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(71) Applicant:
Sumitomo Metal Industries Limited
Osaka-shi, Osaka 541-0041 (JP)

(72) Inventors:
- Kuroda, Atuhiko
Joetu-shi, Niigata 942-0061 (JP)
- Masaki, Yasuhiro
Sakai-shi, Osaka 590-0984 (JP)

(74) Representative:
Woods, Geoffrey Corlett
J.A. KEMP & CO.
Gray's Inn
14 South Square
London WC1R 5LX (GB)

(54) Titanium alloy and method for producing the same

(57) A titanium alloy comprising in weight percent, Cu: not less than 0.01% but less than 2%, Fe: 0.3% or less, O (oxygen): 0.3% or less and the balance being Ti and incidental impurities and a method for producing said alloy.

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a titanium alloy that has excellent antibiotic properties and resistance to fouling organisms (hereinafter called "fouling resistance"), and to a method for producing the titanium alloy. The titanium alloy according to the invention is advantageously used as an interior decoration material which is desired to have antibiotic properties, and as a material for kitchen utensils, wristwatch casings, eyeglass frames, medical tools such as surgical knives, and food production apparatus. The titanium alloy is also advantageously used as a material for marine construction, nets for fish breeding, pipes for heat exchangers utilizing seawater cooling, and desalination apparatus, all of which are required to have the fouling resistance.

2. Description of the Related Art

[0002] Titanium has excellent corrosion resistance and light weight. Therefore, the metal has been used as a material for various members. Titanium has excellent corrosion resistance, particularly in seawater, and therefore has often been used as a material for pipes of a condenser utilizing seawater cooling and desalination apparatus.
[0003] Also, titanium does not cause allergic reaction when brought into contact with human skin, and is therefore preferably used as a material for eyeglass frames and wristwatch casings.
[0004] Moreover, titanium has good biocompatibility, and therefore has been used as a material for prosthetic artificial bones and the like.
[0005] As described above, titanium has been used in a wide range of applications. However, since titanium has good biocompatibility, this metal has caused some problems. For example, when titanium is used as a material for the pipes of heat exchangers utilizing seawater cooling, organisms such as crustaceans enter the pipes and adhere to the inner surfaces thereof. This hinders the flow of cooling water, and impairs heat exchange efficiency. To prevent these problems, the inner surfaces of pipes are periodically brushed.
[0006] Also, titanium has been expected to be applied to nets for fish breeding; however, thus far practical application has been restricted by the hindrance of seawater flow by fouling organisms. Surface treatment with zinc or the like has been investigated; however, this treatment has not yet been brought in practical use, because of high product cost and environmental contamination by zinc.
[0007] One idea for solving the above problems is improving titanium's fouling resistance.
[0008] Japanese Patent Application Laid-Open (*kokai*) No. 8-9836 discloses a float having resistance to fouling by marine organisms and made of titanium alloy. The float is used for floating a fishing net on or in seawater. However, the invention of this publication provides no improvement in the fouling resistance of titanium alloy itself. In the float, resin which has been conventionally used as a material for a float is merely replaced by titanium alloy, resulting in some improvement in fouling resistance.
[0009] Titanium has a disadvantage in that microorganisms can grow on its surface because of its good biocompatibiity. However, no attempt has been made to impart antibiotic properties to titanium.
[0010] In recent years, antibiotic stainless steel has been developed as a material for kitchen utensils and medical tools, since the antibiotic properties of everyday necessities has become a major concern.
[0011] Japanese Patent Application Laid-Open (*kokai*) No. 8-60302 discloses antibiotic austenite stainless steel which comprises, as a base layer, a stainless steel containing Cu in an amount of 0.01-3.5 wt.%, and having a Cu content of 0.1 atom% or more at a depth of 50 angstroms from the surface. Also, this publication discloses that an increase in Cu content to 0.1 atom% or more in the surface layer is achieved by electrolysis by the application of alternating current.
[0012] Japanese Patent Application Laid-Open (*kokai*) No. 9-195016 discloses antibiotic martensitic stainless steel containing Cu in an amount of 0.4-5 wt.%, and in which a second phase comprising Cu as a primary component is suspended in a matrix in an amount of 0.2 vol% or more. The publication also discloses a method of dispersing the Cu-based second phase in the matrix by annealing the material at 500-900 °C for at least one hour.
[0013] However, those types of stainless steel has insufficient corrosion resistance in seawater, and thus is not usable as a material for a desalination apparatus or a heat exchanger utilizing seawater cooling.

