally, the coated workpiece obtained was dried with air at 85 °C.

[0122] No solid foams were formed during this process. The resulting sludge in the reaction bath of I1 was powdery and similar to the sludge formed in an oxalating bath containing Gardobond® AS 4200 from Chemetall GmbH (composition C1, cf. item **2.2**) and could be easily removed from the reaction bath.

2.2 *Treatment with commercially available oxalating solution C1 in a single step*

[0123] Substrate S1 as described hereinbefore was used as workpiece.

[0124] The workpiece was treated as follows:
The workpiece was dipped in a cleaning bath with a 50 g/L aqueous cleaning solution of Gardoclean® 351 available from Chemetall GmbH at 90°C for 10 min. and then rinsed by cold tap water for 1 min. Afterwards, the surface purified workpiece was then pickled by using an aqueous solution containing 20 wt.-% nitric acid and 4 wt.-% hydrofluoric acid at room temperature (23°C) for 1 min. and subsequently rinsed by cold tap water for 1 min.

[0125] Then, in a single step, the workpiece was dipped into a bath containing Gardobond® AS 4200 at 65°C for 10 min.

[0126] Finally, the coated workpiece obtained was dried with air at 85 °C.

2.3 *Treatment by making use of comparative compositions C2, C3, C4 and C5*

[0127] A substrate S1 was treated in the same manner as described hereinbefore in item **2.1** except in that one of compositions C2, C3, C4 and C5 was used instead of I1.

3. Properties of the coated substrates

3.1 *Coated substrate obtained from the 1-step-process* as *outlined in item* ***2.1***

[0128] The resulting coating layer of the coated workpiece is homogenous, thick and adhered firmly on the treated surface of the workpiece. The top coating layer formed by the method is a polymer lubricant layer and the bottom coating layer formed is an oxalate coating layer. Coating layers properties are observed using SEM technology. The bottom oxalate coating layer on the stainless-steel surface was proven to be a sufficiently closed coating layer on the surface of the metal workpiece.

[0129] The coating weights on the substrate were determined using the following test method:
The coated workpiece was weighted. Then, the polymer lubricant coating layer was washed with boiling xylene in order to detach it and subsequently with boiling water. The workpiece was then dried and weighted. The oxalate coating layer was washed with an alkaline solution containing NaOH, triethyl amine and EDTA (PL 83 from Chemetall GmbH) in order to detach it. Finally, the workpiece was rinsed with water, dried and weighted once again.

[0130] The resulting coating weights are listed in Table 2.

Table 2: Coating weights on substrate surfaces (substrate S1) in g/m^2

Substrate	Polymer lubricant coating weight [g/m^2]	Oxalate coating weight [g/m^2)]	Total [g/m^2]
S1	7.5	10.6	18.1

[0131] The coated substrate shows very good lubricating properties and is very suitable for cold forming, even with high drawing speeds, and for cold extrusion. The coating layers adhere firmly on the metal surface of the substrates, even after cold forming.

[0132] After metal cold forming, the remaining coating adhered still firmly on the metal surface and the remaining coating layer can be washed using aqueous alkalic cleaner, e.g. Gardoclean® S 5171 with Gardobond® Additive H 7375 from Chemetall GmbH, or aqueous acidic cleaner, e.g. Gardobond® Additive H 7132 with Gardobond® Additive H 7390 from Chemetall GmbH.

3.2 *Coated substrate obtained from the 1-step-process* as *outlined in item* ***2.2***

[0133] The resulting oxalate coating layer on stainless steel is closed and homogenous.

[0134] The coating weight on the substrate was determined using the following test method:
The oxalated workpiece was weighted. The oxalate coating layer was washed with an alkaline solution containing NaOH, triethyl amine and EDTA (PL 83 from Chemetall GmbH) in order to detach it. Finally, the workpiece was rinsed with water, dried and weighted once again. The resulting oxalate coating weight is 10 g/m^2.

[0135] The coated substrate shows no lubricating properties at all and is thus as such not suitable for cold forming. For this the oxalate coated stainless-steel substrate has to be subjected to lubrication in an additional process step.

3.3 *Coated substrates obtained from the 1-step-processes* as *outlined in item* ***2.3***

[0136] In case of having used comparative composition C2 the resulting coating layer of the coated workpiece was found to have an inferior homogeneity compared to the coated workpiece obtained from having used composition I1. An even inferior homogeneity was observed when comparative composition C3 was used. In case of having used comparative examples C4 and C5 no coating layer at all was found to have been formed on the substrate.

