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(57) Abstract

The powder has an average particle size of less than 8 μm and a loss of mass by reduction in hydrogen of less than 3 % and it contains 10 - 80 % Fe, up to 40 % Co, up to 60 % Ni and up to 15 % M, M being present, at least partially, in the oxidized state and representing one or more of the elements Mn, Cr, V, Al, Mo and Ti, the balance being unavoidable impurities. This powder may be sintered at 650 - 1000 °C to give a matrix having a high hardness.

PRE-ALLOYED POWDER AND ITS USE IN THE MANUFACTURE OF DIAMOND TOOLS

The present invention relates to the use of a pre-alloyed powder containing iron as binder in the manufacture of diamond tools by hot sintering.

In the manufacture of diamond tools by hot sintering, with or without pressure, of an intimate mixture of diamond and of binder, use is made, for the binder, that is to say the material forming the matrix of the tool at the end of the sintering operation, either of fine cobalt powders (1-6 μm) or of mixtures of fine powders, such as a mixture of fine cobalt, nickel and iron powders, or coarse pre-alloyed powders (less than 44 μm), such as a steel powder obtained by atomization.

The use of a fine cobalt powder has very good results from a technical standpoint; its only drawback stems from the high price of the powder.

Using mixtures of fine powders, matrices are obtained whose hardness and, consequently, the wear resistance, are relatively low.

The use of coarse pre-alloyed powders requires a sintering temperature of about 1100-1300°C, at which temperature degradation of the diamond, called graphitization, becomes appreciable.

The object of the present invention is to provide a pre-alloyed powder containing iron, whose use as binder in the manufacture of diamond tools by hot sintering avoids the aforementioned drawbacks.

For this purpose, the powder used according to the invention has an average particle size of less than 8 μm as measured with the Fisher Sub Sieve Sizer and a loss of mass by reduction in hydrogen of less than 3% as measured according to the standard ISO 4491-2:1989; this powder contains, in % by weight, 10 - 80% of iron, up to 40% of cobalt, up to 60% of nickel and up to 15% of M, M being present, at least partially, in the oxidized state and representing one or more of the elements Mn, Cr, V, Al, Mo and Ti, the other components in the powder consisting of unavoidable impurities.

In fact, it has been found that such a powder, which therefore contains at most only 40% of cobalt, may be sintered at moderate temperatures (650 - 1000°C) to give a matrix having a high hardness and that, furthermore, this hardness may be easily adapted to the particular requirements of the users of diamond tools, by varying the composition of the powder.

It is necessary for the particle size to be less than 8 µm in order that the powder be sinterable at moderate temperatures; advantageously, it is less than 5 µm.

The loss of mass by reduction in hydrogen must be less than 3%; otherwise, there is a risk of producing, when the powder mixed with diamonds is sintered in a reducing atmosphere, such a great evolution of gas that porosity appears in the sintered product and/or that the graphitization of the diamond becomes too great; the said loss of mass is preferably less than 2%.

The abovementioned Fe, Co, Ni and M contents are necessary in order that the matrix have a suitable hardness and in order that this hardness be able to be adapted to the requirements of the users of diamond tools. Preference is given to an Fe content of at least 30%, a Co content ranging up to 30%, an Ni content of 10 - 30% and an M content ranging up to 10%, these contents leading to very high hardnesses. The most preferred Fe content is at least 50% and that of M equal to or less than 5%.

The present invention also relates to the above-defined pre-alloyed powder containing iron, this powder therefore being characterized in that it has an average particle size of less than 8 µm as measured with the Fisher Sub Sieve Sizer and a loss of mass by reduction in hydrogen of less than 3% as measured according to the standard ISO 4491-2:1989 and in that it contains, in % by weight, 10 - 80% of iron, up to 40% of cobalt, up to 60% of nickel and up to 15% of M, M being present, at least partially, in the oxidized state and representing one or more of the elements Mn, Cr, V, Al, Mo and Ti, the other components in the powder consisting of unavoidable impurities.

The powder of the invention may be prepared by heating, in a reducing atmosphere, a hydroxide, oxide, carbonate, basic carbonate (mixture of hydroxide and carbonate) or mixed organic salt of the constituents of the alloy so as to obtain a pulverulent product, whose loss of mass by reduction in hydrogen is less than 3%, and by comminuting this product (the expression "constituents of the alloy" is used here to denote all the elements present in the composition of the alloy, apart from oxygen: thus, for example, Fe, Ni, Co and Mn must be regarded as constituents of the Fe-Ni-Co-Mn-O alloy).

