

**FORMAT**  
**for third party submission of information on alternatives for**  
**Applications for Authorisation**

**PUBLIC VERSION**

**Legal name of submitter(s):** Metalcoating S.r.l

**TABLE OF CONTENTS**

1. ALTERNATIVE ID AND PROPERTIES .....	3
2. TECHNICAL FEASIBILITY .....	3
3. ECONOMIC FEASIBILITY .....	28
4. HAZARDS AND RISKS OF THE ALTERNATIVE .....	29
5. AVAILABILITY .....	39
6. CONCLUSION ON SUITABILITY AND AVAILABILITY OF THE ALTERNATIVE .....	39
7. OTHER COMMENTS .....	39
REFERENCES .....	39
APPENDIXES .....	39

**1. ALTERNATIVE ID AND PROPERTIES**

**2. TECHNICAL FEASIBILITY**

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization

International Bureau

(43) International Publication Date  
17 January 2019 (17.01.2019)(10) International Publication Number  
**WO 2019/012496 A1**(51) International Patent Classification:  
C25D 15/00 (2006.01) C25D 3/56 (2006.01)(21) International Application Number:  
PCT/IB2018/055197(22) International Filing Date:  
13 July 2018 (13.07.2018)

(25) Filing Language: Italian

(26) Publication Language: English

(30) Priority Data:  
102017000079843 14 July 2017 (14.07.2017) IT

(71) Applicant: METALCOATING S.R.L. [IT/IT]; Via Turati, 40, 20121 Milano (IT).

(72) Inventor: BURATTI, Marco; c/o METALCOATING S.R.L., Via Turati, 40, 20121 Milano (IT).

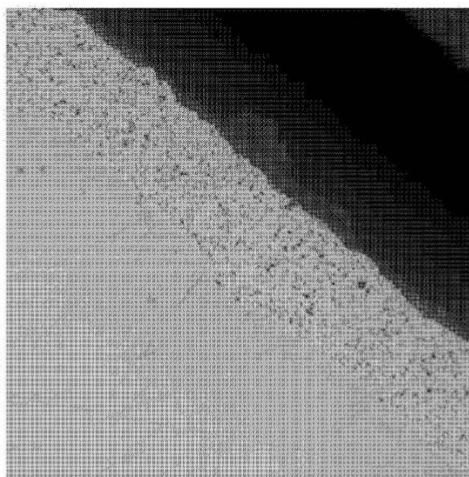
(74) Agent: BOTTERO, Carlo; c/o BARZANO' &amp; ZANARDO MILANO S.P.A., Via Borgonuovo, 10, 20121 Milano (IT).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

(54) Title: ELECTROLYTIC PROCESS FOR COATING METAL SURFACES TO PROVIDE HIGH RESISTANCE TO CORROSION AND ABRASION

Fig. 1



(57) Abstract: Process for coating a metal article, comprising: preparing an electrolytic bath that comprises a suspension of boron carbide particles, having an average size from 0.01  $\mu\text{m}$  a 2  $\mu\text{m}$ , in an aqueous solution comprising at least one nickel (II) salt and at least one phosphorous compound selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or their salts; immersing in the electrolytic bath a cathode which comprises the article to be coated, and an anode, and carrying out an electrodeposition by passing a direct current in the electrolytic bath. The coating layer thus obtained is provided with high thickness uniformity, high wear resistance, even at high temperatures, high hardness (up to 1500 HV), and, at the same time, corrosion resistance at least equal to 400 hours of exposure to neutral saline fog, in accordance with the ISO 9227:2017 standard.

[Continued on next page]

**WO 2019/012496 A1** 

---

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report (Art. 21(3))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

WO 2019/012496

PCT/IB2018/055197

1

ELECTROLYTIC PROCESS FOR COATING METAL SURFACES TO  
PROVIDE HIGH RESISTANCE TO CORROSION AND ABRASION

-----

5       The present invention relates to an electrolytic  
process for coating metal surfaces. More in particular,  
the present invention relates to an electrolytic  
process for coating metal surface with a layer  
comprising a nickel/phosphorus alloy and boron carbide  
10 particles, to provide high resistance against corrosion  
and abrasion.

There is a very pressing need to produce metal  
articles having high resistance against surface wear,  
combined with high corrosion resistance, such as in  
15 particular steel rods and tubes to be used in different  
sectors, for example for the production of industrial  
or agricultural vehicle, forklifts, presses, robotics,  
elevators, hydraulic platforms, or also for special  
applications where high corrosion resistance is  
20 required even in extremely severe conditions, such as  
earth-moving machines, excavators, dredgers, salt  
spreading machines, snowploughs, waste compactors,  
zootechnics machines, cranes, cableways and ski lifts,  
watercraft, off-shore platforms, aircraft, space  
25 vehicles, etc.

Corrosion resistance is generally assessed through  
accelerated aging tests in a saline fog chamber, which  
can be conducted according to different international  
standards, in particular the ISO 9227:2017 standard.  
30 These tests are generally performed in more aggressive  
conditions than those expected in operation, to  
accelerate corrosive processes and reduce the duration

WO 2019/012496

2

PCT/IB2018/055197

of the tests, which normally last from a few tens to a few hundreds of hours.

In general, to obtain the desired combination of wear resistance and corrosion resistance, coatings of metal articles are carried out conventionally by means of nickel plating and subsequent chrome plating, i.e. electrolytic deposition of a layer of nickel and subsequently of a layer of chromium, so as to obtain a layer of coating with total thickness of the order of 100  $\mu\text{m}$ . While chrome plating has low costs, it does not always allow to obtain highly uniform coatings, especially in case of surfaces with complex geometry (for example grooves or other deep etches) in which, because of the tip effect, excessive thickness levels are obtained on the tips and poor thickness levels are obtained in the troughs of the etches. Moreover, the use of hexavalent chromium presents serious problems from the viewpoint of environmental sustainability, because of the high toxicity of this metal, in addition to entailing high costs in terms of energy and disposal.

In recent years, several metal coating processes have been proposed that do not require the use of products containing chromium.

For example, the patent application EP 1 067 220 A2 describes a process for obtaining a coating with boron carbide in nickel phosphorus matrix, in which the article to be coated is subjected to electrodeposition in an electrolytic bath comprising two or more nickel salts, in particular a mixture of nickel sulphate and nickel chloride, at least one complexing agent, at

least one phosphorus salt, an anti-tensioning agent and boron carbide in the form of powder, having a particle dimension from 3 to 6  $\mu\text{m}$ . The cathode consists of the material to be coated, while the anode consists of electrolytic nickel. The electrolytic process is carried out at a temperature from 40°C to 70°C with a current density from 1 to 10 A/dm<sup>2</sup>, under agitation. The article thus coated is then subjected to a heat treatment, in particular at a temperature from 250°C to 400°C.

