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(71) Applicants:
- **CB Trafilati Acciai S.p.A.**
  20124 Milano (IT)
- **Cogne Acciai Speciali S.p.A.**
  11100 Aosta (IT)

(72) Inventors:
- **Fiorio, Luca**
  36056 Tezze sul Brenta (VI) (IT)
- **Massazza, Marco**
  11100 Aosta (AO) (IT)

(74) Representative: **Contessini, Pier Carlo**
Via Pismonte, 2/16
IT-20139 Milano (IT)

(54) Method for preparing a stainless steel wire, rope and/or strand

(57) The present patent application relates to a method for preparing a two-phase austeno-ferritic stainless steel wire, rope and/or strand, said method being characterized by the fact it comprises a stabilization step wherein said wire, rope and/or strand is subjected to a thermal or thermo-mechanical treatment at a temperature between 480°C and 700°C.

This method allows the realization of a two-phase austeno-ferritic stainless steel wire, rope and/or strand having good elongation and necking properties thus ensuring good properties in terms of elasticity and resistance to fragility, still also maintaining at the same time good properties in terms of toughness due to rather good yield snervamento rupture and relaxation features.

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Description

[0001] The present invention relates to a method for preparing a two-phase austeno-ferritic stainless steel wire, rope and/or strand, as well as said wire, rope and/or strand obtained by said method preparation.

[0002] In particular, this invention relates to a method for preparing a two-phase austeno-ferritic low relaxation stainless steel wire, rope and/or strand.

[0003] The two-phase austeno-ferritic stainless steel types, hereinafter defined for simplicity as "duplex steels", are known in the art; they have a mixed austenite and ferrite structure, wherein amounts of chromium, nickel and all other components that have been balanced in such a way to produce a mixed microcrystalline structure are present, wherein the ratio of austenitic versus ferritic phase is close to one.

[0004] The duplex steels basic properties are good resistance to stress corrosion cracking, high tensile strength and yield strength, better passivation level and therefore better resistance to punctiform corrosion as compared to other stainless steel grades.

[0005] These features allow the use of duplex steels in various sectors, the most common uses are in fact in the heat exchangers, material handling machines, tanks and liquid containers with high chlorine concentration, salt water coolers, and the like.

[0006] Steel is the raw material from which wires that can be individually used are obtained or said wires can be braided together to form a rope, wherein at least 2 or 3 wires are twisted together, or to form a strand, wherein seven wires are twisted around one each other or around a central wire.

[0007] This kind of steel has many features that have been reported in technical literature, see, for example, Gunn, "Duplex Stainless Steel: microstructure, properties and applications", Abington Publishing, 1997; however, in this text it is stated that, by subjecting a duplex stainless steel to thermal treatment at a temperature higher than 450°C, a progressive weakening of the steel himself is obtained, with the obvious consequence on decreasing the elastic properties, such as stretching and flexibility, of the desired product to be obtained from said steel.

[0008] British patent application No. GB 2,354,264 discloses a wire, rope or strand comprising 25% chromium super duplex stainless steel, with a microstructure of approximately 50% ferrite and 50% austenite. The stainless steel therein disclosed may be polished before it is subjected to heat treatment prior to the wire formation. Before the final finishing cleaning treatment of the surface, the wire may be subjected to a thermal treatment in the range from 300°C to 550°C.

[0009] US patent No. 5,716,466 discloses a duplex stainless steel wire. The aging temperature therein disclosed is comprised in the range from 200°C to 700°C. Figure 4 of said patent shows a table wherein the high relaxation (HR) values for the steel wire are reported according to the JIS Standard No. G 3536, which considers to perform standard tests after 10 hours treatment, typical for high relaxation steel wires.

[0010] US Patent No. 5,545,482 and patent application No. EP 0,659,896 disclose duplex stainless steel wires, whose aging temperature are comprised in the range from 150°C to 600°C and from 150°C to 700°C, respectively.

[0011] Similarly, patent application No. EP 0,576,802 disclose duplex stainless steel wires, whose aging temperature is in the range from 150°C to 600°C, by considering a maximum aging period of 1 hour.