The hydroxide, carbonate, basic carbonate and the organic salt may be prepared by adding an aqueous solution of the constituents of the alloy to an aqueous solution of, respectively, a base, a carbonate, a base and a carbonate, and a carboxylic acid, separating the precipitate thus obtained from the aqueous phase and by drying the precipitate.

The solution of the constituents of the alloy may be a chloride solution, a sulphate solution, a nitrate solution or a mixed solution of these salts.

It may be useful to add a small quantity of carbon, for example 0.05 - 3%, in the form of an organic compound, to the pre-alloyed powder in order to reduce the risk of graphitization, this risk albeit low at the moderate temperatures used for the sintering.

<u>Example 1</u>

This example relates to the preparation of a powder according to the invention by the precipitation of a mixed oxalate and the subsequent decomposition of this oxalate.

2.47 litres of a chloride solution containing 39 g/1 of Co, 25 g/1 of Ni, 85 g/1 of Fe and 11 g/1 of Mn are added at room temperature and with stirring, to 13.64 litres of an aqueous solution of oxalic acid containing 65 g/1 of $C_2H_2O_4 \cdot 2H_2O$. Thus, 94% of the Co, 85% of the Ni, 81% of the Fe and 48% of the Mn are precipitated in the form of a mixed oxalate. This precipitate is separated by filtration, washed in water and dried at 100°C. The dry precipitate contains 9.2% Co, 5.3% Ni, 17.2% Fe and 1.3% Mn.

The precipitate is heated at 520°C in a stream of hydrogen for 6 hours. A pulverulent metallic product is thus obtained. Grinding this product in a mortar gives a pre-alloyed powder having a loss of mass by reduction in hydrogen of 2% and containing 27.1% Co, 15.7% Ni, 50.8% Fe and 3.9% Mn, and the particles of which have an average diameter of 2.1 µm, measured with the Fisher Sub Sieve Sizer. Examination of the powder using X-ray diffraction shows that virtually all of the Mn is present in the oxidized state.

Example 2

This example relates to the preparation of a powder according to the invention by the precipitation of a mixed hydroxide and the subsequent reduction of this hydroxide.

9.4 litres of a chloride solution containing 24.4 g/1 Co, 13.5 g/1 Ni, 58.6 g/1 Fe and 2.3 g/1 Mn are added, at 80°C and with stirring, to 36.7 litres of an aqueous solution of caustic soda containing 45 g/1 of NaOH. Virtually all of these elements are thus precipitated in the form of a mixed hydroxide. This precipitate is separated by filtration, washed in water, repulped at 80°C in a 45 g/1 NaOH solution, separated once again by filtration, washed in water and dried at 100°C. The dry precipitate contains 14.8% Co, 8.2% Ni, 35.6% Fe and 1.4% Mn.

The precipitate is heated at 510°C in a stream of hydrogen for 7.5 hours. The pulverulent metallic product thus obtained gives, after grinding in a mortar, a pre-alloyed powder having a loss of mass by reduction in hydrogen of 1.65% and containing 24.2% Co, 13.4% Ni, 58% Fe and 2.3% Mn, and the particles of which have an average diameter of 2.1 µm. Examination of the powder using X-ray diffraction shows that virtually all the Mn is present in the oxidized state.

Example 3

This example relates to a series of tests comparing the sinterability of two powders according to the invention, called hereinbelow powder A and powder B, of a fine Co powder (powder C) and of a Co powder obtained by atomization (powder D).

Powder A is that obtained according to Example 1 and powder B is that obtained according to Example 2. Powder C is a commercially available Co powder (1.5 µm) obtained via the oxalate route.
Powder D consists of particles having an average diameter of 9.7 µm.