Claims

1. A method for pretreatment of a metallic substrate for a subsequent metal cold forming process, said method comprising at least steps (1) and (2) and optionally step (3), namely

   (1) providing at least one substrate having at least one surface at least partially made of at least one metal,
   (2) contacting the at least one surface of the substrate provided in step (1) with an aqueous lubricant composition (A) having a pH value below 2.0, wherein the aqueous lubricant composition (A) comprises besides water

      (a1) oxalate anions,
      (a2) thiosulfate anions,
      (a3) chloride anions in an amount in the range of from 0.1 to 25 g/l, calculated as sodium chloride,
      (a4) at least one film-forming polymer, which is a homopolymer and/or copolymer being prepared by polymerization of at least one ethylenically unsaturated monomer,
      (a5) at least one wax, which is different from constituent (a4), and
      (a6) fluoride anions and/or bifluoride anions in each case independently of one another in an amount in the range of from 0.01 to 25 g/l, calculated as sodium fluoride in case of fluoride anions and as sodium bifluoride in case of bifluoride anions,

   and
   (3) optionally drying the coating film obtained after having performed step (2).

2. The method according to claim 1, **characterized in that** composition (A) has a pH value below 1.9, preferably below 1.7, in particular a pH value in a range of from 0.1 to 1.5.

3. The method according to claim 1 or 2, **characterized in that** the at least one film-forming polymer (a4) is a homopolymer and/or copolymer, said homopolymer and/or copolymer being prepared at least from at least one monomer selected from the group consisting of vinyl amine, vinyl alcohol, vinyl formamide, vinyl pyrrolidone, vinyl caprolactam, vinyl acetate and vinyl imidazole, preferably from at least one monomer selected from the group consisting of vinyl pyrrolidone and vinyl acetate, in particular from at least vinyl pyrrolidone.

4. The method according to any one of the preceding claims, **characterized in that** the at least one film-forming polymer (a4) is present in the composition (A) in an amount in the range of from 0.05 to 20 wt.-%, more preferably in the range of from 0.10 to 15 wt.-%, in each case based on the total weight of the composition (A).

5. The method according to any one of the preceding claims, **characterized in that** the at least one wax (a5) is selected from the group consisting of polyolefin waxes, preferably polyethylene waxes and polypropylene waxes, paraffin waxes and natural waxes, preferably montan waxes, bee waxes and carnauba waxes, and mixtures thereof.

6. The method according to any one of the preceding claims, **characterized in that** the at least one wax (a5) is present in the composition (A) in an amount in the range of from 0.1 to 20 wt.-%, more preferably in the range of from 0.5 to 15 wt.-%, in each case based on the total weight of the composition (A).

7. The method according to any one of the preceding claims, **characterized in that**

   oxalate anions (a1) are present in the composition (A) in an amount in the range of from 2 to 500 g/l, more preferably of from 5 to 100 g/l, in particular of from 10 to 50 g/l of oxalic acid, calculated in each case as oxalic acid dihydrate, and/or
   thiosulfate anions (a2) are present in the composition (A) in an amount in the range of from 0.01 to 25 g/l, more preferably of from 0.5 to 10 g/l, in particular of from 1.0 to 5.0 g/l, calculated in each case as sodium thiosulfate,

and/or
chloride anions (a3) are present in the composition (A) in an amount in the range of from 0.5 to 10 g/l, in particular of from 1.0 to 5.0 g/l, calculated in each case as sodium chloride.

8. The method according to any one of the preceding claims, **characterized in that** composition (A) comprises at least one of fluoride anions and bifluoride anions as constituent (a6) in each case independently of one another in an amount in the range of from 0.5 to 10 g/l, in particular of from 1.0 to 5.0 g/l, calculated in each case as sodium fluoride in case of fluoride anions and as sodium bifluoride in case of bifluoride anions.

9. The method according to any one of the preceding claims, **characterized in that** contacting step (2) is performed by at least partially dipping the substrate into a bath containing the aqueous lubricant composition (A) having a bath temperature in the range of from 20 to 95 °C, preferably of from 30 to 90 °C, in particular of from 45 to 85 °C.

10. The method according to any one of the preceding claims, **characterized in that** the at least one surface of the substrate is at least partially made of stainless steel, preferably **in that** the substrate as such is made of stainless steel.

11. A pretreated metallic substrate obtainable by the method according to any one of claims 1 to 10.

12. The pretreated metallic substrate according to claim 11, **characterized in that** the coating film present on the surface of the substrate after having performed step (2) and optionally step (3) has a coating weight in a range of from 1.0 to 40.0 g/m^2, preferably in a range of from 5.0 to 35.0 g/m^2, more preferably in a range of from 10.0 to 30.0 g/m^2.