[0012] All the above cited patents deals therefore with duplex type stainless steel wires or strands, wherein the wire or strand is subjected to a thermal treatment by using very large temperature ranges (up to 700°C).

[0013] However, none of said documents refer to the fact that the final obtained product must show elongation and low relaxation properties according to the standards as indicated in the Italian Ministerial Decree of January 14, 2008 and/or in the European Standard No. EN-10138, namely an elongation breaking percentage higher than 3.5% upon application of a maximum loading force to break the wire, rope and/or strand, and a relaxation percentage (i.e., load losses due to relaxation) lower than 2.5% after 1,000 hours with a load force of 70% of Fma (Effective Maximum Force) and/or lower than 4.5% after 1,000 hours with a load force of 80% of Fma.

[0014] On the other hand, the applicant of the present application has found that, by subjecting a duplex stainless steel to thermal treatment at a temperature lower than 450°C, after the wire, rope and/or strand formation, materials having a too low elongation feature are obtained, not suitable, for example, to satisfy the features requested by the current standards for the low relaxation products, wherein for low relaxation steel products is meant those products having values in accordance to the requirements indicated in the cited above Italian Ministerial Decree of January 14, 2008 and/or in the European Standard No. EN-10138.

[0015] To date, therefore, the technical problem to realize a material, such as a wire, a rope or a strand obtained from a duplex steel, in such a way that said material is able to show good elastic properties, such as stretching and flexibility, still maintaining the good corrosion resistance properties, with a high ultimate tensile strength, is particularly strong. In fact, it has not yet been found a suitable thermal treatment or thermo-mechanical process to which a material is to be subjected in order to achieve the desired characteristics without compromising the typical properties of duplex stainless steels, such as good resistance to embrittlement.

[0016] In a first aspect, the present invention relates to a method for preparing a two-phase austeno-ferritic stainless steel wire, rope and/or strand.

[0017] In fact, the Applicant of the present invention has surprisingly found that a method for preparing a two-phase austeno-ferritic stainless steel wire, rope and/or strand, having relaxation and elongation values according to the standards indicated in the Italian Ministerial Decree of January 14, 2008 and/or in the European Standard No. EN-10138, said method being characterized in that it comprises the stabilization phase wherein said wire, rope or strand is subjected to thermal or thermo-mechanical treatment at a temperature in the range between 480°C and 700°C is able to produce a final material able to meet the high technical performance requirements in specific applications, such as those wherein a wire, rope or strand is required to have a good toughness such as to withstand the minimum ultimate unitary tensile stresses of 1570, 1620 and 1670 N/mm^2 for the regulations concerning the wire product and of 1860 N/mm^2 for rope and strand, combined with a good corrosion resistance. Moreover, the method of the present invention is able to produce a two-phase austeno-ferritic stainless steel wire, rope and/or strand type, with good elongation and striction properties thus ensuring good properties in terms of elasticity and therefore of brittleness resistance, still also maintaining good properties in terms of toughness due to sufficient yield and breaking features. Finally, excellent relaxation properties that meet the parameters set out in the specific standards for this type of product are also obtained.

[0018] In particular, the method of the present invention is able to produce a two-phase austeno-ferritic stainless steel wire, rope and/or strand, wherein said relaxation value is lower than 2.5% after 1,000 hours with a load force of 70% of Fma (Effective Maximum Force) and/or lower than 4.5% after 1,000 hours with a load force of 80% of Fma.

[0019] In addition, the method of the present invention is able to produce a two-phase austeno-ferritic stainless steel wire, rope and/or strand, wherein said elongation value is higher than 3.5% upon application of a maximum loading force to break the wire, rope and/or strand.

[0020] Preferably, said wire, rope or strand are subjected to a thermal or thermo-mechanical treatment at a temperature in the range between 480°C and 600°C, more preferably between 500°C and 580°C.

[0021] Preferably, said wire, rope or strand are subjected to said thermal or thermo-mechanical treatment by an induction heating furnace.

[0022] Preferably, said wire, rope or strand are subjected to said thermal or thermo-mechanical treatment for a period of time lower than 6 minutes, more preferably lower than 3 minutes, still more preferably lower than 2 minutes.

