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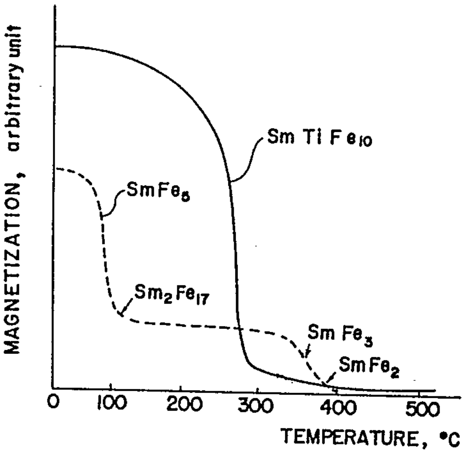
(54) A rare earth-based alloy for permanent magnet.

(57) In contrast to the generally accepted understanding that no excellent magnetically anisotropic sintered permanent magnet can be obtained of a rare earth-iron alloy, rare earth-iron based permanent magnets of high magnetic performance almost equivalent to the samarium-cobalt magnets can be prepared by admixing the rare earth-iron alloy with 0.1 to 10% by weight of titanium. Partial replacement of iron in the alloy with cobalt has an effect to increase the Curie point of the permanent magnet.

FIG. 1



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Description

A RARE EARTH-BASED ALLOY FOR PERMANENT MAGNET

BACKGROUND OF THE INVENTION

The present invention relates to a rare earth-based alloy for permanent magnet having excellent magnetic properties and suitable as a component of various kinds of electric and electronic instruments.

Various kinds of rare earth-based permanent magnet alloys have been developed hitherto and are under production in large quantities including the samarium-cobalt magnet alloys of the chemical composition $SmCo_5$. The magnetic properties of the permanent magnets of this type are so excellent that the maximum energy product $(BH)_{max}$ thereof exceeds 20 MGOe in the magnets manufactured under experimental conditions or is constantly in the range from 16 to 18 MGOe in the magnets manufactured as industrial products. Accordingly, these permanent magnets are widely used in a variety of applications such as speakers, electric motors, metering instruments and the like in which the permanent magnets are required to exhibit high performance. One of the problems in the samarium-based permanent magnets is the high production costs as a consequence of the high content of relatively expensive cobalt metal therein up to 60% by weight or more. It would therefore be a desirable measure to replace the cobalt metal with a less expensive metal such as iron and some attempts have been made hitherto in this direction. No fruitful results, however, have yet been obtained in such an attempt presumably due to the absence of possible solid-solution formation of iron with the $SmCo_5$ intermetallic compound.

On the other hand, several binary intermetallic compounds of rare earths and iron are known including the compounds of the formulas RFe_2, RFe_3 and R_2Fe_{17}, R being a rare earth element. These rare earth-iron intermetallic compounds, however, are not utilized as a permanent magnet due to the low value of either one of the magnetic parameters of Curie point T_c, saturation magnetization $4\pi M_s$ and crystalline magnetic anisotropy constant K_u. In contrast to the series of rare earth-cobalt intermetallic compounds including the RCo_5-type compounds having the crystalline structure of $CaCu_5$, of which the above mentioned $SmCo_5$ alloy is practically utilized as a material of permanent magnets, no RFe_5 type compounds were known for long in the series of rare earth-iron compounds, at least, in the form of a bulk body. It was only in 1984 that Cadieu, et al. reported in Journal of Applied Physics, volume 55, page 2611 (1984) that thin films of $SmFe_5$ and $(SmTi)_xFE_{100-x}$ in which the atomic ratio of Ti:Fe was 1:9 or 1:19, could be formed by the method of sputtering. These intermetallic compounds in the form of a thin film reportedly have a hexagonal crystalline structure of $CaCu_5$. These thin films formed by the sputtering method, however, were in the state of a metastable phase and it was generally understood that such an intermetallic compound could not exist as a bulk body. Therefore, the only permanent magnet based on a rare earth-iron binary compound so far reported is the magnet in a metastable phase prepared by the quenched thin-film method disclosed by Croat, et al. in IEEE Transactions on Magnetics, volume MAG 18, page 1442 (November, 1982). The quenched thin-film magnet prepared by this method is isotropic and based on a metastable phase so that the magnet is not free from the problem of low stability so that the magnets of this type are not in practical use.