SUMMARY OF THE INVENTION

[0014] An objective of this invention is to provide a titanium alloy which has excellent antibiotic properties and fouling resistance and which is usable in a marine environment.

[0015] Another objective of the invention is to provide a method for producing the titanium alloy.

[0016] The gist of the present invention lies in a titanium alloy and a method for producing the same as described below.

(1) A titanium alloy comprising, in weight percent, Cu: not less than 0.01% but less than 2%, Fe: 0.3% or less, O (oxygen):0.3% or less and the balance being Ti and incidental impurities.
(2) A method for producing a titanium alloy, comprising the steps of:

working a titanium alloy comprising, in weight percent, Cu: not less than 0.01% but less than 2%, Fe: 0.3% or less, O (oxygen):0.3% or less and the balance being Ti and incidental impurities, under the condition of 20 percent or more reduction at a temperature not higher than a β transus temperature;and
keeping the worked alloy at a temperature in the range of 600 °C or more, but lower than the β transus temperature, for at least one minute.

[0017] In the present invention, the grain boundary area refers to the grain boundary and its vicinity.

[0018] In an effort to impart antibiotic properties and fouling resistance to the titanium alloy, the inventors conducted various experiments and studies and found the following:

a) Since the solid solubility limit of Cu in α grains of titanium is low, increasing Cu content in α grains is impossible. Therefore, it has been presumed that antibiotic properties or fouling resistance cannot be improved even if Cu is added to titanium. However, when Cu is incorporated into titanium in an amount of from 0.01% to less than 2%, and the titanium is subjected to hot working and then subjected to heat treatment in the temperature range of 600 °C to the β transus temperature; a Cu-rich second phase which is β phase forms in the grain boundary area around grains in the α phase (hereinafter called "α grains"). Consequently, the thus-formed Cu-rich area exerts antibiotic properties and fouling resistance.
b) Copper is repelled out from the inside of the α grain and a Cu-rich phase is formed in the grain boundary areas. The reason why Cu is repelled out from inside of the grain is that Cu is a β former element in the titanium.
c) The micro structure of the titanum alloy is preferably an equiaxed structure whose grains have an average diameter of preferably 100 µm or less. When the average diameter is in excess of 100 µm, the distance between Cu-rich areas becomes so great that bacteria can adhere to the alloy without contacting Cu, with the result that the bacteria survive.
d) Equiaxed crystal grains, whose average diameter is 100 µm or less, are created by the following step; working a titanium alloy to break its acicular crystals completely under the condition of 20 percent or more reduction, at a temperature lower than the β transus temperature and then keeping the worked titanum alloy at the temperature in the region of 600 °C or more and below the β transus temperature.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The titanium alloy and the method for producing the same according to the present invention will next be described in detail. Hereinafter, % in chemical composition refers to weight %.

Chemical Composition of the Titanium Alloy

<u>Cu: 0.01% or more but less than 2%</u>

[0020] For the alloy to exert antibiotic properties and fouling resistance, Cu content must be 0.01% or more. If Cu content is 0.01% or more , a second phase is formed in which the Cu is concentrated at the boundary areas around the α grains at the final step of the production process. Since the solid solubility limit of Cu in an α grain is low and Cu forms a β phase in titanium, Cu is repelled out from the α grain. Therefore, Cu is presumed to be concentrated at the α grain boundary area and its vicinity so as to form a second phase. However, when Cu content is excessively high, the workability of the alloy is impaired to cause cracking of products made of the alloy. In order to avoid this problem, Cu content must be lower than 2%, preferably 1.5% or less.

[0021] The effect of Cu content in titanium alloy on workability was determined by the following tests.

[0022] Several titanium alloys having various Cu contents from 0 % to 2.5% were melt by button arc melting and cast into ingots of 15 mm thickness. Each ingot was heated to 850 °C and rolled to titanium alloy plates of 5 mm thickness. After being annealed at 800 °C for 30 minutes, the plate was subjected to machining in order to remove the oxide scale layer from the surface and thereby finishing with a thickness of 4 mm. The 4 mm thick plate was thinned to 1 mm through cold rolling, and then retained in a 700 °C argon gas atmosphere for one hour. Test pieces of type 13B according to JIS Z 2201 were made from the plate, and the tensile strength and elongation after fracture of each sample was obtained. The results are shown in Table 1.

