(11) EP 2 369 020 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

28.09.2011 Bulletin 2011/39

(51) Int Cl.:

C21D 1/673 (2006.01)

C11D 7/08 (2006.01)

(21) Application number: 10156581.0

(22) Date of filing: 16.03.2010

(84) Designated Contracting States:

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 SE SI SK SM TR

(71) Applicant: Z.A.T. Zinc Anticorosion Technologies SA

1700 Fribourg (CH)

(72) Inventor: Levinski, Leonid 1831 Diegem (BE)

(74) Representative: Ter Smitten, Hans Patentanwälte ter Smitten Burgunder Strasse 29 40549 Düsseldorf (DE)

(54) Method for treating a metal element for an automobile

(57) The invention refers to a method for treating a metal element for an automobile. The method comprises the steps:

Press-hardening the metal element,

removing scale from the press hardened metal element in an ultrasonic liquid by an ultrasonic process, whereby

the ultrasonic liquid is a water solution with an organic carboxylic acid with a concentration of 0,1 to 10 vol. %, and

coating the metal element in a coating process with an anti-corrosion coating.

20

35

40

[0001] The invention refers to a method for treating a metal element for an automobile.

1

[0002] A metal element can be a component of the automobile body or automobile frame made out of a metal sheet as well as a massive metal element of the automobile, such as a bolt, a spring or another massive component not made out of a metal sheet. The metal element has to have a high strength and good anti-corrosive qualities

[0003] For increasing the metal element strength, the metal element is heated in an oven to a temperature of 550°C to 1200°C, and is subsequently quickly cooled down to a temperature below 22C°C in an oil bath or by cooled air. In a so called press-hardening process, the metal element is heated to a temperature of 800°C to 1000°C and is formed into its end shape by pressing and cooled in a press subsequent to the heating. The hardened metal element has a very high strength and allows to produce relatively light metal elements for the automobile. Subsequent to the hardening, the hardened high strength metal element is made anti-corrosive by means of a surface treatment or a surface coating step.

[0004] On the way from the hardening oven to the oil bath or to the press, the heated metal element is, because the high temperature difference with the environment, subject to scaling so that the scale has to be removed from the metal element before the metal element is passed to the surface treatment or surface coating step. A classic method for scale removing is pickling in a cleaning liquid with a strong acid, for example with sulphuric acid. With this scale removing method, even the smallest structures, such as slits, hollow spaces, undercuts etc. are removed from scale. But using a strong acid has the disadvantage that the treated high strength metal element becomes brittle. An alternative method for scale removing is shot blasting which does not effect the inner structure of the metal element but is not suitable to remove scale from small structures, slits, undercuts etc. In addition, the shot blasting stream can mechanically deform a sheet-made metal element.

[0005] It is an object of the invention to improve the scale removing from a automobile metal element between the hardening step and the subsequent coating step.

[0006] This object is, according to the invention, solved with the features of claim 1.

[0007] According to claim 1, the metal element is first hardened. The hardening step can be accomplished by heating the metal element in an oven to a temperature of about 550°C to 1200°C. After heating, the metal element is quickly cooled down to a temperature below 200°C in an oil bath or by cooled air. On the way from the heating oven to the oil bath or to a press for providing a press-hardening step, the metal element is subject to scaling.

[0008] Subsequent to the hardening step, the scale

removing step is provided by an ultrasonic process, whereby the ultrasonic liquid is a water solution with an organic carboxylic with the concentration of 0,1 to 10 vol. %

[0009] As experiments have shown, such a water solution does not significantly affect the metal elements surface, and in particular does not make the metal element brittle. On the other hand, the ultrasonic cleaning method guarantees that the scale is completely removed even from small structures, slits, hollow spaces, undercuts etc.

[0010] Subsequent to the scale removing step, the metal element is coated in a coating process with an anticorrosion coating. This coating process can be realized, for example, by a so-called thermo diffusion process with zinc powder.

[0011] According to the preferred embodiment of the invention, the organic carboxylic acid concentration is between 1,0 and 6,0 vol.%, and preferably between 2,0 and 6,0 vol.%. According to a preferred embodiment, the organic carboxylic acid is a citric acid.

[0012] Preferably, the ultrasonic liquid has a pH value between 3,0 and 5,0.

[0013] According to a preferred embodiment of the invention, is the ultrasonic frequency during the ultrasonic cleaning sequence is between 18 kHz and 60 kHz, whereby the ultrasonic frequency can be a varied during the complete ultrasonic scale removing sequence. Preferably, the ultrasonic activity is provided in intervals with numerous interruptions of less than 30% during the ultrasonic process step. The scale removing sequence can take between one and eight minutes.