The patent application EP 3 098 334 A1 describes a process for coating a metal article, in which the electrodeposition of boron carbide in a nickel/phosphorus alloy matrix is obtained by means of an electrolytic bath containing at least one surfactant, which allows to deposit a significant quantity of boron carbide particles having an average size from 0.01  $\mu\text{m}$  to 2  $\mu\text{m}$ , in general from 10% to 50% by volume, preferably from 5% to 45% by volume, with respect to the total volume of the coating. The coating layer thus obtained is provided with very high wear resistance, even at high temperatures, and high hardness (up to 1500 HV), and at the same time high thickness uniformity.

The Applicant thus addressed the problem of producing metal articles having high surface wear resistance combined with high corrosion resistance, by electrodeposition on the metal of a coating layer that is able to impart these properties without the use of chromium.

These and additional objectives that will be



better illustrated hereafter have been achieved by the Applicant by means of a process as defined in the remainder of the description and in the appended claims, which allows to obtain a coating layer  
5 comprising a nickel/phosphorus (Ni/P) alloy matrix and boron carbide particles having average size from 0.01  $\mu\text{m}$  to 2  $\mu\text{m}$ , having corrosion resistance at least equal to 400 hours, preferably at least equal to 600 hours, of exposure to neutral saline fog, in accordance with  
10 the ISO 9227:2017 standard.

In a first aspect, the present invention therefore relates to a process for coating a metal article, which comprises:

- preparing an electrolytic bath which  
15 comprises a suspension of boron carbide particles, having an average size ranging from 0.01  $\mu\text{m}$  to 2  $\mu\text{m}$ , preferably from 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$ , in an aqueous solution comprising:

at least one nickel (II) salt;  
20 at least one phosphorous compound selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or their salts;

- immersing, in the electrolytic bath, a cathode which comprises the article to be coated, and  
25 an anode, and carrying out an electrodeposition by passing a direct current in the electrolytic bath;

wherein the boron carbide particles have been pre-treated with at least one carboxylic acid or a derivative thereof, having a solubility in water at  
30 20°C higher than 0.10 g/l.

Preferably, said at least one carboxylic acid or a derivative thereof has a solubility in water at 20°C

higher than 10 g/l.

Preferably, said at least one carboxylic acid or a derivative thereof is selected from:

- (i) aliphatic and/or aromatic C<sub>1</sub>-C<sub>8</sub> mono-  
5 carboxylic acids, possibly mono- or poly-hydroxylated, for example: formic acid, acetic acid, propionic acid, butyric acid, valerianic acid, capronic acid, enantic acid, caprylic acid, nonanoic acid, capric acid, acrylic acid, methacrylic acid;
- 10 (ii) aliphatic and/or aromatic C<sub>1</sub>-C<sub>12</sub> di-carboxylic acids, possibly mono- or poly-hydroxylated, for example: oxalic acid, adipic acid, phthalic acid, azelaic acid, sebacic acid, tartaric acid, aldarcic acid;
- 15 or derivatives thereof.

The term "derivatives" means for example salts (in particular salts of alkaline or alkaline-earth metals), esters, amides, anhydrides.

In a preferred embodiment, the boron carbide  
20 particles have been pre-treated with a mixture of tartaric acid and acrylic acid. Preferably, in said mixture the weight ratio between tartaric acid and acrylic acid ranges from 0.2 to 5, more preferably from 0.5 to 2, still more preferably 1.

25 The boron carbide particles have an average size ranging from 0.01 µm to 2 µm, preferably from 0.05 µm to 1 µm.

Within the present description and the appended claims, the term "average particle size" means, unless  
30 otherwise indicated, the diameter d<sub>50</sub> (median value) i.e. the value of the diameter below which 50% by weight of the population of particles is located (see

WO 2019/012496

PCT/IB2018/055197

6

"A Guidebook to Particle Size Analysis" published by Horiba Instruments Inc. - 2016, available at [https://www.horiba.com/fileadmin/uploads/Scientific/eMag/PSA/Guidebook/pdf/PSA\\_Guidebook.pdf](https://www.horiba.com/fileadmin/uploads/Scientific/eMag/PSA/Guidebook/pdf/PSA_Guidebook.pdf)). The diameter  
5 d50 can be determined by laser diffraction technique, according to ISO 13320:2009, or by analysing electronic microscope images (TEM or SEM).

The pretreatment step of the boron carbide particles with at least one carboxylic acid or a  
10 derivative thereof as defined above is preferably carried out by suspending the boron carbide particles in water and adding said at least one carboxylic acid or a derivative thereof to the suspension thus obtained. The suspension thus supplemented is  
15 preferably maintained at a temperature from 30°C to 90°C, more preferably from 40°C to 80°C, for a time that can vary within broad limits, preferably from 20 min and 120 min, more preferably between 40 min and 80 min.

20 Preferably, said at least one carboxylic acid or a derivative thereof is added to the suspension of boron carbide particles in an amount ranging from 1% by weight to 40% by weight, more preferably from 5% by weight to 30% by weight, with respect to the weight of  
25 the boron carbide particles.

In this pretreatment step the boron carbide particles are preferably maintained under stirring, for example by means of a blade mixer. Preferably, the pretreatment, after the addition of the carboxylic  
30 acid, comprises a step of sonication with ultrasound, which is carried out at a pH value of from 1 to 4, more preferably equal to 2.

Once the pretreatment is completed, to the suspension of boron carbide it is possible to add the other components of the electrolytic bath.

In a preferred embodiment, the boron carbide particles are previously purified, before the pretreatment with at least one carboxylic acid. The main purpose of the purification is to eliminate or otherwise significantly reduce the presence of polluting elements that are commonly present in boron carbide, such as ions of aluminium, chromium, copper, iron, manganese, vanadium, calcium, strontium, which can alter the final characteristics of the coating and impair its characteristics, in particular with regard to corrosion resistance. The Applicant has noted that the elimination or otherwise the reduction of these metallic pollutants allows to obtain a more compact coating with improved corrosion resistance. Purification of the boron carbide particles can be carried out according to conventional methods, for example by electrodialysis.

The boron carbide particles in suspension are present in a quantity preferably from 1 g/l to 20 g/l, more preferably from 5 to 15 g/l.

Preferably, the aqueous solution comprises at least one Ni(II) salt having a sulphur-containing anion, for example nickel (II) sulphate. More preferably, it is nickel (II) sulphamate ( $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ ). Use of nickel (II) sulphamate is particularly preferred because it allows to increase the electrodeposition rate, with a substantial improvement in terms of productivity and cost of the process.

Alternatively or additionally to the Ni(II) salt

having a sulphur-containing anion, the aqueous solution can comprise at least another Ni(II) salt, selected preferably from: nickel (II) carbonate, nickel (II) acetate. It is also possible to use nickel (II) chloride, although it is not particularly preferred when the cathode is a nickel cathode, because the presence of chloride ions leads to a consumption of the nickel electrode due to anodic attack, with consequent increase in nickel concentration in the electrolytic bath, altering in a way that is difficult to control the ratios between nickel and the other components (in particular phosphorus).

Preferably, the aqueous solution comprises Ni(II) ions in a total concentration ranging from 0.3 moles/l to 3.0 moles/l, more preferably from 0.5 moles/l to 1.5 moles/l.