Turning now to the recently highlighted neodymium-iron-boron magnets formed of a ternary compound of a chemical composition of the formula $R_2F_{14}B$, they are promising as a high-performance permanent magnet since the base components are inexpensive neodymium and iron and the magnetic properties thereof are even better than those of the samarium-cobalt magnets. These neodymium-iron-boron magnets are, however, not free from a very serious problem that they are highly susceptible to rusting so that the magnets cannot be used practically without providing a protective coating. This disadvantage can hardly be overcome and no practical solution of the problem has yet been obtained to give a possibility of industrial production of the magnets of this type.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to provide a rare earth-based permanent magnet having magnetic properties equivalent to or even better than those of the samarium-cobalt permanent magnets without using or by decreasing the amount of expensive cobalt as well as to provide a rare earth-based alloy as a base material of such a permanent magnet.

Thus, the permanent magnet alloy of the present invention consists essentially of:

(a) form 12 to 45% by weight of a rare earth element or a combination of rare earth elements;
(b) from 0.1 to 10% by weight of titanium; and
(c) the balance of iron or a combination of iron and cobalt, the amount of iron being at least 40% by weight thereof, including unavoidable impurities.

Further, the permanent magnet of the invention is a sintered body of a powder of the above defined rare earth-based alloy having magnetic anisotropy.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a graph showing the magnetization of inventive and conventional samarium-based alloys as a function of temperature.

FIGURE 2 illustrates the X-ray diffraction diagrams of the same alloys using CuKα line.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In respect of the problem of possible existence of RFe_5 phase, the results of experiments hitherto undertaken support that no such a 1:5 phase or, in particular, $SmFe_5$ phase is formed even when samarium and iron are melted together and alloyed in a proportion corresponding to the composition of $SmFe_5$ although three phases of Sm_2Fe_{17}, $SmFe_2$ and $SmFe_3$ could be found as is indicated by the results obtained in the measurement with a vibration magnetometer and in the X-ray diffractometry as is shown in FIGURES 1 and 2.

With an object to obtain a rare earth-iron based permanent magnet having excellent magnetic properties equivalent to those of the imaginary $SmFe_5$ magnet, the inventors have conducted extensive investigations on a third additive element to be added to the rare earth-iron binary magnet alloys and arrived at discoveries that addition of titanium would give a quite satisfactory result and a hitherto unknown ternary intermetallic compound of samarium, titanium and iron can exist in a bulky form by the optimization of the amount of substitution of titanium for the rare earth element or, in particular, samarium. Thus, a ternary alloy of samarium, titanium and iron was prepared in such a proportion as to correspond to the formula of $SmTiFe_{10}$ and the alloy was subjected to the measurement of the magnetization as a function of temperature and X-ray diffractometry to give the results shown in FIGURES 1 and 2, respectively. These figures indicate that, in clear difference from those of the $SmCo_5$-type crystalline structure, crystallographic indices approximately corresponding to those of the tetragonal crystalline structure can be allotted to the peaks in the X-ray diffractometric diagram of the ternary ally and the temperature dependency of the magnetization thereof is also close to that of a single-phase alloy leading to a conclusion that the ternary compound of samarium, titanium and iron is imparted with stability as a result of introduction of titanium into the samarium-iron binary alloy. The further continued investigations have led to confirmation that the above described unique phenomenon is held also for the rare earth elements in general other than samarium including yttrium.