A cylindrical pill, having a diameter of 4 mm and a length of 4 mm, of each of the powders to be tested is produced by cold pressing. These cylinders are heated at a rate of 5°C per minute and the change in length as a function of temperature is measured. The variation of the change (in %) in the length of the cylinders as a function of temperature is given in the figure appended hereto.
The densities (in g/cm^3) of the cylinders before and after heating and the ratio between these densities are given in the table below:

Powder	Density before heating (1)	Density after heating (2)	(1):(2)
A	4.369	7.893	0.55
B	4.091	7.208	0.57
C	5.459	8.591	0.64
D	6.974	7.972	0.87

These results show that the sinterability of the powders according to the invention (A and B) is superior to that of the fine Co powder (C) and far superior to that of the coarse powder D.

<u>Example 4</u>

In this example, the mechanical properties of sintered pieces made from cobalt powder, nickel powder, iron powder, various mixtures of Co, Fe, Ni and Mn powders and various powders according to the invention are compared.

The following powders are used:

- extra-fine cobalt powder from Union Minière, having an average diameter (Fisher) of 1.50 µm and having a loss of mass by reduction in hydrogen (LMRH) of 0.55%;
- ex-carbonyl nickel powder having a Fisher of 2.06 µm and having an LMRH of 0.35%;
- ex-carbonyl iron powder having a Fisher of 4.00 µm and having an LMRH of 0.23%;
- electrolytic manganese powder having a Fisher of 2.80 µm and having an LMRH of 0.23%;
- mixtures of powders, made from the above powders and the Co, Ni, Fe and Mn contents of which are given in Table I below;
- powders according to the invention, the composition of which is given in Table II below, when these are powders prepared via the

oxalate route, and in Table III below, when these are powders prepared via the hydroxide route; these powders have a Fisher of 1.8 - 2.2 µm; their LMRH is less than 2.5%.

The powders were sintered by pressing for 3 minutes at 650, 700, 750, 800, 850 or 900°C under a pressure of 35 MPa in a graphite mould.

The density and the Vickers hardness of all the sintered pieces were measured. A large number of pieces were also subjected to the transverse bending test according to DIN/ISO 3325: the 45 x 10 x 6 mm sintered bar is placed so as to bear freely on two supports separated by 25 mm and the load is applied in the middle of this separation by means of a punch until the piece fails. The results are given in Tables I, II and III below, the first table referring to the elemental powders (Co, Ni, Fe) and to the mixtures of powders, the second table to the ex-oxalate powders of the invention and the third table to the ex-hydroxide powders of the invention.

Table I

Properties of sintered pieces made from elemental powders and mixtures of powders

Test N°	Composition (%) *				Sintering temperature	Properties of the sintered pieces			
	Co	Ni	Fe	Mn	°C	Density g/cm³	Vickers Hardness (HV 10)	Bending test: Failure load N/mm²	Bending test: Deflection mm
1	100	0	0	0	750	8.503	237	1335	0.98
2	0	100	0	0	750	8.098	103	805	3.12
3	0	0	100	0	750	7.201	108	740	2.05
4	50	0	50	0	750	7.338	163	795	0.73
5	45	40	15	0	750	7.580	110	710	1.30
6	40	20	40	0	750	7.438	147	870	1.05
7	40	20	40	0	750	7.589	170	960	1.17
8	40	20	40	0	750	7.558	169	065	1.22
9	40	10	50	0	750	7.305	169	700	0.58
10	40	10	50	0	750	7.629	173	1080	1.16
11	40	10	50	0	850	7.724	231	770	0.56
12	35	30	35	0	750	7.349	117	775	1.04
13	30	10	60	0	750	7.337	158	1130	1.58
14	30	10	60	0	750	7.483	166	1245	1.79
15	30	10	60	0	850	7.557	183	1510	2.25
16	30	0	70	0	750	7.297	130	910	1.40
17	25	40	35	0	750	7.307	104	765	1.25
18	25	20	55	0	750	7.340	155	1125	0.90
19	25	20	55	0	750	7.434	165	1045	1.26
20	25	20	55	0	850	7.375	166	1275	1.53
21	25	10	65	0	750	7.462	155	1120	1.60
22	20	25	55	0	750	7.290	147	1035	1.35
23	20	25	55	0	750	7.297	153	1080	1.36
24	20	25	55	0	850	7.251	155	955	1.03
25	20	10	70	0	750	7.363	148	1050	1.54
26	20	0	80	0	750	7.147	114	885	1.60
27	15	30	35	0	750	7.355	140	1080	1.43
28	15	15	70	0	750	7.352	141	1010	1.33
29	10	50	40	0	750	7.053	92	750	1.32
30	10	0	90	0	750	7.250	112	865	2.12
31	0	50	45	5	750	7.110	129	850	1.11
32	0	50	45	5	750	7.190	133	870	1.00
33	0	50	45	5	850	7.501	151	1115	2.15
34	0	50	50	0	750	7.170	99	740	1.40
35	0	40	60	0	750	7.094	101	760	1.30
36	0	35	60	5	750	7.112	143	865	1.03
37	0	35	60	5	750	7.181	161	1245	1.00
38	0	35	60	5	850	7.513	160	1190	1.80
39	0	20	80	0	750	7.313	116	930	1.80
40	0	10	90	0	750	7.166	105	805	2.08