Preferably, the aqueous solution comprises a Ni(II) salt having a sulphur-containing anion, and a second salt selected from nickel (II) carbonate and nickel (II) acetate, the concentration of the first salt being between 0.3 moles/l and 1.8 moles/l, more preferably between 0.5 moles/l and 1.4 moles/l; the concentration of the second salt being between 0.02 moles/l and 1.0 moles/l, more preferably between 0.05 moles/l and 0.6 moles/l.

With regard to the phosphorous compound, it is selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or their salts. As salts, the following can be used for example: alkali metal (for example potassium, sodium) or alkaline-earth metal (for example magnesium, calcium) salts.

According to a preferred aspect, the phosphorous

compound is a mixture of phosphorous acid/  
hypophosphorous acid, or their salts, preferably in a  
weight ratio ranging from 0.8:1 to 1.2:1. This mixture  
is deemed to allow to further improve the  
5 characteristics of the final coating, obtaining a Ni/P  
alloy having a quantity of phosphorus between 13% and  
16% by weight, to which is accompanied an optimal  
compromise between crystalline phase and amorphous  
phase in the coating material and hence between  
10 hardness and corrosion resistance thereof.

The quantity of phosphorus compound to be added to  
the electrolytic bath is selected mainly according to  
the type of nickel/phosphorus alloy to be obtained,  
i.e. a so-called "low phosphorus" alloy, i.e. in  
15 general with a quantity of phosphorus from 1 to 8% by  
weight, extremes included (with respect to the weight  
of the Ni/P alloy), or a so-called "high phosphorus"  
alloy, i.e. in general with a quantity of phosphorus  
higher than 8% and lower than or equal to 16% by weight  
20 (with respect to the weight of the Ni/P alloy).  
Obtaining a high phosphorus nickel/phosphorus alloy  
allows to further increase the corrosion resistance of  
the coating, in particular resistance to corrosion due  
to contact with water having a high salt content, for  
25 example sea water. On the other hand, a low phosphorus  
nickel/phosphorus alloy has lower corrosion resistance,  
but it is characterised by greater hardness with  
respect to a high phosphorus alloy.

According to a preferred aspect, the aqueous  
30 solution comprises at least one alkali metal iodide,  
preferably potassium iodide. The presence of iodide in  
the electrolytic bath is deemed to allow to further

improve the corrosion resistance of the coating, in particular resistance to corrosion in saline fog, a particular severe test for any material. Preferably, the alkali metal iodide is present in the solution in a  
5 quantity between 0.1 and 10 g/l, more preferably between 0.5 and 3 g/l.

Although it is not strictly necessary, the aqueous solution may comprise at least one surfactant, as described in the patent application EP 3 098 334 A1.  
10 Preferably, the surfactant is a cationic, non-ionic or amphoteric surfactant. The concentration of said at least one surfactant in the aqueous solution is preferably between 0.01 g/l and 2 g/l, more preferably between 0.05 g/l and 1 g/l.

15 The aqueous solution preferably has a pH ranging from 0.5 to 4, more preferably from 1.5 to 3. To obtain values of pH within the intervals indicated above, a strong acid, in particular an aqueous solution of sulphuric acid, is preferably added to the aqueous  
20 solution. In some cases, to maintain the pH within the selected range, adding a buffering agent may be advantageous, for example a boric acid/borate or acetic acid/acetate system.

With regard to the procedure for carrying out the  
25 electrochemical process according to the present invention, it can be achieved according to conventional procedures, provided that a constant and homogeneous movement of the electrolytic bath is assured, mainly for the purpose of maintaining the boron carbide  
30 particles in suspension but without causing perturbations in the electrolytic deposition process. In particular, it is appropriate to prevent the

formation of preferential ways for the flow of the suspension within the electrolytic bath, which could cause lack of homogeneity in the coating layer.

For this purpose, it is particularly advantageous  
5 to carry out the process according to the present invention in an apparatus that comprises an electrolytic tank and a system for recirculating the electrolytic bath, as described in the patent application EP 3 098 334 A1.

10 The electrodeposition step of the process in accordance with the present invention can be accomplished within a broad temperature range, in general from 50°C to 95°C, preferably from 65°C to 85°C. Lower temperatures than the aforesaid ranges  
15 would entail a reduced efficiency of the electrodeposition, while higher temperatures would have the disadvantage of an excessive evaporation of the electrolytic bath, with consequent inefficiency from the energy viewpoint.

20 The electrolytic bath preferably has a pH value from 1 to 5, more preferably from 1.5 to 3.

Into the electrolytic bath is immersed the metal article to be coated, which serves as cathode, and an anode, preferably an insoluble anode, for example an  
25 anode made of titanium coated with platinum or coated with mixed oxides, or a soluble anode, for example a nickel anode.

The passage of current necessary to carry out the electrodeposition process is obtained thanks to the  
30 connection of the electrodes with a direct current generator, so as to obtain a current density in the electrolytic bath generally between 0.5 and 20 A/dm<sup>2</sup>,



preferably between 1 and 10 A/dm<sup>2</sup>.

The electrodeposition is carried out for a time which is such as to obtain the desired coating thickness, which generally ranges from 5 µm to 200 µm, more preferably from 10 µm to 75 µm.

After electrodeposition, the article thus coated may be possibly subjected to a heat treatment, at a temperature generally included between 250°C and 400°C, preferably between 300°C and 375°C, for a time that is variable within wide limits, for example between 1 and 24 hours, preferably between 6 and 18 hours. The heat treatment has mainly the purpose of forming the Ni/P alloy, eliminating the hydrogen formed during the electrolytic process, so as to obtain a stable and homogeneous coating layer, minimising defects and internal stresses and further increasing hardness.

In this regard, the Applicant has observed that the process according to the invention allows, as a matter of fact, to avoid said heat treatment, since satisfactory properties of the coating are anyway obtained with no need to perform annealing processes. Therefore, according to a preferred embodiment the process according to the invention does not comprise a heat treatment of the article at the end of the electrodeposition. This clearly allows to significantly increase the productivity of the process, while reducing production costs.

The present invention will now be further illustrated with reference to the figures accompanying the present description merely for exemplifying purposes, in which:

Figure 1 shows a scanning electron microscope

(SEM) microphotograph of a section of a coated sample according to the invention (200x magnification), where the black portion outside the coating layer is the resin in which the sample was incorporated, lapped and polished to perform the SEM analysis, while the underlying white part is the base metal on which electrodeposition was carried out; the presence of black particles consisting of boron carbide can easily be appreciated;

Figure 2 shows a SEM microphotograph obtained on the same sample at front view, with an enlargement of a portion that highlights the typical mammillary structure of Ni/P alloys; the presence of black particles consisting of boron carbide can easily be appreciated.

The following working examples are provided merely to illustrate the present invention and should not be construed in a sense that would limit the scope of protection defined by the accompanying claims.

EXAMPLE 1.

Boron carbide in the form of particles having average size of 0.4  $\mu\text{m}$  was suspended, in a quantity of 10 g/l, in an aqueous phase having a pH value of 2.0 (obtained by adding a  $\text{H}_2\text{SO}_4$  aqueous solution), containing 1 g/l of tartaric acid and 1 g/l of acrylic acid. The suspension thus obtained was maintained for about 1 hour in an ultrasonic sonicator at 60°C.