Thus, the present invention provides, as an embodiment, a ternary alloy composed of (a) from 12 to 45% by weight of a rare earth element or a combination of rare earth elements; (b) from 0.1 to 10% by wieght of titanium; and (c) the balance of iron including unavoidable impurities. Namely, the magnet alloy can be obtained by melting the component metals together and the alloy is finely pulverized followed by the powder metallurgical processing of the powder by compression molding and sintering. When the amount of the rare earth component in the alloy formulation is outside the above specified range, the ternary compound would be less stable and, therefore, any amounts thereof smaller than 12% by weight and larger than 45% may result in a disadvantageously rapid decrease in the coercive force ${}_iH_c$ and saturation magnetization $4\pi M_s$, respective-ly. The above mentioned range for titanium is also critical because the ternary compound is less stable when the amount of titanium is smaller than 0.1% by weight while the fraction of the phase of the ternary compound is decreased when the amount of titanium is larger than 10% by weight. The rare earth element here implied include the so-called lanthanoid elements having atomic munbers of 57 to 71 and yttrium. Any of these rare earth elements can be used either singly or as a combination of two kinds or more according to need.

The rare earth-based permanent magnet of the invention prepared of the ternary alloy contains the stable phase of the ternary compound as a result of the introduction of titanium so that the Curie point thereof is about 310° C when the rare earth element is samarium which is much higher than 120° C of the Sm_2Fe_{17} phase. In addition, the saturation magnetization is also greatly increased so that the thus obtained permanent magnet has very high magnetic properties. Moreover, the rare earth-titanium-iron permanent magnet of the invention can be imparted with magnetic anistropy by the powder metallurgical method so that the overall magnetic performance of the inventive permanent magnet can be almost equivalent to or even better than the samarium-cobalt based magnets.

Despite the high content of iron in the alloy of the inventive permanent magnet, which is formed mainly of a tetragonally crystalline phase, the inventive permanent mgnet is highly corrosion-resistant and free from rusting in clear contrast to the neodymium-iron based magnets. Accordingly, the inventive permanent magnets can be used in practical applications without any prtective coating on the surface although the corrosion resistance thereof can of course be further increased by a protective coating or surface treatment by forming a resinous layer or a metallic layer formed by electrolytic or electroless plating, vacuum vapor deposition, sputtering or ion plating.

Further, the ternary alloy can be processed into a thin film having a high coercive force by the quenched thin-film method and the thin film can be finely pulverized into fine particles of which magnetically isotropic permanent magnets can be prepared. It is of course that the magnetically anisotropic sintered magnet is pulverized into fine particles of which anisotropic plastic magnets can be prepared.

As is mentioned above, the permanent magnet of the ternary alloy of samarium, titanium and iron has a Curie point of about 310°C. Although this Curie point is well within the practically acceptable range, it is of course desirable to have a higher Curie point when comparison is made with the $SmCo_5$ permanent magnets having a Curie point at about 740°C. In this regard, the inventors have further continued extensive investigations and arrived at a discovery that a magnetic alloy suitable for the purpose can be obtained when a solid solution is formed of the above described ternary compound of rare earth, titanium and iron with cobalt. For example, an increase by about 40 to 100° C can be obtained in the Curie point of the ternary alloy when 10 atomic % of iron in the alloy is replaced with cobalt although the increment depends on the kind of the rare earth element. The Curie point T_c is increased approximately linearly with the increase in the amount of replacement of iron with cobalt up to 50% replacement by weight but thereafter the increment in the Curie point is relatively small with further increased replacement of iron with cobalt to finally level off. In addition, the saturation magnetization of the magnet is increased as a trend though dependent on the kind of the rare earth element by the substitution of cobalt for a part of iron in the ternary magnet alloy of rare earth, titanium and iron to level off with increase of the proportion of cobalt relative to iron.

It should be noted, however, that replacement of iron with cobalt has some adverse effect of decreasing the coercive force of the magnet. For example, more than 40% replacement of iron with cobalt is undesirable due to the great decrease in the coercive force of the magnet. This is the reason for the limitation that more than 60% by weight or, preferably, more than 40% by weight of iron should not be replaced with cobalt.

In the following, the rare earth-based alloy for permanent magnets and the sintered permanent magnet of the alloy accord ing to the invention are described in more detail by way of examples.

Example 1.