[0023] A 13B type test piece according to JIS Z 2201 has the following dimensions: parallel length 60 mm, width 12.5 mm, and gauge length 50 mm.

Table 1

Cu Content (weight %)	Tensile strength (N / mm^2)	Elongation (%)
0	363	43.8
0.11	379	43.5
0.52	403	43.2
0.98	468	35.6
1.56	515	33.3
2.01	532	24.6
2.49	559	20.8

[0024] Table 1 clearly shows that when the Cu content is 2% or more, the elongation decreases significantly to impair workability.

Fe: 0.3% or less

[0025] Fe may be added in addition to Cu. When incorporated into titanium alloy, Fe is effective in accelerating the formation of the second phase and in making the grains finer. As a result, the antibiotic properties and fouling resistance of the titanium alloy are improved. Also, Fe is effective in increasing strength. Usually, the Fe content is about 0.03%; however, in order to obtain sufficient effect, the Fe content is preferably in excess of 0.03%. When Fe content is excessively high, corrosion resistance and workability tend to be impaired. Therefore, Fe content is preferably 0.3% or less.

Oxygen (O): 0.3% or less

[0026] Oxygen may be added in addition to Cu. Generally, the oxygen content is about 0.05%. Oxygen is effective in increasing strength and therefore may be added intentionally. However, when oxygen content becomes excessively high, workability, especially cold workability, is impaired. Therefore, the oxygen content is preferably 0.3% or less.

The impurities include the following:

Ni:

[0027] Ni is inevitably contained in sponge titanium which is a raw material of the titanum alloy. When Ni content is in excess of 0.05%, workability is impaired. Therefore, Ni content is preferably 0.05% or less.

Cr:

[0028] Cr is also inevitably contained in sponge titanium, a raw material. When Cr content is in excess of 0.05%, workability is impaired. Therefore, Cr content is preferably 0.05% or less.

Nitrogen (N):

[0029] Nitrogen is contained in sponge titanium and is also mixed into the alloy during the melting process. When N content is in excess of 0.02%, workability is impaired. Therefore, N content is preferably 0.02% or less.

Hydrogen (H):

[0030] Hydrogen is mixed into the alloy during the melting process or during a heat treatment described later. When

H content is in excess of 0.015%, workability is impaired. Therefore, H content is desirably 0.015% or less.

Carbon (C):

[0031] Carbon is inevitably contained in sponge titanium. When C content is in excess of 0.01%, workability is impaired. Therefore, C content is desirably 0.01% or less.

Microstructure and Average Grain Diameter

[0032] The microstructure of the alloy of the present invention is not particularly limited, but preferably is an equiaxed structure, since an equiaxed structure is more advantageous than an acicular structure in terms of antibiotic effect and workability.

[0033] In the case of an acicular structure, prior β grains are divided into so-called "colonies" during the transformation step. The Cu content at colony boundaries is lower than that at the boundaries of the prior β grains. Also, at a temperature range where the microstructure of titanum is a β phase, the grain growth rate is very high; therefore, in general, large grains are formed. Therefore, in an acicular structure, a Cu -rich area is present only at boundaries of the large prior β grains. Thus, the probability that bacteria could come into contact with Cu is low compared with the equiaxed structure, and this results in a correspondingly weaker abtibiotic properties.

[0034] In the case of an equiaxed structure, a Cu-rich area is located in the α grain boundary area, but not within the α grains themselves. Therefore, the grain diameter of α grains is preferably smaller. When the diameter is in excess of 100 μm, the distance between the grain boundaries become excessively large, resulting in poor antibiotic properties. In this respect, the average grain diameter is preferably 100 μm or less.

[0035] As used herein, the average grain diameter refers to a grain diameter determined by the cutting method specified in JIS H 501.

[0036] According to the above cutting method, grains which are cut by a 100 mm line in a 100 times magnification microphotograph are counted and the average diameter is calculated. In the present invention, five measurements were obtained, and the average value was calculated.