To the suspension was then added an aqueous solution consisting of:

- nickel sulphate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ )	75 g/l
- phosphorous acid	15 g/l

- sodium hypophosphite 40 g/l
- sodium acetate ( $\text{CH}_3\text{COONa}$ ) 120 g/l.

The electrolytic bath thus obtained was brought to a pH value of 2.0 with a  $\text{H}_2\text{SO}_4$  aqueous solution.

5 The electrodeposition process was carried out on a steel plate, used as cathode, while the anode used was a titanium anode coated with mixed oxides. During the electrodeposition, the electrolytic bath was maintained for three hours at a temperature of about  $80^\circ\text{C}$  and the  
10 current density at a value of about  $10 \text{ A/dm}^2$ .

At the end of the electrodeposition process, a coating layer of the plate was obtained with a thickness of about  $25 \mu\text{m}$ , containing about 15% by weight in phosphorus, having Vickers hardness of 900  
15 HV. It should be noted that such a high hardness was obtained without subjecting the specimen to a subsequent heat treatment (annealing) step, which is usually carried out for this type of coatings for the purpose of increasing its hardness.

20 On the specimen thus treated, corrosion resistance was measured in neutral saline fog, according to the ISO 9227:2017 standard, obtaining a value of 1000 hour (rating: 10).

The sample thus coated was subjected to scanning  
25 electron microscope (SEM) analysis, and the microphotographs thus obtained are shown in Figure 1 (section) and Figure 2 (surface). The coating layer showed a substantially homogeneous distribution of boron carbide particles in the Ni/P matrix, with a  
30 mammillary surface structure that is typical of the Ni/P alloy.

WO 2019/012496

15

PCT/IB2018/055197

EXAMPLE 2 (comparative).

Example 1 was repeated in the same operating conditions, the only difference being that the boron carbide particles were not pre-treated with tartaric acid and acrylic acid, but rather used as such.

At the end of the electrodeposition process, a coating layer of the plate was obtained with a thickness of about 25  $\mu\text{m}$ , containing about 15% by weight of phosphorus, having Vickers hardness of 550 HV (without annealing).

On the specimen thus treated, corrosion resistance was measured in neutral saline fog, according to the ISO 9227:2017 standard, obtaining a value of 120 hours (rating: 8).

15

CLAIMS

1. A process for coating a metal article, which comprises:

5 - preparing an electrolytic bath which comprises a suspension of boron carbide particles, having an average size ranging from 0.01  $\mu\text{m}$  to 2  $\mu\text{m}$ , preferably from 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$ , in an aqueous solution comprising:

at least one nickel (II) salt;

10 at least one phosphorous compound selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or their salts;

- immersing, in the electrolytic bath, a cathode which comprises the article to be coated, and an anode, 15 and carrying out an electrodeposition by passing a direct current in the electrolytic bath;

wherein the boron carbide particles have been pretreated with at least one carboxylic acid or a derivative thereof, having a solubility in water at 20  $^{\circ}\text{C}$  higher than 0.10 g/l. 20

2. The process according to claim 1, wherein said at least one carboxylic acid or a derivative thereof has a solubility in water at 20  $^{\circ}\text{C}$  higher than 10 g/l.

3. The process according to any one of the previous 25 claims, wherein said at least one carboxylic acid or a derivative thereof is selected from:

(i) aliphatic and/or aromatic  $\text{C}_1\text{-C}_8$  mono-carboxylic acids, possibly mono- or poly-hydroxylated, for example: formic acid, acetic acid, propionic acid, 30 butyric acid, valerianic acid, capronic acid, enantic acid, caprylic acid, nonanoic acid, capric acid, acrylic acid, methacrylic acid.

(ii) aliphatic and/or aromatic C<sub>1</sub>-C<sub>12</sub> di-carboxylic acids, possibly mono- or poly-hydroxylated, for example: oxalic acid, adipic acid, phthalic acid, azelaic acid, sebacic acid, tartaric acid, aldarcic

5 acid;

or derivatives thereof.

4. The process according to any one of the previous claims, wherein the boron carbide particles have been pretreated with a mixture of tartaric acid and acrylic  
10 acid.

5. The process according to claim 4, wherein the weight ratio between tartaric acid and acrylic acid ranges from 0.2 to 5, preferably from 0.5 to 2, more preferably is 1.

15 6. The process according to any one of the previous claims, wherein the pretreatment step of the boron carbide particles is carried out by suspending the boron carbide particles in water and adding said at least one carboxylic acid or a derivative thereof to  
20 the suspension thus obtained.

7. The process according to claim 6, wherein said at least one carboxylic acid or a derivative thereof is added to the suspension of boron carbide particles in an amount ranging from 1% by weight to 40% by weight,  
25 preferably from 5% by weight to 30% by weight, with respect to the weight of the boron carbide particles.

8. The process according to any one of the previous claims, wherein the pretreatment step of the boron carbide particles is carried out at a temperature  
30 ranging from 30°C to 90°C, preferably from 40°C to 80°C, for a time ranging from 20 minutes to 120 minutes, preferably from 40 minutes to 80 minutes.

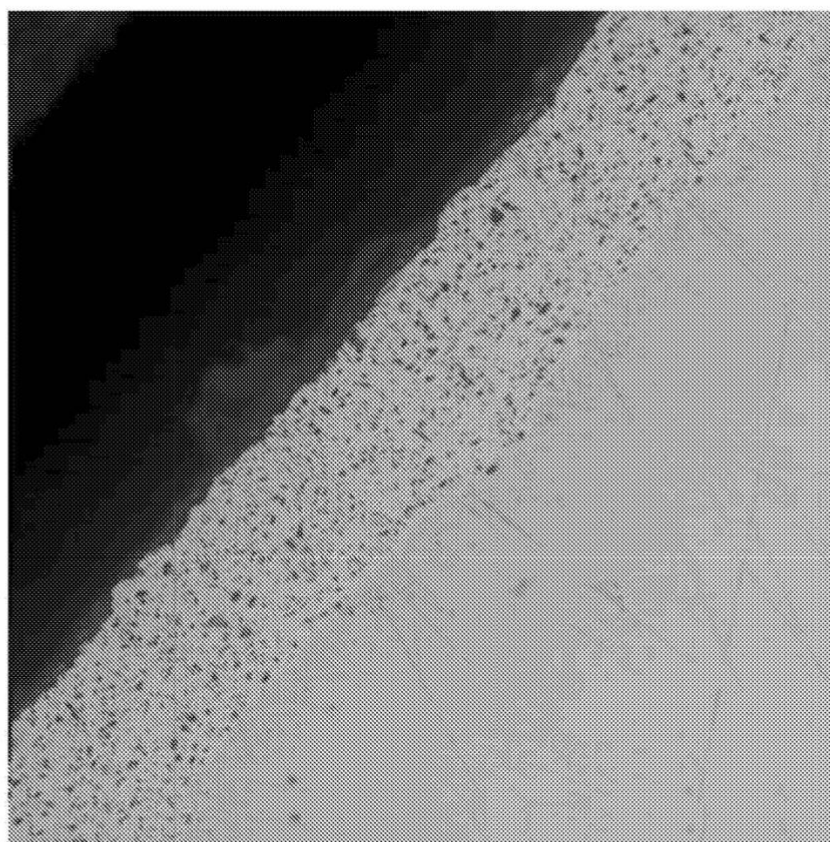
9. The process according to any of the previous claims, wherein the boron carbide particles have an average size ranging from 0.01  $\mu\text{m}$  to 2  $\mu\text{m}$ , preferably from 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$ .
- 5 10. The process according to any one of the previous claims, wherein the boron carbide particles are previously purified, before the pretreatment with at least one carboxylic acid.
11. The process according to any one of the previous
- 10 claims, wherein the aqueous solution comprises Ni(II) ions in a total concentration ranging from 0.3 moles/l to 3.0 moles/l, preferably from 0.5 moles/l to 1.5 moles/l.
12. The process according to any one of the previous
- 15 claims, wherein the phosphorous compound is a mixture of phosphorous acid/hypophosphorous acid, or their salts, preferably in a weight ratio ranging from 0.8:1 to 1.2:1.
13. The process according to any one of the previous
- 20 claims, wherein the aqueous solution has a pH ranging from 0.5 to 4, preferably from 1.5 to 3.
14. The process according to any of the previous claims, wherein the electrodeposition step is carried out for a time so as to obtain a coating thickness
- 25 ranging from 5  $\mu\text{m}$  to 200  $\mu\text{m}$ , preferably from 10  $\mu\text{m}$  to 75  $\mu\text{m}$ .