* the total of the elements Co, Ni, Fe and Mn being regarded as 100%.

Table II

Properties of sintered pieces obtained from powders of the invention : oxalate root

Test N°	Composition (%)*				Sintering temperature	Properties of the sintered pieces			
	Co	Ni	Fe	Mn	°C	Density g/cm³	Vickers Hardness (HV 10)	Bending test Failure load N/mm²	Deflection mm
41	37.7	0	57.3	5	750	7.589	415		
42	37.7	0	57.3	5	800	7.567	405	1212	0.48
43	37.7	0	57.3	5	850	7.676	390		
44	33.4	0	59	7.6	750	7.676	435		
45	33.4	0	59	7.6	800	7.541	400	1041	0.43
46	33.4	0	59	7.6	850	7.634	385		
47	33.3	9.5	57.2	0	750	8.076	425		
48	33.3	9.5	57.2	0	800	8.006	395	1893	0.70
49	33.3	9.5	57.2	0	850	8.034	400		
50	33.1	29.5	32.4	5	750	8.090	330		
51	33.1	29.5	32.4	5	850	8.115	295		
52	29.3	0	60	10.7	750	7.318	485		
53	29.3	0	60	10.7	800	7.316	440	896	0.40
54	29.3	0	60	10.7	850	7.435	395		
55	28.4	13.6	50.4	7.6	750	7.719	478		
56	28.4	13.6	50.4	7.6	850	7.768	439		
57	28.4	10.9	60.7	0	750	7.844	430	1320	0.69
58	28.4	10.9	60.7	0	750	7.778	445		
59	28.4	10.9	60.7	0	850	7.946	392	1615	0.83
60	28.4	10.9	60.7	0	850	7.919	421		
61	27.8	16.1	52.1	4	750	7.839	470		
62	27.8	16.1	52.1	4	800	7.779	495	1928	0.85
63	27.8	16.1	52.1	4	850	7.831	345		
64	27.1	12.6	54.3	6	750	7.632	550		
65	27.1	12.6	54.3	6	800	7.568	470	1117	0.50
66	27.1	12.6	54.3	6	850	7.638	440		
67	22.5	13.7	57.1	6.7	750	7.636	430		
68	22.5	13.7	57.1	6.7	850	7.662	473		
69	18	24.2	52.4	5.4	750	7.883	238		
70	18	24.2	52.4	5.4	850	7.805	271		
71	0	56.5	41	2.5	750	8.367	307		
72	0	56.5	41	2.5	850	8.655	299		
73	0	53.3	41.1	5.6	750	8.470	347		
74	0	53.3	41.1	5.6	850	8.235	309		
75	0	34.1	60.4	5.5	750	7.824	238		
76	0	34.1	60.4	5.5	850	7.879	235		
77	0	33.3	60.1	6.6	750	7.806	270		
78	0	33.3	60.1	6.6	800	7.624	260	990	0.55
79	0	33.3	60.1	6.6	850	7.758	240		

* the total of the elements Co, Ni, Fe and Mn being regarded as 100%.