[0023] By this phase (known as stabilization phase), the further advantage to have a wire, rope and/or strand with particularly high elastic properties, due to an excellent elongation percentage value, is obtained.

[0024] Preferably, during said stabilization phase, said wire, strand or rope is subjected to a tensioning phase. More preferably, during said tensioning phase, said tensed wire, rope or strand is stretched (dynamic stretching) by a pair of flywheels, named traction capstans, synchronously working one each other with an angular velocity difference of a few percentage points in favor of the leading capstan. By this way, fibers relaxation is obtained.

[0025] Preferably, the stretching dynamics of said wire, rope or strand is in the range between 35 and 70%, more preferably between 40 and 60% of its ultimate tensile strength.

[0026] Preferably, immediately after they have been subjected to said thermal or thermo-mechanical treatment and while they are still subjected to said tensioning phase, said wire, rope or strand is subjected to a cooling phase, letting them pass through, for example, a cooling box filled with water maintained at a controlled temperature, for example at 30°C.

[0027] By this way, the sudden cooling causes a "freezing" of the aforementioned fiber relaxation.

[0028] At the end of said cooling stage, said wire, rope or strand is ready to be packed.

[0029] In order to further improve certain characteristics of the final product (wire, rope or strand) to be obtained by the method of the present invention, some optional steps may precede said stabilization phase.

[0030] In fact, preferably, the method of the present invention further comprises the preparation phase of the single stainless steel duplex wire and, then, the drawing phase of said single thread, said preparation phase and drawing phase both preceding said stabilization phase.

[0031] More preferably, said preparation phase of the single stainless steel duplex wire comprises the melting step of the raw materials constituting said stainless steel, the hot rolling phase and the pickling phase.

[0032] Preferably, said duplex stainless steel has a chemical composition comprising 0,001-0,10% by weight of carbon, 0,0001-0,030% by weight of sulfur, 0,005-0,050% by weight of phosphorus, 0,1-1,5% by weight of silicon, 0,30-1,80% by weight of manganese, 18-35% by weight of chromium, 2,5-9,0% by weight of nickel, 0,5-5,0% by weight of molybdenum, and 0,05-0,50% by weight of nitrogen, and the balance being made up of iron and some minimum impurity percentages.

[0033] More preferably, said two-phase stainless steel has a chemical composition comprising 0,01-0,08% by weight of carbon, 0,0005-0,020% by weight of sulfur, 0,010-0,040% by weight of phosphorus, 0,2 -1,0% by weight of silicon, 0,50-1,50% by weight of manganese, 20-30% by weight of chromium, 3,5-8,0% by weight of nickel, 1,5-4,5 % by weight of molybdenum, and 0,10-0,40% by weight of nitrogen, and the balance being made up of iron and some minimum impurity percentages.

[0034] Preferably, said raw materials are melted in an electric furnace; then, said melted raw materials are continuously casted to form billets or blooms of semi-finished steel which are then hot rolled to obtain wire rod, that is a semi-finished steel bar, usually with a circular section, the section being generally in the range between 10 and 25 mm, wrapped in coils.

[0035] Preferably, said wire rod is then subjected to the pickling phase, through which a deoxidation of the substance occurs, in other words the wire rod is freed from surface impurities and passivated, allowing the wire rod to return to its original characteristics. By this way, the wire rod appears clean and protected from atmospheric agents aggression.

[0036] Preferably, once said wire rod has been subjected to such hot rolling and pickling phases, said hot rolled and pickled wire rod is subjected to at least one drawing phase, whose goal is to reduce its diameter up to obtain a wire.

[0037] In fact, in the drawing phase, which occurs through a plant defined as a draw plate plant, the wire rod undergoes forced passages through dies having progressively decreasing diameter holes that reduce the section. The wire volume remains constant due to the fact that the drawing phase is only a cold plastic deformation treatment with no material removal; by reducing the diameter an increase of the length is obtained.

[0038] The drawing diagram must be properly proportioned to the rod type in comparison with the finished wire diameter, depending upon the desired strength to be obtained on the final product and upon the rod starting properties.