13. A method of cold forming a metallic substrate, **characterized in that** it comprises a step of subjecting the pretreated metallic substrate according to claim 11 or 12 to a cold forming process, preferably by drawing.

14. An aqueous lubricant composition (A) as defined in any of claims 1 to 8.

15. A master batch to produce the aqueous composition (A) according to claim 14 by diluting the master batch with water and if applicable by adjusting the pH value.

Patentansprüche

1. Verfahren zur Vorbehandlung eines metallischen Substrats für ein nachfolgendes Metall-Kaltformverfahren, wobei das Verfahren wenigstens Schritte (1) und (2) und gegebenenfalls Schritt (3) umfasst, nämlich

   (1) Bereitstellen wenigstens eines Substrats mit wenigstens einer Oberfläche, die wenigstens zum Teil aus wenigstens einem Metall besteht,
   (2) Inkontaktbringen der wenigstens einen Oberfläche des bei Schritt (1) bereitgestellten Substrats mit einer wässrigen Schmiermittelzusammensetzung (A) mit einem pH-Wert unter 2,0, wobei die wässrige Schmiermittelzusammensetzung (A) neben Wasser Folgendes umfasst:

      (a1) Oxalat-Anionen,
      (a2) Thiosulfat-Anionen,
      (a3) Chlorid-Anionen in einer Menge im Bereich von 0,1 bis 25 g/l, berechnet als Natriumchlorid,
      (a4) wenigstens ein filmbildendes Polymer, das ein Homopolymer und/oder Copolymer ist, das durch Polymerisation von wenigstens einem ethylenisch ungesättigten Monomer hergestellt wird,
      (a5) wenigstens ein Wachs, das von Bestandteil (a4) verschieden ist, und
      (a6) Fluorid-Anionen und/oder Bifluorid-Anionen, jeweils unabhängig voneinander in einer Menge im Bereich von 0,01 bis 25 g/l, berechnet als Natriumfluorid im Fall von Fluorid-Anionen und als Natriumbifluorid im Fall von Bifluorid-Anionen,

   und
   (3) gegebenenfalls Trocknen des nach Durchführung von Schritt (2) erhaltenen Beschichtungsfilms.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** Zusammensetzung (A) einen pH-Wert unter 1,9, vorzugsweise unter 1,7, und insbesondere einen pH-Wert im Bereich von 0,1 bis 1,5 aufweist.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** das wenigstens eine filmbildende Polymer (a4) ein Homopolymer und/oder Copolymer ist, wobei das Homopolymer und/oder Copolymer wenigstens aus wenigstens einem Monomer ausgewählt aus der Gruppe bestehend aus Vinylamin, Vinylalkohol, Vinylformamid, Vinylpyrrolidon, Vinylcaprolactam, Vinylacetat und Vinylimidazol, vorzugsweise aus wenigstens einem Monomer ausgewählt aus der Gruppe bestehend aus Vinylpyrrolidon und Vinylacetat, insbesondere aus wenigstens Vinylpyrrolidon, hergestellt wird.

4. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das wenigstens eine filmbildende Polymer (a4) in der Zusammensetzung (A) in einer Menge im Bereich von 0,05 bis 20 Gew.-%, weiter bevorzugt im Bereich von 0,10 bis 15 Gew.-%, jeweils bezogen auf das Gesamtgewicht der Zusammensetzung (A), vorhanden ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das wenigstens eine Wachs (a5) ausgewählt ist aus der Gruppe bestehend aus Polyolefinwachsen, vorzugsweise Polyethylenwachsen und Polypropylenwachsen, Paraffinwachsen und natürlichen Wachsen, vorzugsweise Montanwachsen, Bienenwachsen und Carnaubawachsen, und Gemischen davon.

6. Verfahren gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das wenigstens eine Wachs (a5) in der Zusammensetzung (A) in einer Menge im Bereich von 0,1 bis 20 Gew.-%, weiter bevorzugt im Bereich von 0,5 bis 15 Gew.-%, jeweils bezogen auf das Gesamtgewicht der Zusammensetzung (A), vorhanden ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** Oxalat-Anionen (a1) in der Zusammensetzung (A) in einer Menge im Bereich von 2 bis 500 g/l, weiter bevorzugt von 5 bis 100 g/l, insbesondere von 10 bis 50 g/l, Oxalsäure, jeweils berechnet als Oxalsäuredihydrat, vorhanden sind, und/oder

   Thiosulfat-Anionen (a2) in der Zusammensetzung (A) in einer Menge im Bereich von 0,01 bis 25 g/l, weiter bevorzugt von 0,5 bis 10 g/l, insbesondere von 1,0 bis 5,0 g/l, jeweils berechnet als Natriumthiosulfat, vorhanden sind, und/oder
   Chlorid-Anionen (a3) in der Zusammensetzung (A) in einer Menge im Bereich von 0,5 bis 10 g/l, insbesondere von 1,0 bis 5,0 g/l, jeweils berechnet als Natriumchlorid, vorhanden sind.

8. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** Zusammensetzung (A) Fluorid-Anionen und/oder Bifluorid-Anionen als Bestandteil (a6) jeweils unabhängig voneinander in einer Menge im Bereich von 0,5 bis 10 g/l, insbesondere von 1,0 bis 5,0 g/l, jeweils berechnet als Natriumfluorid im Fall von Fluorid-Anionen und als Natriumbifluorid im Fall von Bifluorid-Anionen, umfasst.

9. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Schritt des Inkontaktbringens (2) durch wenigstens teilweises Eintauchen des Substrats in ein Bad, das die wässrige Schmiermittelzusammensetzung (A) enthält, mit einer Badtemperatur im Bereich von 20 bis 95 °C, vorzugsweise von 30 bis 90 °C, insbesondere von 45 bis 85 °C, durchgeführt wird.

10. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die wenigstens eine Oberfläche des Substrats wenigstens zum Teil aus nichtrostendem Stahl besteht, vorzugsweise **dadurch gekennzeichnet, dass** das Substrat als solches aus nichtrostendem Stahl besteht.

11. Vorbehandeltes metallisches Substrat, erhältlich durch das Verfahren nach einem der Ansprüche 1 bis 10.

12. Vorbehandeltes metallisches Substrat nach Anspruch 11, **dadurch gekennzeichnet, dass** der nach Durchführung von Schritt (2) und gegebenenfalls Schritt (3) auf der Oberfläche des Substrats vorhandene Beschichtungsfilm ein Beschichtungsgewicht in einem Bereich von 1,0 bis 40,0 g/m^2, vorzugsweise in einem Bereich von 5,0 bis 35,0 g/m^2, weiter bevorzugt in einem Bereich von 10,0 bis 30,0 g/m^2, aufweist.

13. Verfahren zum Kaltformen eines metallischen Substrats, **dadurch gekennzeichnet, dass** es einen Schritt umfasst, bei dem man das vorbehandelte metallische Substrat nach Anspruch 11 oder 12 einem Kaltformverfahren, vorzugsweise durch Ziehen, unterwirft.

14. Wässrige Schmiermittelzusammensetzung (A) gemäß einem der Ansprüche 1 bis 8.

15. Masterbatch zur Herstellung der wässrigen Zusammensetzung (A) nach Anspruch 14 durch Verdünnen des Masterbatch mit Wasser und gegebenenfalls Einstellen des pH-Werts.

Revendications

1. Procédé de prétraitement d'un substrat métallique pour un processus de formage à froid de métal subséquent, ledit procédé comprenant au moins les étapes (1) et (2) et éventuellement l'étape (3), à savoir

(1) la fourniture d'au moins un substrat ayant au moins une surface partiellement composée d'au moins un métal,
(2) la mise en contact de l'au moins une surface du substrat fourni à l'étape (1) avec une composition aqueuse de lubrifiant (A) ayant une valeur de pH inférieure à 2,0, la composition aqueuse de lubrifiant (A) comprenant outre de l'eau

(a1) des anions oxalate,
(a2) des anions thiosulfate,
(a3) des anions chlorure en une quantité dans la plage de 0,1 à 25 g/l, calculée en chlorure de sodium,
(a4) au moins un polymère filmogène, qui est un homopolymère et/ou un copolymère préparé par polymérisation d'au moins un monomère éthyléniquement insaturé,
(a5) au moins une cire, qui est différente du constituant (a4), et
(a6) des anions fluorure et/ou des anions bifluorure, en chaque cas indépendamment les uns des autres en une quantité dans la plage de 0,01 à 25 g/l, calculée en fluorure de sodium pour les anions fluorure et en bifluorure de sodium pour les anions bifluorure,

et
(3) éventuellement séchage du film de revêtement obtenu après avoir effectué l'étape (2).