Table III

Properties of sintered pieces obtained from powders of the invention : hydroxide route

Test N°	Composition (%)*				Sintering temperature	Properties of the sintered pieces	
	Co	Ni	Fe	Mn	°C	Density g/cm³	Vickers Hardness (HV 10)
80	24.7	13.7	59.3	2.3	650	7.848	401
					700	7.853	439
					750	7.704	401
					800	7.719	381
					850	7.736	368
					900	7.708	367
81	25.8	13.4	58.5	2.3	750	7.763	412
82	35.3	10.4	54.2	0.1	650	7.952	462
					700	7.969	421
					750	7.393	420
					800	7.904	420
					850	7.964	400
					900	7.904	386
83	32.9	11.5	55.0	0.6	650	8.034	473
					700	7.871	425
					750	8.170	420
					800	7.931	425
					850	8.013	417
					900	7.906	414

* the total of the elements Co, Ni, Fe and Mn being regarded as 100%.

These results show that, after sintering, superior mechanical properties are obtained with the pre-alloyed powders according to the invention than with mixtures of elemental powders. For comparable compositions (see, for example, test No. 14 versus test No. 57), the hardness obtained with the powders of the invention is from 2 to 3 times higher than that obtained with mixtures of powders. With regard to the failure load, higher values were measured with the pre-alloyed powders than with the mixed powders within the 25 - 35% Co, 5 - 20% Ni and 45 - 55% Fe range; outside this range, the failure loads are comparable.

Example 5

This example relates to the use of a powder according to the invention in the manufacture of diamond tools.

Powder obtained in Example 1 is mixed with 1% of synthetic diamonds. The mixture is sintered by pressing under vacuum at 800°C and 35 MPa.

Microscope examination of the sintered material shows that the manganese oxide is finely dispersed in the metallic matrix, that the diamonds remain intact and that they are firmly embedded in the metallic matrix.

CLAIMS

1. Use of a pre-alloyed powder containing iron as binder in the manufacture of diamond tools by hot sintering, characterized in that the powder has an average particle size of less than 8 µm as measured with the Fisher Sub Sieve Sizer and a loss of mass by reduction in hydrogen of less than 3% as measured according to the standard ISO 4491-2:1989 and in that it contains, in % by weight, 10 - 80% of iron, up to 40% of cobalt, up to 60% of nickel and up to 15% of M, M being present, at least partially, in the oxidized state and representing one or more of the elements Mn, Cr, V, Al, Mo and Ti, the other components in the powder consisting of unavoidable impurities.

2. Use according to Claim 1, characterized in that the powder has an average particle size of less than 5 µm.

3. Use according to Claim 1 or 2, characterized in that the powder contains at least 30% of Fe and preferably at least 50%.

4. Use according to Claim 1, 2 or 3, characterized in that the powder contains up to 30% of Co.

5. Use according to Claim 1, 2, 3 or 4, characterized in that the powder contains 10 - 30% of Ni.

6. Use according to any one of Claims 1 - 5, characterized in that the powder contains up to 10% of M, preferably up to 5%.