[0039] For example, to reduce a rod having an initial section of 8 mm to a wire of 2 mm in diameter a dozen passages through decreasing dies are executed.

[0040] Preferably, said rod is subjected to a repeated series of n "cold" drawing phases, wherein n preferably varies from 2 to 20, more preferably from 5 to 15, during which the diameter of said wire is progressively reduced.

[0041] Preferably, for technical and plants reasons connected to the structure of duplex stainless steels and to the thermal and mechanical characteristics of the die used, the total reduction coefficient of the finished wire is preferably lower than or equal to 94% of the overall reduction.

[0042] Preferably, at the end of a drawing phases cycle according to the present application, a wire rod having an initial section in the range between 10 and 20 mm, is reduced to a wire of up to 7 mm.

[0043] By this way, not only the advantage of reducing the section diameter of said rod is obtained, but the geometrical and mechanical characteristics are also improved; in fact, for example, if a not subject to the drawing phase rod generally has a wire ultimate tensile stress equal to 700N/mm^2 with a diameter ovalization of about 5/100, the same wire rod subjected to at least one drawing phase is able to have a tolerance of 1/100 on the diameter ovalization and 1700 N/mm^2 of ultimate tensile stress.

[0044] At the end of the drawing phase, and before the beginning of the stabilization phase, the thus obtained wire can optionally be subjected to a further phase, named stranding treatment, which consists in taking two or more wires and twisting one to each other in order to obtain compact wire groups. In particular, if two or three wires are used a rope is obtained; on the other side, if seven wires are used a strand is obtained. In the case of twisting a strand, the wires can twist around a central wire.

[0045] In a second aspect, the present invention relates to a two-phase austeno-ferritic stainless steel wire, rope and/or strand, prepared by the above described method. Additional features and advantages of the present invention will be better highlighted by the examination of the following detailed description of a preferred, but not exclusive embodiment, illustrated as purposes only and without limitation.

Detailed description of the invention.

[0046] A duplex steel V wire rod having a diameter of 15 mm and the following cast analysis was prepared:

Element	wt%
C	0.02
S	0.001
P	0.025
Si	0.59
Mn	1.1
Cr	22.74
Ni	5.33
Mo	3.17
N2	0.15

the balance being made up of iron and some minimum percentage of impurities.

[0047] The V wire rod was pickled in hydrochloric acid and passivated with a protective and lubricant material.

[0048] The V wire rod so treated was then ready to be drawn. 13 steps to progressively reduce the diameter of the V wire rod were carried out, to pass from the initial value of 15 mm for the wire rod diameter to a final one of a F wire of 5.02 mm, as shown in table 1 below. For some of the intermediate obtained diameters the "hardening" values, i.e. the wire increase tensile strength values as the diameter was reduced by means of a traction 500 KN Metrocom apparatus, and the necking percentages derived from the calculation of the breaking section area compared to the initial area were measured by sampling.

Table 1

No of steps	diameter in mm	strength in N/mm^2	necking %
0	15	811	
1	13,74818		
2	12,60701	1160	
3	11,56624		
4	10,61659	1319	
5	9,74969		
6	8,95797		
7	8,23457		
8	7,57331		
9	6,96857		
10	6,41526	1648	58
11	5,90878		
12	5,44495	1743	56
13	5,02	1801	53

[0049] The data for strength and necking percentage showed the good quality of duplex stainless steel wire obtained after 13 steps, because the necking values exceeded the limit of 35%, generally considered the minimum acceptable value. Moreover, the resistance values showed a gradual increase as the diameter was reduced; however, the obtained F wire resistance value was still inadequate in order to allow the use of the F wire in applications where a minimum strength of 1860 N/mm^2 is required.

[0050] Subsequently, 7 samples of the F wires so obtained after drawing of the V wire rod were then twisted together to form a T strand, using a wire as a central core of the strand, and twisting around it the remaining 6 wires.

Examples

Example 1.

[0051] 7 samples of the obtained T strand were taken and each of them was subjected to a different stabilization phase to get the stabilized TS1-TS7 strands.

