

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 350 867 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

08.10.2003 Bulletin 2003/41

(51) Int Cl.7: **C23C 22/23, C10M 173/02**

(21) Application number: **03007463.7**

(22) Date of filing: **04.04.2003**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**

Designated Extension States:

AL LT LV MK RO

(30) Priority: **04.04.2002 EP 02007662**

(71) Applicant: **Zepf, Walter**

78467 Konstanz/Bodensee (DE)

(72) Inventor: **Zepf, Walter**

78467 Konstanz/Bodensee (DE)

(74) Representative: **Müller-Boré & Partner**

Patentanwälte

Grafinger Strasse 2

81671 München (DE)

(54) **A coating solution for metals and metal alloys**

(57) The present invention relates to a coating solution to be applied on the surface of metals or metal alloys, a process for cold forming of metals and metal alloys using said coating solution, and a coated blank made of a metal or a metal alloy.

EP 1 350 867 A1

Description

[0001] The present invention relates to a coating solution to be applied onto the surface of metals or metal alloys, a process for cold forming of metals and metal alloys using said coating solution, and a coated blank made of a metal or a metal alloy.

[0002] In cold forming, no heat is applied to the metallic workpiece before forming. However, its temperature can increase during the forming process, as the energy expended in forming is almost completely converted into heat. The main advantages of cold forming are the saving of materials and working time, the use of lower strength steels, the improved quality of workpieces, lower machine costs, better size accuracy, high surface quality and an extended tool life. In order to achieve these advantages, a protective film must be formed between the tool and the work piece, which must remain intact during the working process. Such a protective film is mainly made up of molybdenum disulfide dispersions or graphite as lubricants. Hitherto, in order to obtain such a protective lubricating film in cold forming processes, lubricant carriers are applied onto the surface of the workpiece, which can absorb about five times the quantity of lubricants compared to the untreated metal surface. However, the application of such lubricant carriers onto the surface of workpieces is carried out by applying aggressive acids and metallic soaps in huge amounts, which is not desirable from an ecological standpoint.

[0003] Therefore, the technical problem underlying the present invention is to provide a new system for cold forming of metals and metal alloys, which should avoid the treatment of the working piece with aggressive acids and/or metallic soaps prior to the cold forming process, but should exhibit at least the same results compared to a cold forming process using workpieces treated with aggressive acids and/or metallic soaps.

[0004] The solution to the above technical problem is achieved by providing the embodiments characterized in the claims.

[0005] In particular, there is provided a coating solution to be applied onto the surface of a metal or a metal alloy, comprising a polyphosphate and a dithiocarbamate.

[0006] In a preferred embodiment of the present invention, the polyphosphate is selected from the group consisting of ammonium polyphosphate and alkali metal polyphosphates, such as sodium polyphosphate, or mixtures thereof. The amount of said polyphosphate is preferably in the range of from about 0.1% (w/v) to about 80% (w/v).

[0007] The dithiocarbamate is preferably a dialkyl dithiocarbamate, wherein the alkyl groups are the same or different and can have 1 to 12 carbon atoms. In a preferred embodiment of the present invention the dithiocarbamate is a heavy metal dithiocarbamate, wherein the heavy metal is for example molybdenum. In a more preferred embodiment of the present invention the dithiocarbamate is a molybdenum dibutyldithiocarbamate. The amount of said dithiocarbamate is preferably in the range of from about 0.1% (w/v) to about 80% (w/v).

[0008] The coating solution of the present invention can further include graphite and/or molybdenum disulfide, each of which can be present preferably in an amount of from about 0.1% (w/v) to about 80% (w/v).

[0009] In a preferred embodiment of the present invention the coating solution may further contain at least one component selected from the group consisting of alcohols in an amount of from 0 % to about 100% (v/v); waxes such as polyalkylene waxes, e.g. polyethylene waxes, microcrystalline waxes, and Montan ester® waxes, in an amount of from 0 % to about 80 (v/v); emulsifying agents such as alkyloxyethylates and alkylaryloxyethylates, in an amount of from 0 % to about 50% (v/v); pH-modulating agents such as buffers, e.g. phosphorous acid and esters thereof, in an amount of from 0 % to about 50% (v/v); polymeric compounds such as polyethylene glycols, preferably having a weight average molecular weight of from 500 to 1,000,000, polysaccharides and methylcellulose, in an amount of from 0% to about 50% (v/v); oxides such as silicon dioxide, in an amount of from 0% to about 50% (v/v); friction-reducing agents such as sodium stearate, in an amount of from 0% to about 80% (v/v); defoaming agents such as fatty alcohol polyglycol ethers, in an amount of from 0% to about 50% (v/v); carboxylic acids and derivatives thereof such as 2-phosphonobutanetricarboxylic acid, in an amount of from 0% to about 50% (v/v); organophosphorous compounds such as alkylphosphates, in an amount of from 0% to about 5% (v/v); and phosphates such as boron phosphate, sodium phosphate, P₂O₅ etc., in an amount of from 0% to about 80% (v/v); and mixtures thereof containing two or more of said components.