[0037] Usually, an equiaxed structure comprises α grains having an aspect ratio close to 1, but in some cases, the aspect ratio may be greater. In the titanium alloy of the invention, the aspect ratio is preferably about 1 - 4. The antibiotic properties are improved when the aspect ratio is close to 1; therefore, the aspect ratio is desirably within the range of 1-3.

Method for Producing Titanium Alloy

[0038] The ingot of titanium alloy according to the present invention is produced by melting, for example, sponge titanium in an argon gas atmosphere, adding elements thereto for achieving the chemical composition defined by the invention. The ingots are worked by conventional plastic working, such as forging or rolling so as to form sheets, bars, pipes, or the like. Also, the alloy can be cast into product shape; however, when no plastic working is performed, the microstructure retains cast structure, and therefore the antibiotic properties is not as good as that of the material produced through plastic working.

[0039] In order to produce a titanium alloy having improved antibiotic properties and fouling resistance; that is, having α grains of an average grain diameter of 100 μm or less, the chemical composition must fall within the aforementioned ranges. In the final step of production, processing and heat treatment under the following specific conditions are effective in forming α grains of the appropriate size.

[0040] First, the above-mentioned titanium alloy is worked under the condition of 20 percent or more reduction, at a temperature below the β transus temperature, and the worked titanium alloy is then heated to a temperature of 600 °C or higher, but lower than the β transus temperature for at least one minute. Here, "reduction" refers to reduction in cross sectional area of the alloy through forging and rolling, and is obtained from the following equation.

Percent Reduction (%) = {(cross sectional area of the alloy before processing) - (cross sectional area of the alloy after processing) × 100} ÷ (cross section area of the alloy before processing)

[0041] When the percent reduction at the β transus temperature or below is less than 20%, the acicular structure formed in an ingot casting step or in an initial hot working step at a temperature not lower than the β transus temperature is retained without decomposition. If the acicular structure remains, however workability is impaired and cracking may occur. Also, since Cu concentrates along the boundaries of the large prior β grains, and the distance between Cu-rich areas becomes too great, significant antibiotic properties may not be obtained. The lower limit of working temperature is not defined, since cold working is available. The upper limit of the working temperature is not defined either. After the above-mentioned working, the alloy is subjected to a heat treatment in which the alloy is kept at a temperature of 600 °C or more, but below the β transus temperature, for one minute or more. By the combination of this heat treatment and the aforementioned working, equiaxed α grains are formed and Cu concentrates at α grain boundary areas. When the temperature is lower than 600 °C, an equiaxed α phase is not formed. When the temperature is higher than the β transus temperature, only the β phase is formed and grains become coarse, resulting in an acicular structure and impaired workability.

[0042] When the treatment time is shorter than one minute, the equiaxed α grain structure is not formed, and the old structure is retained. The upper limit of the treatment time is not defined, but the conditions for obtaining an average α grain diameter of 100 μm or less may be advantageously selected.

[0043] The reason why an equiaxed structure imparts excellent antibiotic properties and fouling resistance is that Cu concentrates on equiaxed grain boundaries that are formed through heat treatment. Briefly, a Cu-rich area is an area providing antibiotic properties which are in close(tight) formation.on the surface of the material.

EXAMPLE 1

[0044] Titanium alloy was melted in an button arc melting furnace in an argon gas atmosphere, and ingots measuring 100 mm wide, 300 mm long, and 25 mm thick were prepared. The chemical composition of each ingot is shown in Table 2.

Table 2

No	Chemical Composition (Wt.% , balance:Ti)			α Grain Diameter (μm)	** Antibiotic Action	Example Categories
	Cu	Fe	○			
1	0.009 *	0.025	0.049	50	X	Comparative
2	0.011	0.029	0.051	45	△	Invention
3	0.115	0.022	0.051	50	○	
4	0.513	0.027	0.052	45	○	
5	1.080	0.025	0.051	40	○	
6	1.557	0.022	0.050	45	○	
7	1.984	0.028	0.048	40	○	
8	0.015	0.081	0.050	30	○	
9	0.012	0.253	0.051	15	○	
10	0.504	0.023	0.021	40	○	
11	2.110 *	0.025	0.049	40	○	Comparative

*: Falling outside the scope of the present of invention
**: Antibiotic properties
○: Antibiotic properties exhibited (less than 30% of bacteria survived)
△: Antibiotic properties exhibited (30% to less than 70% of bacteria survived)
X: Ineffective (70% or more of bacteria survived)

[0045] The ingots were heated to 1000 °C (not lower than the β transus temperature). Subsequently, through hot rolling, a 12 mm thick plate was prepared with slow cooling according to a conventional method.