WO 2019/012496

1/2

PCT/IB2018/055197

Fig. 1



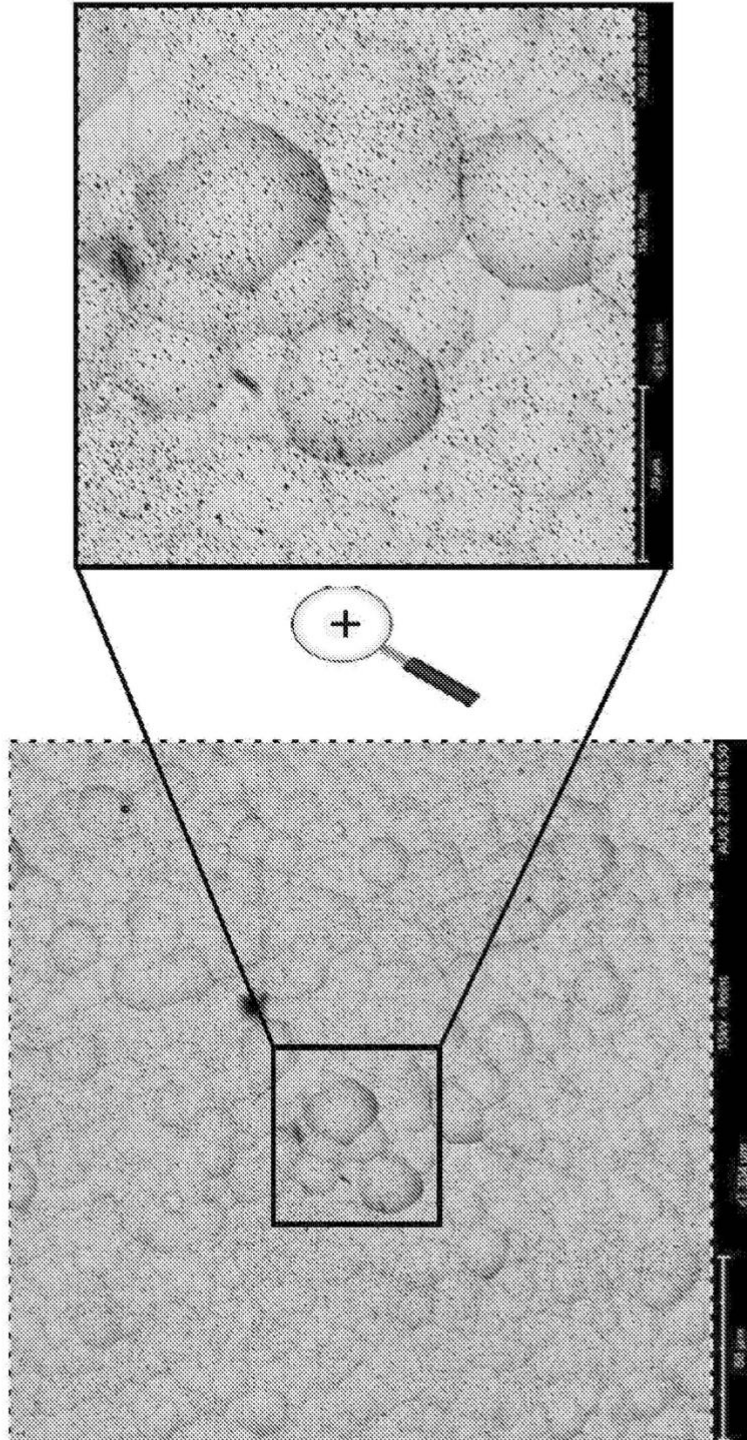


WO 2019/012496

2/2

PCT/IB2018/055197

Fig. 2



## INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2018/055197

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C25D15/00 C25D3/56  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25D C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 3 098 334 A1 (METALCOATING S R L [IT]) 30 November 2016 (2016-11-30) paragraphs [0001], [0003], [0005], [0007], [0010], [0017], [0029], [0035], [0048], [0080]; example 4 -----	1-14
Y	WO 02/052063 A1 (MCCOMAS EDWARD [US]; MCCOMAS TECHNOLOGIES AG [DE]) 4 July 2002 (2002-07-04) page 5, lines 1-15, 30-36; claim 11; examples 1-4 page 6, lines 5,6 -----	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

28 September 2018

Date of mailing of the international search report

08/10/2018

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Suárez Ramón, C

Form PCT/ISA/210 (second sheet) (April 2005)

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2018/055197

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3098334	A1	30-11-2016	NONE
WO 02052063	A1	04-07-2002	
		BR 0017389 A	13-01-2004
		CA 2432100 A1	04-07-2002
		EP 1352108 A1	15-10-2003
		JP 2004537647 A	16-12-2004
		KR 20030065560 A	06-08-2003
		MX PA03005563 A	24-10-2003
		US 6319308 B1	20-11-2001
		WO 02052063 A1	04-07-2002

Form PCT/ISA/210 (patent family annex) (April 2005)

### **3. ECONOMIC FEASIBILITY**

Carbonip is already placed on the market for use in batch and for a specific application has been developed in line.

This technology shows interesting peculiarities.

Due to the high energy efficiency of the process, a considerable energy saving is obtained from this process.

No cooling system is required to maintain the temperature constant; Joule effect is almost negligible for Carbonip.

A substantial reduction in consumptions and disposal costs complete the description.

Specific data concerning the production costs are available on request.

