

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 657 564 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **94203574.2**(51) Int. Cl.⁶: **C25F 1/04**, C25F 1/00,
C25F 1/02(22) Date of filing: **07.12.94**(30) Priority: **09.12.93 IT MI932585**(43) Date of publication of application:
14.06.95 Bulletin 95/24(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IE LI SE(71) Applicant: **Felisari, Dario**
Via Comasina 123 Bis
I-20050 Verano Brianza,
Milan (IT)(72) Inventor: **Felisari, Dario**
Via Comasina 123 Bis
I-20050 Verano Brianza,
Milan (IT)(74) Representative: **Appoloni, Romano**
ING. BARZANO' & ZANARDO MILANO S.p.A.
Via Borgonuovo 10
I-20121 Milano (IT)(54) **Process for cleaning and conditioning the surface of an electrolytically oxidizable metal alloy by hyperanodizing said surface.**

(57) The process consists in submitting the surface layer of an electrolytically oxidizable metal to the action of an electrical field with a higher field intensity than the breakdown intensity during an anodizing step.

Under such conditions, extremely intense energy exchanges occur in a region confined on the surface of the immersed article; the resulting physical and chemical processes cause, among others, any impurities to be nearly immediately removed, and a useful surface conditioning layer for subsequent processes to be produced.

The process is particularly useful for high-speed treatment of bands of light alloy or other oxidizable materials.

EP 0 657 564 A1

According to the present state of the art, the washing process commonly used by aluminum alloy manufacturers or fabricators essentially consists in a band degreasing step carried out in order to remove greases or similar organic substances used in the rolling process.

Such a removal is carried out by bringing the band to be washed into contact with a liquid phase displaying strong affinity for the impurities, substantially performing the task of transferring the latter from the solid into the liquid phase.

Said processes are usually carried out with solvent liquids (e.g., trichloroethylene) or alkaline solutions which are suitably buffered, therefore with reduced reactivity towards aluminum; in order to cause the impurities to diffuse, the processes known from the prior art rely on diffusion (high-temperature processes), or on kinds of fluxing (castings), or on the supply of mechanical energy to the interface (brushing, sonication).

A rinsing step follows, often followed, in its turn, by steps of anchoring functional groups for surface protection, or acting as adhesion promoters (oxidation, chromate treatment, phosphating treatment or phospho-chromate treatment).

In order to be effective, these processes require a long enough surface-liquid contact time as to make it possible material to diffuse between the metal, the limit layer, and the liquid, which time, when bands are submitted to such a continuous, high-speed treatment, may require that considerably long facilities are used, with consequent large overall dimensions and high costs; furthermore, the use of hydrogenated rolling lubricants, such as, e.g., lauryl alcohol, and the like, having electronic affinity for aluminum, compromises the transfer of impurities to the liquid phase, sometimes rendering necessary a preliminary chemical etching step prior to the subsequent treatments, with problems of disposal of the resulting waste products consequently arising.

Electrochemical processes are known as well in the practice of metal articles degreasing, which consist in submitting the metal surface to an anodic or cathodic action, while said surface is immersed in suitable electrolytic solutions.

This practice, useful in order to activate the surface as a preliminary step to electrodepositions is, unfortunately, ineffective for degreasing purposes, because the flow of the ionic species, and of the released gases does not interact with the presence of grease or oleol impurities.

Due to such a reason, in the practical operations of facilities for continuous band degreasing, this solution is not applied.

The process according to the present patent application consists in an action of ionic type which exclusively occurs at high current density values

5

(superficial electrical intensity comprised within the range of from some tens, up to one hundred A/dm²), in the presence of a polybasic acidic electrolyte, when the electrolytically oxidizable material is submitted to anodizing with a higher voltage than the stopping potential of formed oxide.

10

Under such conditions, a sharp potential decrease takes place on that layer which is the nearest to the metal, with unstable ionic species (radicals) being generated, which are capable of destroying the degradable organic substances, or of reducing their affinity for the metal.

15

In other terms, the voltage gradient, concentrated in the immediate nearby of the surface of the metal to be treated, promotes a violent, localized energy development with the results disclosed hereinabove being accomplished.

20

A process results which is governed by easily modulated electrical parameters in which, following a supply of electrical energy (of the order of 1 kW/dm² of exposed surface) a nearly immediate decontamination of band surface is attained.

25

Therefore, the essential parameters are constituted by the electrical conductivity of the bath and the local current density on the surface to be treated.

30

The present electrodes, necessary for the above events to take place prevalingly perform transport functions, and therefore their composition slowly varies during the process.

35

In practical tests, several low-concentration (2 ÷ 5 %) acidic electrolytes were successfully tested under moderately high temperature (80 ÷ 90 °C) conditions.