[0052] TS1 sample (comparison). A F strand sample was subjected to the stabilization phase, which consisted in placing the strand in an induction furnace at a temperature of 330°C with sample controlled tension values for a staying period in the oven lower than one minute. Thus, the stabilized TS1 strand was obtained.

[0053] TS2 sample (comparison). The stabilized TS2 strand was obtained by the same procedure for obtaining the stabilized TS1 strand, this time the temperature being 400°C.

[0054] TS3 sample (comparison). Similarly, the stabilized TS3 strand was obtained using a temperature of 450°C.

[0055] TS4 sample (invention). Similarly, the stabilized TS4 strand was obtained using a temperature of 520°C.

[0056] TS5 sample (invention). Similarly, the stabilized TS5 strand was obtained using a temperature of 550°C.

[0057] TS6 sample (invention). The stabilized TS6 strand was obtained by the same procedure for obtaining the stabilized TS5 strand of the invention, this time by subjecting the F strand to a thermal treatment for a period of two minutes, still at a temperature of 550°C.

[0058] TS7 sample (invention). The stabilized TS7 strand was obtained by the same procedure for obtaining the stabilized TS5 strand of the invention, this time by subjecting the F strand to a thermal treatment for a period of five minutes, still at a temperature of 550°C.

[0059] After being subjected to said stabilization phase, for each of the 7 stabilized TS1-TS7 strands elongation and tensile strength, measured as previously described, were measured, obtaining the results reported in Table 2 below:

Table 2

Sample	Temperature °C	Time minutes	Elongation %	Necking %	Ulltimate tensile strength in N/mm^2
TS1 (comparison)	330	1	2,0	—	1945
TS2 (comparison)	400	1	1,9	—	1946
TS3 (comparison)	450	1	2,2	—	1894
TS4 (invention)	520	1	5,3	38,4	1905
TS5 (invention)	550	1	6,7	56,4	1928
TS6 (invention)	550	2	5,8	39,2	2107
TS7 (invention)	550	5	5,2	48,2	2090

[0060] Table 2 clearly shows that the comparison TS1-TS3 samples showed not satisfactory elongation percentage values, even lower than the 3.5% value required by Italian law, as stated in DM 14.01.2008, and by the European standard EN-10138-2000 entitled "Prestressing steels". Surprisingly, however, TS4-TS7 samples of the invention showed excellent elongation percentage values, thus giving TS4-TS7 samples a considerable flexibility, still maintaining a very high ultimate tensile strength, higher than the minimum toughness value of 1860 N/mm^2 required for certain applications.

[0061] In particular, Table 2 shows that, among the TS4-TS7 samples of the invention, TS5 sample, subjected to thermal treatment at 550°C for a maximum time of only one minute, was the one who showed the best results from the elasticity point of view, due to both elongation and necking percentages significantly greater than the values of the other samples, still maintaining good ultimate tensile strength values.

[0062] Sample TS5 was also subjected to relaxation tests (loss of load due to relaxation) in accordance to UNI 15630 standard, producing acceptable results in the range between 0.29% and 0.96% after 120 hours.

[0063] All the above features related to the strand also occurred on tests run on a single wire, tested in laboratory and pilot plants for stranding and stabilization, wherein said single strand was subjected under the same parameters related to stress, temperature furnace and time maintenance in the oven used to obtain the above strand samples.

[0064] Subsequent tests on wire samples having a final diameter of 5.22 mm, subjected at 550°C, with a dynamic tension or stretching of 40% of its ultimate tensile strength, showed relaxation values of 0.8% after 120 hours, values in any case lower than the maximum value of 2.5% after 1000 hours required by the above cited standards.

[0065] Similarly, a test performed under the same conditions on the same wire sample, but with a dynamic tension or stretching of 60% of its ultimate tensile strength, showed acceptable relaxation values of 0.9% after 120 hours.

[0066] On the other way, a similar wire sample but not thermal treated showed relaxation values of 3.8% after 120 hours, thus a surely high value that exceeds the maximum allowed limit and therefore not acceptable.