[0046] The plate was heated to 800 °C, (lower than the β transus temperature), and subjected to hot rolling such that a 38 percent reduction was attained and a 7.5 mm thick plate was formed. Through mechanical working for removing a scale layer from the surface, a finished 7 mm thick plate was produced.

[0047] The resultant 7 mm hot-rolled thick plate was subjected to conventional cold rolling to form a 3 mm thick sheet. Then annealing was performed for one hour at a temperature not lower than 600 °C and lower than the β transus temperature; i.e., 700 °C, to thereby obtain a titanium alloy plate.

[0048] The antibiotic properties, fouling resistance, and microstructure of the prepared titanium alloy plate were assayed. The antibiotic assay was performed as follows. *Escherichia coli* (W3110 strain) was suspended in 1/500-

diluted bouillon medium, to thereby prepare inoculation liquid containing microbes. The bouillon medium was prepared by dissolving 5 g meat extract, 10.0 g peptone, and 5 g sodium chloride in one liter of purified water.

[0049] Then a test piece (50 mm square titanium alloy plate) which had been disinfected by wiping with ethanol was placed in a sterilized Petri dish, and the test piece was inoculated with the inoculation liquid containing microbes (bacteria density: 2.0×10^5 /0.5 ml). The specimen was covered with a 50 mm square sterilized film and maintained at 35 ± 1 °C and 95% relative humidity.

[0050] After a lapse of 24 hours, the bacteria on the film and the surface of the test piece were rinsed off with 9.5 ml of physiological saline solution, the saline solution was put on the standard agar medium, and the medium was incubated at 35 ± 1 °C for 48 hours. The grown colonies were counted and survival rate was calculated for antibiotic assay, to thereby obtain indices for antibiotic properties. Fouling resistance was recognized to be directly proportional to antibiotic effect, as it expresses the ease with which a microbe adheres to the test piece. Therefore, fouling resistance was determined and evaluated on the premise that the better the antibiotic properties, the better the fouling resistance.

[0051] A specimen was cut out of the cross section along the elongation direction for examination of microstructure. After being polished and subjected to corrosion, the specimen was observed through a optical microscope (magnitude: 100 times), grain diameter was determined, and an average value was estimated.

[0052] The results of assay of antibiotic properties and microstructure are shown in Table 2.

[0053] Antibiotic properties is expressed in terms of the following ratings:

◯: (30% or less of bacteria survived), △: (30% to less than 70% of bacteria survived), X: (70% or more of bacteria survived).

[0054] Table 2 clearly shows that the titanium alloy according to the present invention is superior in antibiotic properties, but Specimen No. 1, whose Cu content is below the lower limit of the present invention, has insufficient antibiotic properties. Also, Specimen Nos. 8 and 9, which contain Fe, are somewhat better in antibiotic properties than Specimens which do not contain Fe.

EXAMPLE 2

[0055] By the same method as described in Example 1, ingots measuring 100 mm wide, 300 mm long, and 25 mm thick were prepared. The chemical composition of these ingots was as follows, Cu: 0.5 wt.%, Fe: 0.1 wt.%, Oxygen (O): 0.05 wt.%. The test pieces for antibiotic assay and microstructure examination were prepared from these ingots through treatments performed under various sets of conditions; i.e., percent reduction, working temperature, annealing temperature, and annealing time. The β transus temperature of the specimen alloy is approximately 840 °C.

[0056] According to the present invention, each ingot was heated to 1000 °C, as in Example 1, then subjected to hot working and mechanical working to produce a 7.5 mm thick hot plate. Each plate was then worked under the conditions, temperature, and percent reduction listed in Table 3. Thus, plates of various thicknesses were prepared and then annealed.