Metals of samarium, titanium and iron each having a purity of 99.9% were taken by weighing in the proportion indicated in Table 1 below and melted together in a high-frequency induction furnace. The melt was cast into a water-cooled, copper-made casting mold to form an ingot of the alloy. The ingot was crushed and then pulverized in a jet mill using nitrogen gas as the ject gas to give a fine powder having an average particle diameter in the range from 2 to 10 μm. The powder was compression-molded under a pressure of 1.5 tons/cm^2 with the particles oriented in a static magnetic field of 15 KOe into a green body, which was sintered by heating in an atmosphere of argon gas for 1 hour at a temperature in the range form 1000 to 1200 °C and then subjected to thermal aging for 4 hours at a temperature in the range from 500 to 900 °C followed by quenching.

The thus obtained magnetically anisotropic sintered body after the thermal aging was subjected to the measurement of the density of residual magnetic flux B_r, coercive force $_iH_c$ and maximum energy product $(BH)_{max}$ to give the results shown in Table 1 for the three different formulations of the alloys No. 1, No. 2 and No. 3. For comparison, Table 1 also includes the results of the magnetic measurement of a sintered body of a samarium-iron al loy corresponding to $SmFe_5$ (No. 4) prepared in the same manner as above. As is shown in the table, this comparative sintered body had only negligibly small values of coercive force and maximum energy product.

Table 1

No.	Composition, % by weight			Magnetic properties		
	Sm	Ti	Fe	Br, kG	iHc, kOe	(BH)max, MGOe
1	28.6	2.3	69.1	8.2	7.7	16.1
2	20.0	6.5	73.5	10.8	9.8	26.5
3	14.8	9.5	75.7	9.1	6.1	19.2
4	35.0	0	65.0	3.0	ca. 0	ca. 0

Example 2.

Metals of praseodymium, samarium, cerium, titanium and iron were taken by weighing in the proportion indicated in Table 2 and magnetically anisotropic sintered bodies were prepared each in the same manner as in Example 1. The coercive force $_iH_c$ of these sintered bodies was measured to give the results shown in the table which supports the conclusion that the coercive force is little affected by the replacement of samarium with other rare earth elements.

Table 2

No.	Composition, % by weight					$_iH_c$, kOe
	Pr	Sm	Ce	Ti	Fe	
1	19.4	0	0	6.6	74.0	9.0
2	12.0	0	8.0	6.8	73.2	7.0
3	7.9	4.2	7.8	6.7	73.4	7.8

Example 3.

Magnetically anisotropic sintered permanent magnets No. 1 to No. 4 were prepared each in the same manner as in Example 1 except that the magnetic alloy was prepared from metals of neodymium, titanium, iron and cobalt each having a purity of 99.9% taken by weighing in the proportion indicated in Table 3.

These sintered permanent magnets were subjected to the measurement of the density of residual magnetic flux B_r, coercive force $_iH_c$ and maximum energy product $(BH)_{max}$ as well as Curie point to give the results shown in the table, in which ΔT_c means the increment of the Curie point T_c in °C obtained by the replacement of a part of iron with cobalt.

Table 3

No.	Composition, % by weight				Magnetic properties			
	Nd	Ti	Fe	Co	B_r, kG	iHc, KOe	(BH)max, MGOe	ΔT_c, °C
1	19	7	64	9	10.8	8.5	26.5	90
2	19	7	44	29	11.3	8.0	30.0	220
3	28	3	48	21	9.4	6.7	21.2	19.0
4	16	9	52	23	10.5	7.1	25.0	190

Example 4.

Magnetically anisotropic sintered permanent magnets No. 1 and No. 2 were prepared in the same manner as in the preceding examples from metals of samarium, cerium, titanium, iron and cobalt taken by weighing in the proportion indicated in Table 4 below. These sintered permanent magnets were subjected to the measurement of the magnetic properties to give the results shown in the table.

Table 4

No.	Composition, % by weight					$_iH_c$, kOe
	Pr	Sm	Ce	Ti	Fe	
1	19.4	0	0	6.6	74.0	9.0
2	12.0	0	8.0	6.8	73.2	7.0
3	7.9	4.2	7.8	6.7	73.4	7.8

Claims

1. A rare earth-based alloy for permanent magnet consisting essentially of:
   (a) from 12 to 45% by weight of a rare earth element or a combination of rare earth elements;
   (b) from 0.1 to 10% by weight of titanium; and
   (c) the balance of iron or a combination of iron and cobalt, the amount of iron being at least 60% by weight thereof, including unavoidable impurities.
2. The rare earth-based alloy for permanent magnet as claimed in claim 1 wherein the rare earth element is selected form the group consisting of the elements of the atomic number of from 57 to 71 and yttrium.
3. A permanent magnet which is a sintered body of a powder of a rare earth-based alloy consisting essentially of:
   (a) from 12 to 45% by weight of a rare earth element or a combination of rare earth elements;
   (b) from 0.1 to 10% by weight of titanium; and
   (c) the balance of iron or a combination of iron and cobalt, the amount of iron being at least 60% by weight thereof, including unavoidable impurities.