[0010] In a preferred embodiment of the present invention, the coating solution has a pH-value ranging from about 3 to about 4, adjusted by the above-defined pH-modulating agent.

[0011] The solvent used for the coating solution of the present invention is H₂O in an amount of from 0% to 100% (v/v), alcohols, preferably alcohols having up to 10 carbon atoms such as methanol, ethanol, etc., or a mixture of different alcohols, in an amount of from 0% to 100% (v/v), or a H₂O/alcohol-mixture in an amount of from 0% to 100% (v/v).

[0012] Further, the present invention relates to a process for cold forming of metals or metal alloys, comprising the steps of:

- (a) immersing a blank of a metal or a metal alloy in a bath containing the above-defined coating solution for a time period of from about 30 seconds to about 10 minutes;

(b) drying said blank having the coating solution on its surface at a temperature ranging from about room temperature to about 80°C, preferably from about 50°C to about 60°C, wherein the drying is carried out preferably in hot air or in a drying stove; and

(c) subjecting the thus-coated blank to cold forming.

[0013] In the preferred embodiment, the blank can be sand-blasted prior to the above process step (a).

[0014] Further, there is provided a blank made of a metal or a metal alloy such as steel, having a coating obtainable by the above-defined process steps (a) and (b).

[0015] When using the above-defined coating solution for the treatment of blanks ("workpieces") to be processed in cold forming, there can be observed that on the one hand the coating solution of the present invention does not exhibit the severe drawbacks with respect to environmental pollution, and on the other hand the blanks having a coating based on the coating solution of the present invention show at least the same results for the processed workpiece and the tool when compared with blanks having a coating known in the prior art. Moreover, the cold forming process using blanks treated with the coating solution of the present invention is superior from an economical standpoint, i.e. the weight of the coating on the blank is much less as compared to the weight of a coating known in the art. Additionally, in comparison with a coating procedure known in the art, wherein about eleven steps for applying the coating on the blank are necessary, only two steps - (i) immersing the blank in the coating solution according to the present invention and then (ii) drying the blank - are necessary resulting in a drastically saving of time.

[0016] The present invention will now be further illustrated in the following examples, without being limited thereto.

Examples

[0017] 25 cylindrically shaped steel blanks (examples 1 to 25) having a length of 500 mm are immersed in a coating solution containing 2-8 % (w/v) polyphosphate, 2-5 % (w/v) dithiocarbamate, 5-12 % (w/v) graphite and 5-12 % (w/v) molybdenum disulfide for a time period of about 1 min. Then, the blanks having the coating solution on their surfaces are transferred to a drying stove wherein they are dried at a temperature of about 60°C for about 30 min. For comparison, 5 cylindrically shaped steel blanks (Comp. Examples 1 to 5) having a length of 500 mm are coated using the agents and procedure known in the art. The results are summarised in Table 1.

Table 1

Examples	blank weight before coating [g]	blank weight after coating [g]	weight of coating [g]	cold forming of coated blanks
1	5583.2	5584.3	1.1	+
2	5558.1	5559.6	1.5	+
3	5560.3	5561.2	0.9	+
4	5562.1	5563.0	0.9	+
5	5552.7	5553.9	1.2	+
6	5532.6	5533.6	1.0	+
7	5538.4	5539.3	0.9	+
8	5552.9	5554.8	1.9	+
9	5564.1	5565.1	1.0	+
10	5554.2	5555.9	1.7	+
11	5553.9	5558.7	2.8	+
12	5547.6	5556.6	1.0	+
13	5560.0	5561.1	1.1	+
14	5568.7	5569.6	0.9	+
15	5573.0	5571.2	0.9	+
16	5563.0	5563.8	0.8	+

Table 1 (continued)

Examples	blank weight before coating [g]	blank weight after coating [g]	weight of coating [g]	cold forming of coated blanks
17	5572.0	5573.0	1.0	+
18	5570.6	5571.5	0.9	+
19	5562.1	5563.0	0.9	+
20	5559.1	5559.9	0.8	+
21	5570.7	5571.8	1.1	+
22	5572.8	5573.4	0.6	+
23	5561.1	5562.7	1.6	+
24	5563.2	5564.0	0.8	+
25	5563.7	5564.8	1.1	+
Comp. Example				
1	5531.0	5560.1	29.1	+
2	5526.8	5557.0	30.2	+
3	5535.4	5562.3	26.9	+
4	5533.4	5563.1	29.7	+
5	5532.6	5551.5	18.9	+

[0018] As can be taken from Table 1, the coated blanks according to the present invention exhibit a drastically reduced coating weight, but the coating reveals at least the same properties for the blank to be cold formed as the coating of blanks obtained according to the prior art, upon evaluation of the processed coated blanks during and after their cold forming (+=good results of the formed blanks after 3 operations in a cold forming process).