2. Procédé selon la revendication 1, **caractérisé en ce que** la composition (A) présente une valeur de pH inférieure à 1,9, préférablement inférieure à 1,7, en particulier une valeur de pH dans une plage de 0,1 à 1,5.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** l'au moins un polymère filmogène (a4) est un homopolymère et/ou copolymère, ledit homopolymère et/ou copolymère étant préparé au moins à partir d'un monomère choisi dans le groupe constitué par la vinylamine, l'alcool vinylique, le vinylformamide, la vinylpyrrolidone, le vinylcaprolactame, l'acétate de vinyle et le vinylimidazole, préférablement parmi au moins un monomère choisi dans le groupe constitué par la vinylpyrrolidone et l'acétate de vinyle, en particulier parmi au moins la vinylpyrrolidone.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'au moins un polymère filmogène (a4) est présent dans la composition (A) en une quantité dans la plage allant de 0,05 à 20 % en poids, plus préférablement dans la plage allant de 0,10 à 15 % en poids, en chaque cas sur la base du poids total de la composition (A).

5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'au moins une cire (a5) est choisie dans le groupe constitué par des cires de polyoléfine, préférablement des cires de polyéthylène et des cires de polypropylène, des cires de paraffine et des cires naturelles, préférablement des cires de montan, des cires d'abeilles et des cires de carnauba, et des mélanges correspondants.

6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'au moins une cire (a5) est présente dans la composition (A) en une quantité dans la plage allant de 0,1 à 20 % en poids, plus préférablement dans la plage allant de 0,5 à 15 % en poids, en chaque cas sur la base du poids total de la composition (A).

7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** des anions oxalate (a1) sont présents dans la composition (A) en une quantité dans la plage de 2 à 500 g/l, plus préférablement de 5 à 100 g/l, en particulier de 10 à 50 g/l d'acide oxalique, en chaque cas calculée en dihydrate d'acide oxalique, et/ou

des anions thiosulfate (a2) sont présents dans la composition (A) en une quantité dans la plage de 0,01 à 25 g/l, plus préférablement de 0,5 à 10 g/l, en particulier de 1,0 à 5,0 g/l, en chaque cas calculée en thiosulfate de sodium, et/ou
des anions chlorure (a3) sont présents dans la composition (A) en une quantité dans la plage de 0,5 à 10 g/l, en

particulier de 1,0 à 5,0 g/l, en chaque cas calculée en chlorure de sodium.

8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la composition (A) contient au moins l'un parmi des anions fluorure et des anions bifluorure en tant que constituant (a6) en chaque cas indépendamment l'un de l'autre en une quantité dans la plage de 0,5 à 10 g/l, en particulier de 1,0 à 5,0 g/l, en chaque cas calculée en fluorure de sodium pour les anions fluorure et en bifluorure de sodium pour les anions bifluorure.

9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'étape de mise contact (2), est réalisée en trempant au moins partiellement le substrat dans un bain contenant la composition aqueuse de lubrifiant (A) ayant une température de bain dans la plage allant de 20 à 95 °C, préférablement allant de 30 à 90 °C, en particulier allant de 45 à 85 °C.

10. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'au moins une surface du substrat est au moins partiellement composée d'acier inoxydable, préférablement **en ce que** le substrat en tant que tel est composé d'acier inoxydable.

11. Substrat métallique prétraité pouvant être obtenu par le procédé selon l'une quelconque des revendications 1 à 10.

12. Substrat métallique prétraité selon la revendication 11, **caractérisé en ce que** le film de revêtement présent sur la surface du substrat après avoir effectué l'étape (2) et éventuellement l'étape (3) a un poids de revêtement dans la plage allant de 1,0 à 40,0 g/m^2, préférablement dans une plage allant de 5,0 à 35,0 g/m^2, plus préférablement dans une plage allant de 10,0 à 30,0 g/m^2.

13. Procédé de formage à froid d'un substrat métallique, **caractérisé en ce qu'**il comprend une étape de soumission du substrat métallique prétraité selon la revendication 11 ou 12 à un processus de formage à froid, préférablement par étirage.

14. Composition aqueuse de lubrifiant (A) telle que définie dans l'une quelconque des revendications 1 à 8.

15. Mélange maître pour produire la composition aqueuse (A) selon la revendication 14 en diluant le mélange maître avec de l'eau et, le cas échéant, en ajustant la valeur du pH.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- DE 1179437 **[0003]**
- DE 1196467 **[0003] [0004]**
- EP 0233503 A1 **[0003] [0005]**
- EP 0232929 A1 **[0006] [0007] [0013]**
- WO 9416119 A1 **[0006] [0008]**
- WO 2009095373 A1 **[0006] [0009] [0012] [0013]**
- WO 2009095375 A1 **[0006] [0010] [0013]**
- WO 2009095374 A1 **[0006] [0010] [0013]**
- JP 56072090 A **[0006]**
- JP S5672090 A **[0011] [0013]**
- EP 3290544 A1 **[0014]**
- JP S545847 A **[0015]**