Claims

1. Method for preparing a two-phase austeno-ferritic stainless steel wire, rope and/or strand, having relaxation and elongation values according to the standards as indicated in the Italian Ministerial Decree of January 14, 2008 and/or in the European Standard No. EN-10138, said method being **characterized by** the fact it comprises a stabilization step wherein said wire, rope and/or strand is subjected to a thermal or thermo-mechanical treatment at a temperature between 480°C and 700°C.

2. Method according to any one of the preceding claims, wherein said relaxation value is lower than 2.5% after 1,000 hours with a load force of 70% of Fma (Effective Maximum Force) and/or lower than 4.5% after 1,000 hours with a load force of 80% of Fma.

3. Method according to any one of the preceding claims, wherein said elongation value is higher than 3.5% upon application of a maximum loading force to break the wire, rope and/or strand.

4. Method according to any one of the preceding claims, wherein said temperature is between 480°C and 600°C.

5. Method according to any one of the preceding claims, wherein said temperature is between 500°C and 580°C.

6. Method according to any one of the preceding claims, wherein said thermal or thermo-mechanical treatment is for a period of time lower than 6 minutes.

7. Method according to any one of the preceding claims, wherein said two-phase austeno-ferritic stainless steel has a chemical composition comprising 0.001-0.10 wt. % of C, 0.0001-0.030 wt. % of S, 0.005-0.050 wt. % of P, 0.1-1.5 wt. % of Si, 0.30-1.80 wt. % of Mn, 18-35 wt. % of Cr, 2.5-9.0 wt. % of Ni, 0.5-5.0 wt. % of Mo, and 0.05-0.50 wt. % of N, the balance being Fe and impurities.

8. Method according to any one of the preceding claims, wherein said method comprises at least a wire drawing step, preceding said stabilization step, in order to progressively reducing the wire diameter.

9. Method according to any one of the preceding claims, wherein said method comprises a stranding step, preceding said stabilization step, wherein two or more wires are braided together to form a stainless steel rope.

10. Method according to any one of claims 1 to 8, wherein said method comprises a stranding step, before said stabilization step, wherein seven wires are corded together to form a stainless steel strand.

11. Method according to any one of the preceding claims, wherein said wire, rope and/or strand, after being subjected to said thermal or thermo-mechanical treatment, is subjected to a cooling step.

12. Method according to any one of the preceding claims, wherein said method comprises, in order, said at least a wire drawing step, said stranding step, said stabilization step and said cooling step.

13. Method according to any one of the preceding claims, wherein, during said stabilization step and said cooling step, said wire, rope and/or strand is subjected to a tensioning step.

14. Method according to claim 13, wherein during said tensioning step, the dynamic strength of said wire, rope and/or strand is between 35% and 70% of its tensile strength.

15. Wire or set of wires corded together to form a two-phase austeno-ferritic stainless steel rope or strand having relaxation and elongation values according to the standards as indicated in the Italian Ministerial Decree of January 14, 2008 and/or in the European Standard No. EN-10138, obtained according to the preparation method as described in any one of the preceding claims.

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EUROPEAN SEARCH REPORT

Application Number
EP 10 01 6127

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	GB 2 354 264 A (ADVANCED METALS INTERNAT LTD [GB]) 21 March 2001 (2001-03-21) * page 5, line 29 * -----	1-15	INV. C22C38/44 C21D8/06 C21D9/52
X	US 5 716 466 A (YAMAOKA YUKIO [JP] ET AL) 10 February 1998 (1998-02-10) * page 5, line 45 - line 50; figure 6 * -----	1-15	
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X	EP 0 659 896 A1 (SHINKO WIRE CO LTD [JP]) 28 June 1995 (1995-06-28) * page 3, line 47 - line 56; figures 4,6; table 4 * -----	1-15	
X	EP 0 576 802 A1 (SHINKO WIRE COMPANY LTD ALSO K [JP]) 5 January 1994 (1994-01-05) * claims 1-6; figure 3 * -----	1-15	

TECHNICAL FIELDS SEARCHED (IPC)

C22C
C21D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	12 May 2011	Badcock, Gordon

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
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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

1

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 10 01 6127

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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