Any other process and new application must be subjected to a specific study in order to evaluate a correct feasibility. Metalcoating S.r.l. is opened to provide help to any company who are interested in this technology.

#### **4. HAZARDS AND RISKS OF THE ALTERNATIVE**

Safety data sheets  
According to 1907/2006/EC and 453/2010/EC  
regulations and subsequent updates

Page: 1/9

29.10.2016

Vers. 1

Update date: 29.10.2016

**SECTION 1: Identification of the substance or the mixture and of the company**

- 1.1 Identification of the product
- Commercial designation: CARBONIP COMPLEX
- 1.2 Identified recommended applications of the substance or mixture and not recommended ones  
Complexant solution through Nichel galvanic deposition
- Uptake of the Substance  
Complexant solution through Nichel galvanic deposition
- 1.3 Informations about the safety datasheet's supplier:
- Supplier:  
Metalcoating Srl  
Via Tagliamento 14  
20098 San Giuliano Milanese (MI) - Italy  
Phone: (02)98490672 - Time schedule: 8.30 - 12.30, 13.30 - 17.30  
Fax: (02)98249752  
metalcoating@metalcoating.com  
E-mail address of the qualified person responsible for the safety datasheet:  
metalcoating@metalcoating.com
- Information provided by: Reparto sicurezza prodotti
- 1.4 Emergency phone number: 3356359285  
Centro Antiveleni Osp. Niguarda Milano Tel. 0266101029  
(available 24 hours on 24)

**SECTION 2: Hazard identification**

- 2.1 Classificazione of the substance or the mixture  
Classification according to Regulation (EC) no 1272/2008

**0**

GHS07

Acute Tox. 4 H302 harmful if swallowed.  
Skin Irrit. 2 H315 Causes skin irritation.  
Eye Irrit. 2 H319 Causes severe eye irritation.

- 2.2 Label elements
- Labelling according to Regulation (EC) no 1272/2008  
The product is classified and labelled in conformity with the regulation CLP.
- Hazard pictograms



GHS07

- Warning Caution
- Dangerous components that feature the labelling:  
Phosphoric acid  
Sodium hydroxide
- Hazard statements:  
H302 Harmful if swallowed.  
H315 Cause skin irritation.

(continued on page 2)

**Safety data sheets**  
According to 1907/2006/EC and 453/2010/EC  
regulations and subsequent updates

Page: 2/9

29.10.2016

Vers. 1

Update date: 29.10.2016

**Commercial designation: CARBONIP COMPLEX**

(continued from pagina 1)

H319 Cause severe eye irritation.

**- Safety advices**

P280 Wear protective gloves.

P280 Wear personal protective equipment for eyes and face.

P305+P351+P338 IN CASE OF CONTACT WITH THE EYES: rinse carefully for several minutes. Remove contact lenses, if present and easy to do. Continue to rinse off the eyes.

P321 Specific treatment (check on this label).

P301+P312 IN CASE OF INGESTION: contact a POISON CONTROL CENTER/ in case of discomfort contact a doctor.

P501 Pour the product/tank in conformity with the local / regional / national / international regulations.

**- 2.3 Further hazards****- Outcome of the PBT and vPvB assessments****- PBT:** Not applicable.**- vPvB:** Not applicable.**SECTION 3: Composition/Information on the ingredients****- 3.2 Chemical properties: Mixture****- Description:** Mixture of the below substances with non-hazardous additives**- Hazardous substances:**

CAS: 13598-36-2	phosphonic acid	20-25%
EINECS: 237-066-7	Met. Corr.1, H290; Skin Corr. 1A,	
Reg.nr.: 01-2119488030-46	H314; Eye Dam. 1, H318; Acute Tox. 4, H302	
CAS: 1310-73-2	Sodium hydroxide	4-5%
EINECS: 215-185-5	Met. Corr.1, H290; Skin Corr. 1A,	
Reg.nr.: 01-2119457892-27	H314	

**- Additional informations:**

The warnings sheet about the hazards cited above can be acquired from section 16.

**SECTION 4: First-aid measures****- 4.1 Description of the first aid measures****- General guidance:**

Pull away immediately the contaminated clothes from the product. Sintoms of poisoning can show up after many hours, for this reason it is necessary medical surveillance during the subsequent 48 hours after the accident.

**- After inhalation:**

If the subject is unconscious provide to hold him in a stable lateral position during the transport.

Supply fresh air; in case of complaints consult a doctor.

**- After skin contact:**

Rinse immediately with water.

Remove immediately the contaminated clothes.

Rinse immediately under abundant running water the areas of the body which could be come into contact with the product.

(continued on page 3)



Safety data sheets  
According to 1907/2006/EC and 453/2010/EC  
regulations and subsequent updates

Page: 3/9

29.10.2016

Vers. 1

Update date: 29.10.2016

Commercial designation: CARBONIP COMPLEX

(continued from page 2)

- **After eye contact**  
Rinse with running water for several minutes holding the eyelids apart. If the pain continues, consult a doctor.
- **After ingestion:**  
Call at once the doctor, undergo medical treatments
- **4.2 Main symptoms and effects, both acute and delayed.**  
Other information is not available.
- **4.3 Indication of any immediate medical attention and special treatment needed**  
Other information is not available.

#### SECTION 5: Fire-fighting measures

- **5.1 Extinguishing media**
- **Suitable extinguishing media:**  
CO<sub>2</sub> powder or water jet. Extinguish large-scales fires with water jet or with alcohol resistant foam.
- **5.2 Special hazards arising from the substance or mixture**  
No further information available.
- **5.3 Guidelines for the operators taking part to the extinction of the fires**
- **Specific protective media:**  
Don't inhale the gases arising from explosions and fires.

#### SECTION 6: Accidental release measures

- **6.1 Personal recommendations, protective equipment and emergency procedure**  
Wear protective equipment. Keep non equipped people at a distance.
- **For non-emergency personnel** Proceed to a safer place.
- **For emergency responders**  
Wear protective equipment. Keep non equipped people at a distance.
- **6.2 Environmental precautions:** Particular measures are not required.
- **6.3 Methods and materials for the containment and cleaning up**  
Absorb the liquid with liquid-binding material (sand, universal binders, sawdust).  
Disposal of the contaminated material in accordance with point 13.
- **6.4 Reference to other sections**  
For information on safe handling see Section 7.  
For information on personal protective equipment see Section 8.  
For information on the waste disposal see Section 13.

#### SECTION 7: Handling and storage

- **7.1 Precautions for safe handling**  
Store in cool, dry conditions in well-sealed containers.
- **Information about fire and explosion protection:**  
No special measures required.

(continued on page 4)



Safety data sheets  
According to 1907/2006/EC and 453/2010/EC  
regulations and subsequent updates

Page: 4/9

29.10.2016

Vers. 1

Update date: 29.10.2016

Commercial designation: CARBONIP COMPLEX

(Continued from page 3)

**7.2 Condition for safe storage, including any incompatibilities****Storage:**

- **Requirements to be met by storerooms and receptacles:**  
No special requirements.
- **Information about storage in one common storage facility:** Not required.
- **Further information about storage conditions:**  
Store in cool, dry conditions in well-sealed containers.  
Store under lock and key and out of the reach of children.  
Protect from heat and direct sunlight.  
Protect from contamination.
- **7.3 Specific end uses** No further relevant information available.