[0014] Preferably, the temperature of the ultrasonic liquid is between 30 and 70°C. In this temperature range, the ultrasonic liquid is very effective.

[0015] According to a preferred embodiment of the invention, the metal element is moved with respect to the ultrasonic liquid during the ultrasonic cleaning sequence. Preferably, the metal element is rotated in the ultrasonic liquid during the ultrasonic treatment. Preferably, the metal element is rotated by a rotor in the ultrasonic liquid during the ultrasonic treatment. The rotor holds the metal element in a rotor cradle or with rotor fingers attached to the metal element.

[0016] Preferably, the metal element is a complex structural automobile element,

[0017] The following is a description of one embodiment of the method according to the invention.

[0018] A metal element to be treated can be any metal automobile component which has to have high strength and good anticorrosive qualifies, Especially automobile components made out of thin metal sheets but also massive parts as springs and bolts are predestinated to be treated accordingly. The following example refers to a sheet-like metal element which is formed to a component of the automobile body or automobile frame.

[0019] In a hardening step, the metal sheet element is transferred to a hardening oven wherein the metal sheet element is heated to a temperature of 700°C to 1000°C

10

15

20

25

30

35

40

45

50

in an oven, and subsequently is formed into its end shape by pressing under high pressure in a press-hardening press. As soon as the heated metal sheet element is removed from the oven, the metal sheet element is subject to scaling on the way to the press so that the metal sheet element is covered with a layer of scale after leaving the press-hardening oven. After the press-hardening step in the press, the press is opened, and the metal sheet element is removed from the press.

[0020] Before the metal sheet element is transferred to a coating step for coating the high strength metal sheet element with an anticorrosion coating, the scale layer has to be removed from the metal sheet element.

[0021] The scale removing step is carried out in a scale removing device, wherein the high strength metal sheet element is fixed to a rotor which rotates the metal sheet element in an ultrasonic liquid. The ultrasonic liquid is a water solution with an organic carboxylic acid with a concentration of about 4,0 vol%, Preferably, the acid is a citric acid. The ultrasonic liquid has a temperature of about 50°C and a pH value of 4.

[0022] As soon as the metal sheet element is fixed to the rotor and immersed into the ultrasonic liquid, the scale removing process starts: an ultrasonic element induces ultrasonic waves into the ultrasonic liquid. The frequency of the ultrasonic waves varies between 20 kHz and 40 kHz, and is provided in intervals of for example 50 seconds separated by interruptions of 10 seconds. During the complete ultrasonic treatment step, the metal sheet element is rotated by the rotor in the ultrasonic liquid. The ultrasonic treatment of one metal sheet element takes about 5 minutes in total.

[0023] After the scale removing step is finished, the metal sheet element is removed from the ultrasonic scale removing device, and is transferred to a coating process step whereby the metal sheet element is provided with an anticorrosion treatment by a so-called thermo diffusion process with zinc powder.

Claims

1. Method for treating a metal element for an automobile, with the steps:

hardening the metal element, removing scale from the press hardened metal element in an ultrasonic liquid by an ultrasonic process, whereby the ultrasonic liquid is a water solution with an organic carboxylic acid with a concentration of 0,1 to 10 vol. %, and coating the metal element in a coating process with an anti-corrosion coating.