Claims

1. A coating solution to be applied on the surface of metals or metal alloys, comprising a polyphosphate and a dithiocarbamate.
2. The coating solution according to claim 1, wherein said polyphosphate is selected from the group consisting of ammonium polyphosphate and alkali metal polyphosphates, or a mixture thereof.
3. The coating solution according to claim 1 of 2, wherein the amount of said polyphosphate is in the range of from about 0.1% (w/v) to about 80% (w/v).
4. The coating solution according to any one of claims 1 to 3, wherein said dithiocarbamate is a dialkyl dithiocarbamate.
5. The coating solution according to claim 4, wherein said dithiocarbamate is a heavy metal dithiocarbamate.
6. The coating solution according to any one of claims 1 to 5, wherein the amount of said dithiocarbamate is in the range of from about 0.1% (w/v) to about 80% (w/v).
7. The coating solution according to any one of claims 1 to 6, further comprising at least one component selected from the group consisting of graphite and molybdenum disulfide, or a mixture thereof.
8. The coating solution according to any one of claims 1 to 7, further comprising at least one component selected from the group consisting of alcohols, waxes, emulsifying agents, pH-modulating agents, polymeric compounds, oxides, friction-reducing agents, defoaming agents, carboxylic acids and derivatives thereof, organophosphorous

compounds, and phosphates, or mixtures thereof containing two or more of said components.

9. The coating solution according to any one of claims 1 to 8, having a pH-value ranging from about 3 to about 4.

5 10. A process for cold forming of metals or metal alloys, comprising the steps of:

(a) immersing a blank of a metal or a metal alloy in a bath containing the coating solution according to any one of claims 1 to 9, for a time period of from about 30 seconds to about 10 minutes;

10 (b) drying said blank having the coating solution on its surface at a temperature ranging from about room temperature to about 80°C; and

(c) subjecting the thus-coated blank to cold forming.

15 11. The process according to claim 10, wherein prior to step (a) the blank is sand-blasted.

12. A blank having a coating obtainable by

20 (a) immersing a blank of a metal or a metal alloy in a bath containing the coating solution according to any one of claims 1 to 9, for a time period of from about 30 seconds to about 10 minutes; and

(b) drying said blank having the coating solution on its surface at a temperature ranging from about room temperature to about 80°C, resulting in a coated blank.

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 00 7463

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 6 309 477 B1 (WADA YUTAKA ET AL) 30 October 2001 (2001-10-30) * the whole document *	1-6,8,9	C23C22/23 C10M173/02
X	--- DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; IZAKI, TERUAKI ET AL: "Plated steel sheet covered with organic film for high corrosion resistance" retrieved from STN Database accession no. 135:347629 CA XP002213347 * abstract * & JP 2001 303262 A (NIPPON STEEL CORP., JAPAN) 31 October 2001 (2001-10-31) ---	1,4,5,8	
A	FR 2 378 084 A (ROSTOVSKY O NEFTEMASLOZAVOD) 18 August 1978 (1978-08-18) ---		
A	EP 0 613 939 A (KYODO YUSHI ;NISSAN MOTOR (JP)) 7 September 1994 (1994-09-07) ---		
A	EP 0 714 975 A (SHOWA SHELL SEKIYU) 5 June 1996 (1996-06-05) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 May 2003	Examiner Van Leeuwen, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EPO FORM 1503 03/02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 00 7463

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-05-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6309477 B1	30-10-2001	JP 2001073162 A	21-03-2001
		EP 0979880 A1	16-02-2000
		KR 2000017277 A	25-03-2000
JP 2001303262 A	31-10-2001	NONE	
FR 2378084 A	18-08-1978	FR 2378084 A1	18-08-1978
EP 0613939 A	07-09-1994	JP 2586871 B2	05-03-1997
		JP 6256784 A	13-09-1994
		DE 69420600 D1	21-10-1999
		DE 69420600 T2	16-03-2000
		EP 0613939 A2	07-09-1994
		ES 2138055 T3	01-01-2000
		US 5460737 A	24-10-1995
EP 0714975 A	05-06-1996	JP 8157859 A	18-06-1996
		AU 696648 B2	17-09-1998
		AU 3919595 A	13-06-1996
		BR 9505614 A	16-09-1997
		CA 2164053 A1	03-06-1996
		CN 1132781 A ,B	09-10-1996
		DE 69502164 D1	28-05-1998
		DE 69502164 T2	24-09-1998
		EP 0714975 A1	05-06-1996
		ES 2116030 T3	01-07-1998
		HK 1010459 A1	17-06-1999
		US 5624889 A	29-04-1997