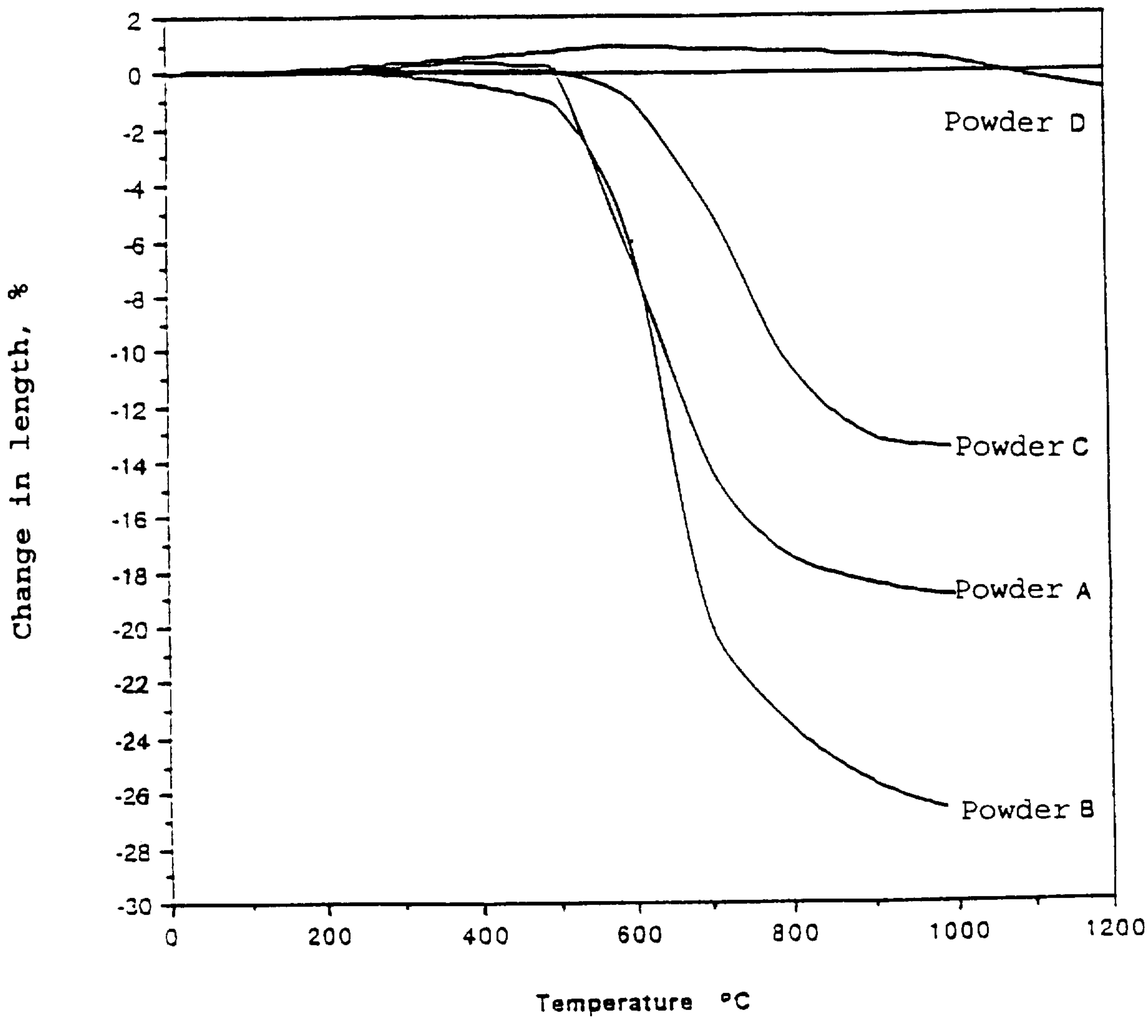
7. Use according to any one of Claims 1 - 6, characterized in that the said loss of mass is less than 2%.

8. Use according to any one of Claims 1 - 7, characterized in that the powder was prepared by heating, in a reducing atmosphere, a mixed hydroxide or a mixed oxalate of its constituents.

9. Use according to Claim 8, characterized in that 0.05 - 3% of carbon in the form of an organic compound is added to the powder.

10. Use according to any one of Claims 1 - 9, characterized in that the sintering is carried out at 650 - 1000°C.

11. Pre-alloyed powder containing iron, the use of which forms the subject of Claims 1 - 9.



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1200
Change in length, %
Temperature °C
Powder D
Powder C
Powder A
Powder B

Fig. 1

INTERNATIONAL SEARCH REPORT

Inte   onal Application No
PCT/EP 96/05125

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22C26/00 B24D3/06

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)
IPC 6 C22C B24D

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 231 762 A (HARA AKIO ET AL) 4 November 1980 see claim 1; example 4 ---	1-11
A	CHEMICAL ABSTRACTS, vol. 108, no. 22, 30 May 1988 Columbus, Ohio, US; abstract no. 191222, TSUCHIYA, SHINJIRO ET AL: "Copper-iron alloy binder in diamond tools for cutting and polishing of fine ceramics" XP002011548 see abstract & JP 62 287 035 A (FUJI DIE CO., LTD., JAPAN) -----	1-11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
6 March 1997	14.03.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Schruers, H

INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/EP 96/05125

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4231762 A	04-11-80	JP 1397299 C	24-08-87
		JP 54114513 A	06-09-79
		JP 61058432 B	11-12-86
		JP 1394395 C	11-08-87
		JP 53136790 A	29-11-78
		JP 61056067 B	01-12-86
		AU 518306 B	24-09-81
		AU 3566778 A	08-11-79
		CA 1103042 A	16-06-81
		DE 2905452 A	06-09-79
		FR 2389437 A	01-12-78
		GB 1598775 A	23-09-81
		US 4171973 A	23-10-79
		DE 2819532 A	07-06-79