40

In order to maintain the temperature level, the energy excess turned into heat must be transferred to a secondary fluid, and can be recovered for the rinsing or drying process.

45

From a practical viewpoint, the band to be treated is electrically connected to the positive terminal of power supply unit.

50

The ionic action takes place inside a tank inside which the band can run while being immersed, exposed to the surfaces of opposite polarity electrodes (cathodes).

55

Current flow is so controlled as to keep constant energy developed at band surface, correlating it, e.g., to the running speed of said band. In other words the process consists in submitting the surface layer of an electrolytically oxidizable metal to the action of an electrical field with a higher field intensity than the breakdown intensity during an anodizing step.

Under such conditions, extremely intense energy exchanges occur in a region confined on the surface of the immersed article; the resulting physical and chemical processes cause, among others, any impurities to be nearly immediately removed,

and a useful surface conditioning layer for subsequent processes to be produced.

The process is particularly useful for high-speed treatment of bands of light alloy or other oxidizable materials.

16. Materials treated by means of process according to claim 11.

5

Claims

1. Surface washing and conditioning process accomplished by means of a hyperanodizing process of electrolytically oxidizable alloys. 10
2. Process according to claim 1, characterized in that the anodizing voltage exceeds the breakdown potential of generated oxide. 15
3. Process according to claim 2, characterized in that as process liquid an acidic electrolyte is used. 20
4. Process according to claim 3, characterized in that as process liquid a phosphoric acid acidic electrolyte is used. 25
5. Process according to claim 4, characterized in that concentrations of from 1 to 6 %, by weight, are used. 30
6. Process according to claim 5, characterized in that temperatures are used which are comprised within the range of from 50 to 100 ° C. 35
7. Process according to claim 2, applied to light alloy bands. 40
8. Process according to claim 3, applied to light alloy bands. 45
9. Process according to claim 4, applied to light alloy bands. 50
10. Process according to claim 5, applied to light alloy bands. 55
11. Process according to claim 6, applied to light alloy bands.
12. Materials treated by means of process according to claim 7.
13. Materials treated by means of process according to claim 8.
14. Materials treated by means of process according to claim 9.
15. Materials treated by means of process according to claim 10.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 3574

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.6)
X,Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 87-077758 & SU-A-1 244 216 (GORYACHKIN AGRIC ENG)	1-5	C25F1/04 C25F1/00 C25F1/02
Y	* abstract * ---	6-16	
X,Y	PATENT ABSTRACTS OF JAPAN vol. 14, no. 458 (C-0766) & JP-A-02 182 900 (SKY ALUM CO. LTD)	1,2	
Y	* abstract * ---	3-16	
X,Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 85-219648 & JP-A-60 140 199 (HITACHI PLANT ENG. CONST.)	1,2	
Y	* abstract * ---	6-16	
X,Y	EP-A-0 059 527 (ALLEGHENY LUDLUM STEEL CORPORATION)	1,2	
Y	* the whole document * ---	6,11,16	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X,Y	DE-B-10 21 229 (MAGNESIUM ELEKTRON LIMITED)	1,2	C25F
Y	* the whole document * ---	5,7-16	
X,Y	GB-A-1 071 249 (RUTHNER INDUSTRIEPLANUNGS-AKTIENGESELLSCHAFT)	1-3	
Y	* the whole document * ---	4-8,12,13	
X,Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 76-71063X & JP-A-51 088 435 (HAKUSUI KAGAKU KOGY)	1,2	
	* abstract * ---		
	-/--		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 March 1995	Examiner Fischer, W
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			



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 3574

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.6)
Y	US-A-4 397 721 (R. EXALTO ET AL.) * the whole document * ---	3,6-16	
Y	US-A-4 640 752 (TAYLOR ET AL.) * the whole document * ---	7-11	
A	FR-A-1 544 974 (REVERE COPPER ANDBRAS INCORPORATED) ---		
A	US-A-3 756 931 (C. M. DE BOER) ---		
A	DE-A-43 10 749 (SIEMENS AG) ---		
A	GB-A-517 415 (S. J. BLAUT ET AL.) ---		
A	LU-A-53 840 (PECHINEY-COMPAGNIE DE PRODUITS CHIMIQUES ET ELECTROMETALLURGIQUES) ---		
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 94-149436 & SU-A-1 798 393 (HARWARE IND. RES. INST.) 28 February 1993 * abstract * ---		
A	PATENT ABSTRACTS OF JAPAN vol. 7, no. 143 (C-172) & JP-A-58 055 597 (KOGYO GIJUTSUIN) * abstract * -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 March 1995	Examiner Fischer, W
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			