FIG. 1

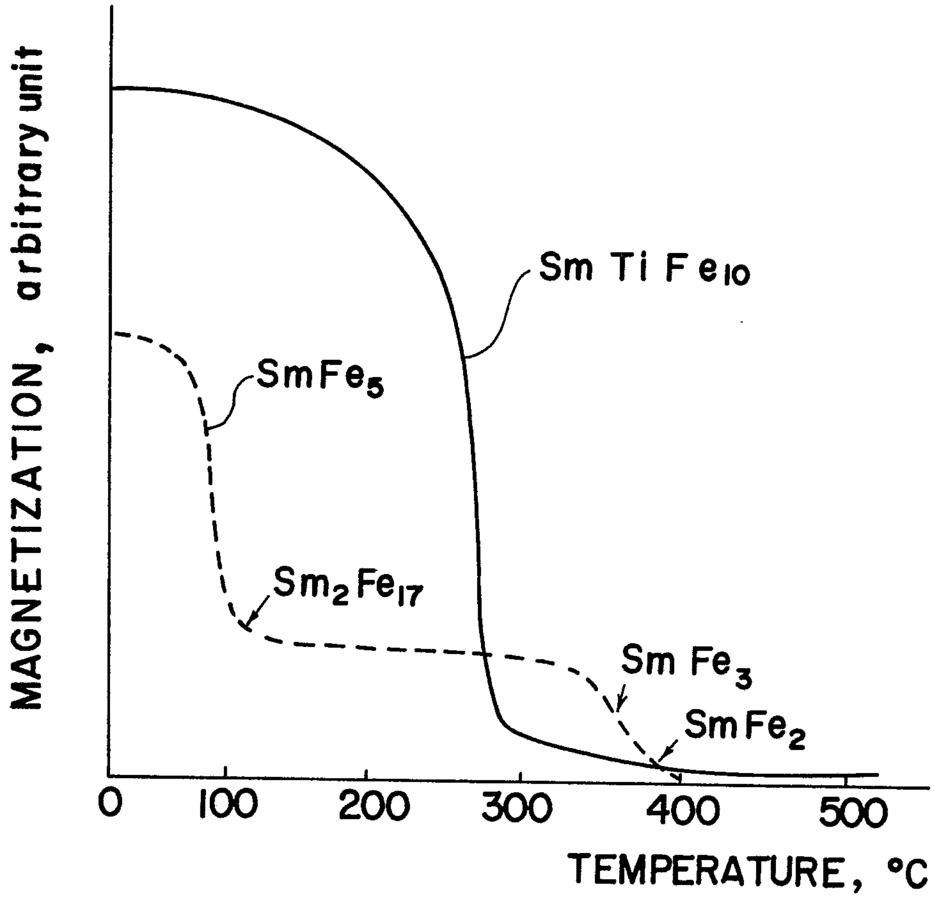
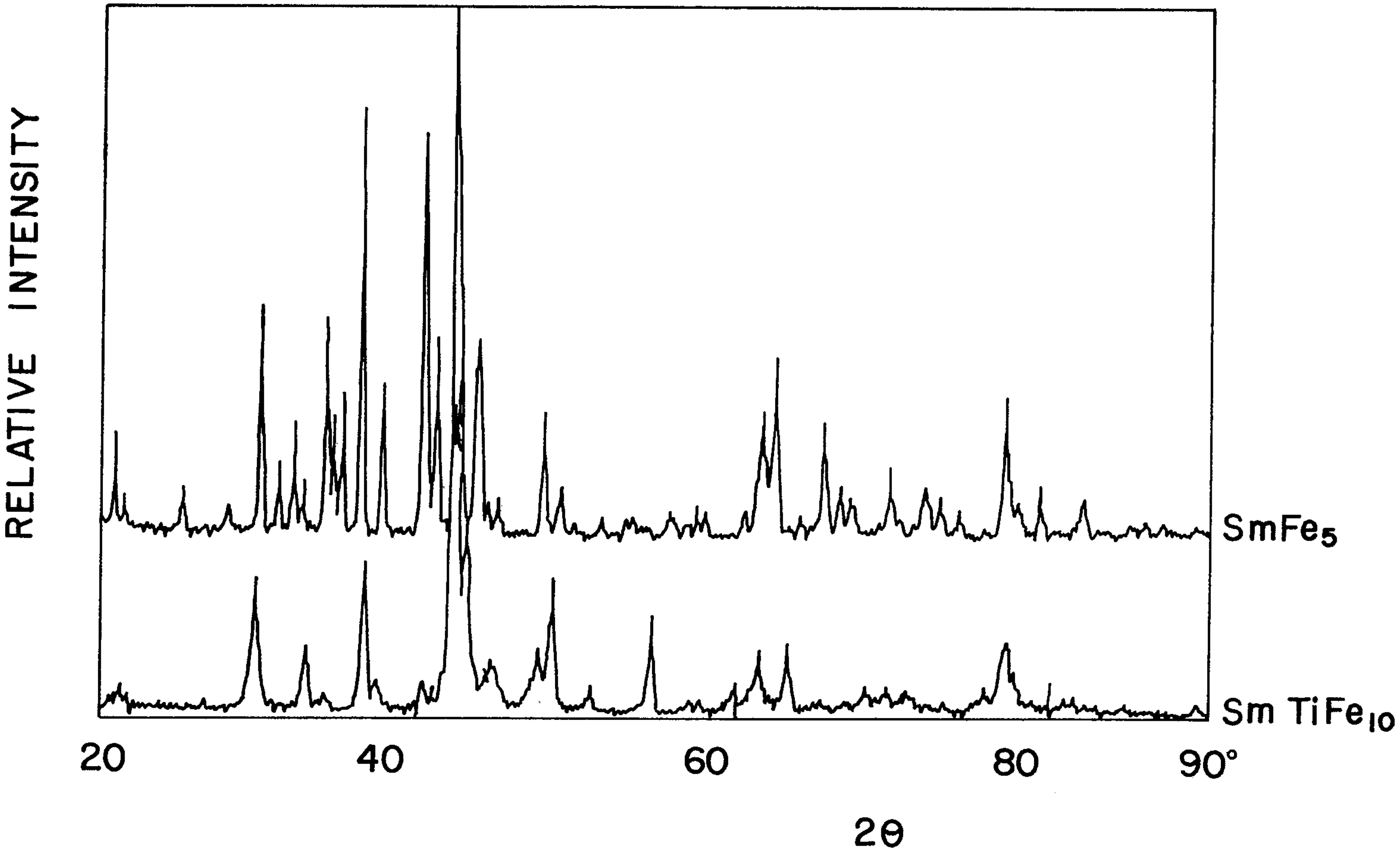

MAGNETIZATION, arbitrary unit
Sm Ti Fe10
SmFe5
Sm2Fe17
Sm Fe3
SmFe2
0
100
200
300
400
500
TEMPERATURE, °C

FIG. 2



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EUROPEAN SEARCH REPORT

Application number

EP 87400808.9

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 4)
A	CHEMICAL ABSTRACTS, vol. 85, no. 18, November 1, 1976, Columbus, Ohio, USA TOKYO SHIBAURA ELECTRIC CO., "Sintered alloy permanent magnets" page 903, column 1, abstract no. 136255z & Jpn. Kokai Tokkyo Koho JP 76 47,296, 22 April 1976 --	1,2	C 22 C 38/14 H 01 F 1/08
A	US - A - 4 221 613 (IMAIZUMI et al.) * Abstract * ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl 4)
			C 22 C H 01 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	10-07-1987	LUX

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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