**SECTION 8: Exposure controls/personal protection**

- **8.1 Control parameters**
- **Components with limit values that require monitoring at the workplace:**  
The product does not contain any relevant quantities of materials with limit values that require monitoring in the workplace.

**- DNEL****1310-73-2 Sodium hydroxide**

By inhalation	Long term systemic effects on employees	mg/m3 (-)
	Long term systemic effects on population	1 mg/m3 (-)

- **Further information:**  
The lists valid during the making were used as basis.
- **8.2 Exposure controls**
- **Personal protection equipment**  
**General protective and hygienic measures:**  
Keep away from food, beverages and feed.  
Take off contaminated clothing immediately.  
Wash hands before breaks and at the end of work.  
Avoid contact with eyes and skin.
- **Protective mask:**  
If the threshold value for one or more of the substances present in the preparation for daily exposure in the workplace or to a fraction established by the company prevention and protection service is exceeded, wear a mask with an B or universal filter, the class (1,2 or 3) of which must be chosen according to the limit concentration of use (reference standard EN 141). The use of respiratory tract protection equipment, such as masks like that indicated above, is necessary to reduce worker exposure in the absence of technical measures. The protection provided by the mask is in any case limited.  
If the considered substance is odorless or its odor threshold is higher than the relative limit of exposure and in case of emergency, or when the levels of exposure are unknown or the oxygen concentration in the work room falls below 17% in volume, use independent respirator with an open circle on the compressed air (reference standard EN 137) or a fresh air hose breathing apparatus for use with full face mask, half mask or mouthpiece (reference standard EN 138) In case of inadequate ventilation, wear respiratory protection.

(continued on page 5)

Safety data sheets  
According to 1907/2006/EC and 453/2010/EC  
regulations and subsequent updates

Page: 5/9

29.10.2016

Vers. 1

Update date: 29.10.2016

Commercial designation: CARBONIP COMPLEX

(Continued from page 4)

- **Protective gloves:**  
The glove material must be impermeable and resistant to the product/ the substance/ the preparation.
- **Gloves material:**  
The selection of the suitable gloves does not only depend on the material, but also on further marks of quality and varies from manufacturer to manufacturer. Since the product is to be considered a mixture of more substances, the durability of the glove's materials could not be calculated in advance and must therefore be tested before use. For preparations of the pure product use protective gloves resistant to chemical products (EN 374-1/EN374-2/EN374-3)
- **Safety glasses:** Tightly sealed goggles.
- **Body protection:** Body protection.
- **Environmental exposure controls-**

### SECTION 9: Physical and chemical properties

- |   |  |
|---|--|
| - 9.1 Information on basic physical and chemical properties |  |
| - General aspects   |  |
| - Appearance:   |  |
| Form:   | Liquid                                     |
| Colour:   | Yellow                                     |
| - Odour:  | Characteristic aroma                       |
| - pH value at 20 °C:  | 2 (internal approach)                      |
| - Melting temperature/ melting range:                       | not defined                                |
| - Boiling temperature/ boiling range :                      | 120 °C                                     |
| - Flashpoint:   | not applicable                             |
| - Self-ignition:  | Product is not self-igniting.              |
| - Explosion hazard:   | Product is not explosive.                  |
| - Explosion limits:   |  |
| lower:  | not applicable                             |
| higher:   | not applicable                             |
| Oxidizing properties  | not applicable                             |
| - Vapour pressure at 20 °C:                                 | 23 hPa                                     |
| - Density at 20 °C:   | 1,33 g/cm <sup>3</sup> (internal approach) |
| - Solubility in/Miscibility with Water:                     | Completely miscible                        |
| - Solvent content:  |  |
| Organic solvent:  | 0,0 %                                      |
| Water:  | 71,8 %                                     |
| - 9.2 Further information                                   | No further relevant information available. |

### SECTION 10: Stability and reactivity

- 10.1 Reactivity No further relevant information available.

(continued on page 6)

Safety data sheets  
According to 1907/2006/EC and 453/2010/EC  
regulations and subsequent updates

Page: 6/9

29.10.2016

Vers. 1

Update date: 29.10.2016

Commercial designation: CARBONIP COMPLEX

(continued from pagina 5)

- 10.2 Chemical stability
- Thermal decomposition/conditions to be avoided:  
No decomposition if the product is used according to specifications.
- 10.3 Possibility of hazardous reactions:  
No dangerous reactions known.
- 10.4 Conditions to avoid: No further information available.
- 10.5 Incompatible materials: No further information available.
- 10.6 Hazardous decomposition products:  
No dangerous decomposition products known.

\*

**SECTION 11: Toxicological information**

- 11.1 Information on toxicological effects
  - Acute toxicity  
Harmful if swallowed.
  - LD/LC50 values that are relevant for classification
- |                            |                        |
|----------------------------|------------------------|
| 1310-73-2 Sodium hydroxide |                        |
| Oral                       | LD 50 2000 mg/kg (Rat) |
| Cutaneous                  | LD50 1350 mg/kg (Rat)  |
- Primary irritancy:
  - On skin:  
Causes skin irritation.
  - On eyes:  
Causes serious eye irritation.
  - Respiratory or skin sensitisation  
Based on available data, no effect.
  - CMR effects (carcinogenity, mutagenity and toxicity for reproduction)
  - Germ cell mutagenicity  
Based on available data, no effect.
  - Carcinogenicity Based on available data, no effect.
  - Reproductive toxicity  
Based on available data, no effect.
  - Specific target organ toxicity (STOT) - single exposure  
Based on available data, no effect.
  - Tossicità specifica per organi bersaglio (STOT) - repeated exposure  
Based on available data, no effect.
  - Aspiration hazard  
Based on available data no effect.

\*

**SECTION 12: Ecological information**

- 12.1 Toxicity
  - Aquatic toxicity:
- |                            |                                |
|----------------------------|--------------------------------|
| 1310-73-2 Sodium hydroxide |                                |
| LC50/96h                   | 35-189 mg/l (Fish)             |
| EC50/48h                   | 40,4 mg/l (Ceriodaphnia Dubia) |
- 12.2 Persistence and degradability: No further information available.
  - 12.3 Bioaccumulation potential No further information available.
  - 12.4 Mobility in soil No further information available.

(continued on page 7)

Safety data sheets  
According to 1907/2006/EC and 453/2010/EC  
regulations and subsequent updates

Page: 7/9

29.10.2016

Vers. 1

Update date: 29.10.2016

Commercial designation: CARBONIP COMPLEX

(continued from page 6)

- Behaviour in environmental systems:
- Further indications:  
Not known to be hazardous to water.
- 12.5 Results of PBT and vPvB assessment
- PBT: Not applicable.
- vPvB: Not applicable.
- 12.6 Other adverse effects No further information available.