Table 3

No	Hot rolling			Annealing		Micro structure			Antibiotic Action **
	Heating temp. (°C)	Reduction (%)	Thickness (mm)	Temperature (°C)	Time (min)	Structure	Grain Dia. μm	Aspect Ratio	
1	850	70.0	1.5	700	60	acicular	-	≧ 10	△
2	800	70.0	1.5	700	60	equiaxed	30	1.5	○
3	800	10.0	4.5	700	60	acicular	-	≧ 10	△
4	800	20.0	4.0	700	60	equiaxed	50	3.5	○
5	800	50.0	2.5	700	60	"	40	1.5	○
6	800	70.0	1.5	850	60	acicular	-	≧ 10	△
7	800	50.0	2.5	800	60	equiaxed	80	1.1	○
8	800	50.0	2.5	800	180	"	120	1.1	△
9	800	50.0	2.5	700	0.5	unrecrystalized	-	≧ 10	△
10	800	50.0	2.5	700	1.0	equiaxed	20	1.6	○
11	800	50.0	2.5	700	5.0	"	30	1.4	○

* * ○: Antibiotic properties exhibited (less than 30% of bacteria survived)
△: Insufficient antibiotic properties exhibited (30% to less than 70% of bacteria survived)

[0057] The plates were annealed, and test pieces were punched therefrom. The test pieces were evaluated for their antibiotic properties and fouling resistance. The test methods were identical with those employed in Example 1. Evaluation of antibiotic properties was expressed in terms of the following ratings: ○: sufficiently antibiotic (less than 30% of bacteria survived), △: insufficiently antibiotic (30% to less than 70% of bacteria survived).

[0058] Table 3 shows the results of the assay and the examination of antibiotic properties and microstructure.

[0059] The specimens prepared according to the invention clearly exhibit good antibiotic properties and workability. Specifically, specimens Nos. 1, 3, and 6, in which an acicular structure is retained, are somewhat inferior in antibiotic properties. The reason for this is conceivably that the acicular structure comprises large grains, the distance between Cu-rich areas present near grain boundaries becomes great, and probability of contact between bacteria and the Cu-rich areas decreases, whereby the antibiotic properties is suppressed. For the same reason, specimen No. 8, which has an equiaxed structure but an excessively large grain diameter, exhibits insufficient antibiotic properties.

[0060] The titanium alloy according to the present invention exhibits excellent antibiotic properties and fouling resistance, and may be used for a variety of applications which require these properties. Also by production process according to the present invention, the titanium alloy exhibiting excellent antibiotic properties and fouling resistance can be produced with ease.

Claims

1. A titanium alloy comprising in weight percent, Cu: not less than 0.01% but less than 2%, Fe: 0.3% or less, O (oxygen): 0.3% or less, the balance being Ti and incidental impurities.

2. An alloy according to claim 1, which has a microstructure comprising grains of an α phase and a Cu-rich second phase in the boundary area of the α grains.

3. An alloy according to claim 2, wherein the α grains are equiaxed crystals having an average grain diameter of 100 μm or less.

4. An alloy according to claim 2 or 3, further comprising a Ti_2Cu phase.

5. An alloy according to any one of claims 2 to 4, wherein the α grains have an aspect ratio of 1 to 4.

6. A method for producing a titanium alloy as claimed in claim 1, comprising the steps of:

working a titanium alloy comprising, in weight percent, Cu: not less than 0.01% but less than 2%, Fe: 0.3% or less, O (oxygen): 0.3% or less, the balance being Ti and incidental impurities under conditions of 20 percent or more reduction, at a temperature not higher than a β transus temperature; and
maintaining the worked alloy at a temperature of 600°C or more, but lower than the β transus temperature for at least one minute.

7. Use of a titanium alloy as claimed in any one of claims 1 to 5 in an application requiring antibiotic properties and fouling resistance.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 6954

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X A	US 4 744 878 A (RIGGS JR OLEN L) 17 May 1988 (1988-05-17) * claims 1-10 * * column 1, line 5 - column 4, line 46 * * examples 1-10 *	1 2-7	C22C14/00 C22F1/18
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X A	GB 944 130 A (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 11 December 1963 (1963-12-11) * claims 1-6 * * page 1, line 1 - page 2, line 109 * * tables I-IV *	1 2-7	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 February 2000	Vlassi, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 30 6954

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