2. Method for treating a metal element of claim 1, wherein the hardening step is realized by presshardening.

- **3.** Method for treating a metal element of one of the preceding claims, wherein the organic carboxylic acid concentration is between 1,0 and 8,0 vol.%.
- **4.** Method for treating a metal element of one of the preceding claims, wherein the organic carboxylic acid concentration is between 2,0 and 6,0 vol.%.
- **5.** Method for treating a metal element of one of the preceding claims, wherein the organic carboxylic acid is a citric acid.
- **6.** Method for treating a metal element of one of the preceding claims, wherein the ultrasonic liquid has a pH-value between 3,0 and 5,0.
- 7. Method for treating a metal element of one of the preceding claim, wherein the ultrasonic frequency during the ultrasonic process step is between 18 kHz and 60 kHz.
- **8.** Method for treating a metal element of one of the preceding claim, wherein the ultrasonic frequency is varied during the complete ultrasonic process step.
- **9.** Method for treating a metal element of one of the preceding claims, wherein the ultrasonic activity is provided in intervals with numerous interruptions of less than 30% during the ultrasonic process step.
- **10.** Method for treating a metal element of one of the preceding claims, wherein the cleaning sequence takes 1 to 8 minutes.
- **12.** Method for treating a metal element of one of the preceding claims, wherein the temperature of the ultrasonic liquid is between +30 and +70°C.
- **13.** Method for treating a metal element of one of the preceding claims, wherein the metal element is moved with respect to the ultrasonic liquid during the ultrasonic process step.
- **14.** Method for treating a metal element of one of the preceding claims, wherein the metal element is rotated in the ultrasonic liquid during the ultrasonic process step.
- **15.** Method for treating a metal element of one of the preceding claim, wherein the metal element is rotated by a rotor in the ultrasonic liquid during the ultrasonic process step.
- **16.** Method for treating a metal element of one of the preceding claims, wherein the metal element is a complex structural automobile element which is hardened by press-hardening.

17. Method for treating a metal element of one of the preceding claims, wherein the metal element is a massive element which is hardened by heating and subsequently cooling in an oil bath.

18. Method for treating a metal element of one of the preceding claims, wherein the coating is realized by a thermal-diffusion procedure with zinc powder.



EUROPEAN SEARCH REPORT

Application Number EP 10 15 6581

	DOCUMENTS CONSIDER	ED TO BE RELEVANT				
Category	Citation of document with indica of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)			
Υ	US 2006/219334 A1 (BRC AL) 5 October 2006 (20 * paragraphs [0001], [0017], [0032]; clair 1,3 *	006-10-05) [0002], [0014] -	1	INV. C21D1/673 C11D7/08		
Υ	US 2006/131185 A1 (LEV AL) 22 June 2006 (2006 * paragraphs [0003], [0011], [0013], [001	5-06-22) [0004], [0005],	1	TECHNICAL FIELDS SEARCHED (IPC) C21D C23C B21D C23F C11D C25F		
Υ	JP 2008 222823 A (ADEI 25 September 2008 (200 * abstract *		1			
А	US 2002/197491 A1 (R002 C26 December 2002 (2002 * paragraphs [0057], 1,16,17 *	2-12-26)	1,5,6, 10,12			
A	US 2008/202550 A1 (MCI [US] ET AL) 28 August * paragraphs [0044], *	2008 (2008-08-28)	1,7-9			
Α	US 6 277 799 B1 (SACHI AL) 21 August 2001 (20 * the whole document	001-08-21)	1-10, 12-18			
A	US 4 401 479 A (QUICK 30 August 1983 (1983-0 * the whole document	98-30)	1-10, 12-18			
Α	US 2006/137779 A1 (BROAL) 29 June 2006 (2000) * the whole document	5-06-29)	1			
	The present search report has been	,	_			
		Date of completion of the search	C	Examiner		
	Munich	21 July 2010	·			
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		E : earlier patent doc after the filing dat D : document cited in L : document cited fo	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document oited in the application L : document oited for other reasons			
O : non-written disclosure P : intermediate document		& : member of the sa document	& : member of the same patent family, corresponding document			

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

EP 10 15 6581

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.

21-07-2010

cite	Patent document ed in search report		Publication date		Patent family member(s)		Publication date
US	2006219334	A1	05-10-2006	DE EP WO JP ZA	10333165 1646458 2005018848 2007500782 200600593	A1 A1 T	24-02-200 19-04-200 03-03-200 18-01-200 26-08-200
US	2006131185	A1	22-06-2006	DE GB WO	112005002977 2436269 2006065436	Α	31-10-200 19-09-200 22-06-200
JP	2008222823	Α	25-09-2008	NONE			
US	2002197491	A1	26-12-2002	AT AU WO CN DE EP JP	250646 1377101 0140378 1402759 19957276 1238013 2003515650	A A1 A A1 A1	15-10-200 12-06-200 07-06-200 12-03-200 11-10-200 11-09-200 07-05-200
US	2008202550	A1	28-08-2008	EP JP KR TW US	1570918 2005246376 20060043031 246944 2005183739	A A B	07-09-200 15-09-200 15-05-200 11-01-200 25-08-200
US	6277799	B1	21-08-2001	NON	 Е		
US	4401479	Α	30-08-1983	NON	E		
US	2006137779	A1	29-06-2006	WO EP JP JP	2004033126 1536898 4319987 2005539145	A1	22-04-200 08-06-200 26-08-200 22-12-200

FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82