#### SEZIONE 14: Disposal considerations

- 13.1 Waste treatment methods
- Recommendation:  
Must not be disposed together with household garbage.
- Uncleaned packaging:
- Recommendation: Disposal must be made according to official regulations.
- Recommended cleaning agent: Water, if necessary with cleaning agent.

#### SECTION 14: Transport information

- |   |  |
|---|--|
| - 14.1 ON number  |  |
| - ADR, ADN, IMDG, IATA  | not needed   |
| - 14.2 ON proper shipping name  |  |
| - ADR, ADN, IMDG, IATA  | not needed   |
| - 14.3 Transport hazard classes   |  |
| - ADR, ADN, IMDG, IATA  |  |
| - Class   | not needed   |
| - 14.4 Packaging group  |  |
| - ADR, IMDG, IATA   | not needed   |
| - 14.5 Environmental hazard:  | Not applicable.                                      |
| - 14.6 Special precautions for user                                       | Non applicable.                                      |
| - 14.7 Transport in bulk according to Annex II of MARPOL and the IBC code | Not applicable.                                      |
| - Transport/Additional information:                                       | Not dangerous according to the above specifications. |
| - UN "Model Regulation":  | not needed   |

#### SEZIONE 15: Regulatory information

General bibliography:  
Regulation (EC) 1907/2006 of the European Parliament (REACH)  
Regulation (EC) 1272/2008 of the European Parliament (CLP) and subsequent adjustments  
Regulation (EU) 830/2015 of the European Commission  
Web site ECHA Agency  
Lgs D 81/2008 (Consolidated Law on the protection of health and safety)  
(continued on page 8)



Safety data sheets  
According to 1907/2006/EC and 453/2010/EC  
regulations and subsequent updates

Page: 8/9

29.10.2016

Vers. 1

Update date: 29.10.2016

**Commercial designation: CARBONIP COMPLEX**

(Continued from page 7)

In the workplace) and subsequent modifications  
Regulation 648/2004/EC on detergents and subsequent modifications;  
Regulations for the transport of dangerous goods by road/rail: ADR/ RIO  
agreement.

Raw material supplier's safety data sheets

Niosh - Registry of Toxic Effects of Chemical Substances

Patty - Industrial Hygiene and Toxicology, 6th Edition, 2012

N.I. Sax - Dangerous properties of Industrial Materials-11th Ed., 2004

- **15.1 Specific laws and regulations provisions on health, safety and environment for the substance or the mixture**

- **Directive 2012/18/EU**

- **Specified hazardous substances - ANNEX I**

None of the components is present.

- **15.2 Chemical safety assessment:**

A chemical safety assessment has not been carried out.

#### **SECTION 16: Other information**

Further information:

This fact sheet has been written according to our actual knowledge and has the aim to provide technical and scientific information.

Working conditions at the intended user facility are however beyond our control.

The end user is responsible for the observance of legal provisions.

#### **KEY:**

ADR: Accord européen relative au transport international des marchandises dangereuses par route (European agreement concerning the international carriage of dangerous goods by road)

ASTM: ASTM International, originally known as American Society for Testing and Materials (ASTM)

EINECS: European Inventory of Existing Commercial Chemical Substances

EC(0/50/100): Effective Concentration 0/50/100

LC(0/50/100): Lethal Concentration 0/50/100

IC50: Inhibitor Concentration 50

NOEL: No Observed Effect Level

NOEC: No Observed Effect Concentration

LOEC: Lowest Observed Effect Concentration

DNEL: Derived No Effect Level (Derived dose of no effect)

DMEL: Derived Minimum Effect Level (Derived dose of minimum effect)

CLP: Classification, Labelling and Packaging

CSR: Chemical Safety Report LD(0/50/100): Lethal Dose 0/50/100

IATA: International Air Transport Association

ICAO: International Civil Aviation Organization

Codice IMDG: International Maritime Dangerous Goods code

PBT: Persistent, bioaccumulative and toxic

RIO: Règlement concernant le transport International ferroviare des marchandises dangereuses (regulations concerning the international transport of dangerous goods by rail)

STEL: Short term exposure limit

TLV: Threshold limit value

TWA: Time Weighted Average

EU: European Union

(continued on page 9)

**Safety data sheets**  
**According to 1907/2006/EC and 453/2010/EC**  
**regulations and subsequent updates**

Page: 9/9

29.10.2016

Vers. 1

Update date: 29.10.2016

**Commercial designation: CARBONIP COMPLEX**

(Continued from page 8)

vPvB: Very persistent very bioaccumulative  
 N.D.: Not available  
 N.A.: Non applicabile  
 VwVwS.: Text of Administrative Regulation on the Classification of Substances hazardous to waters into Water Hazard Classes (Verwaltungsvorschrift wassergefahrdende Stoffe - VwVwS)  
 PNEC: Predicted No Effect Concentration  
 PNOS: Particulates not Otherwise Specified  
 BOD: Biochemical Oxygen Demand  
 COD: Chemical Oxygen Demand  
 BCF: BioConcentrationFactor

- **Relevant phrases**  
 H290 May be corrosive to metals.  
 H302 Harmful if swallowed.  
 H314 Causes severe skin burns and eye damage.  
 H318 Causes severe eye damage.

- **Data sheets provided by:** Reparto Sicurezza Prodotti

- **Abbreviations and acronyms:**  
 ADR: Accord européen sur le transport des marchandises dangereuses par Route (European Agreement concerning the International Carriage of Dangerous Goods by Road)  
 IMDG: International Maritime Code for Dangerous Goods  
 IATA: International Air Transport Association  
 GHS: Globally Harmonised System of Classification and Labelling of Chemicals  
 EINECS: European Inventory of Existing Commercial Chemical Substances  
 ELINCS: European List of Notified Chemical Substances  
 CAS: Chemical Abstracts Service (division of the American Chemical Society)  
 DNEL: Derived No-Effect Level (REACH)  
 LC50: Lethal concentration, 50 percent  
 LD50: Lethal dose, 50 percent  
 PBT: Persistent, Bioaccumulative and Toxic  
 vPvB: very Persistent and very Bioaccumulative  
 Met. Corr. 1: Substances or mixtures corrosive for metals - Category 1  
 Acute Tox. 4: Acute toxicity - Category 4  
 Skin Corr. 1A: Skin corrosion/irritation - Categoria 1A  
 Skin Irrit. 2: Skin corrosion/irritation - Categoria 2  
 Eye Dam. 1: Serious eye damage/irritation - Category 1  
 Eye Irrit. 2: Serious eye damage/irritation - Category 2

- **Sources** Safety data sheets from our suppliers

## **5. AVAILABILITY**

As described in chapter 3. Economic feasibility.

## **6. CONCLUSION ON SUITABILITY AND AVAILABILITY OF THE ALTERNATIVE**

Metalcoating S.r.l. considers the Carbonip coating a suitable and sustainable alternative for this application and is available to further evaluations.

## **7. OTHER COMMENTS**

## **REFERENCES**

Metalcoating S.r.l. is already working with Aso H&P S.r.l., Fabbrica d'armi PIETRO BERETTA S.p.A. and Cromatura Dura S.r.l..

## **APPENDIXES**