

"PERMANENT MAGNET AND METHOD OF MAKING THE SAME"

This invention relates to permanent magnets and to methods of making the same.

According to one aspect of the present invention there is provided a permanent magnet made from a powdered alloy composed of samarium, cobalt, copper, iron and any one or more of zirconium, titanium, hafnium, tantalum, niobium and vanadium and formed predominantly of $\text{Sm}_2\text{Co}_{17}$ crystals with a predominantly columnar macrostructure.

Preferably the permanent magnet comprises 21% to 28% by weight of samarium, 3% to 10% by weight of copper, 14% to 35% by weight of iron and 0.5% to 5% by weight of any one or more of zirconium, titanium, hafnium, tantalum, niobium and vanadium, the balance being cobalt.

According to another aspect of the present invention there is provided a method of making a permanent magnet as recited above comprising the steps of subjecting the alloy to a heat treatment for magnetic alloy hardening, forming a magnetic powder from the heat treated alloy having an average particle size of not more than $50\mu\text{m}$, mixing the magnetic powder with a binder, and compacting the mixture so formed into a desired shape under the influence of a magnetic field.

The binder may be an organic resin or a metal or metal alloy.

The invention is illustrated, merely by way of example, in

the accompanying drawings, in which:-

Figure 1 illustrates, in cross-section, the macrostructure of an alloy ingot for the purpose of explaining the present invention;

5 Figure 2 is a flow diagram illustrating a method of making a permanent magnet according to the present invention;

Figure 3 illustrates a mould for producing a permanent magnet according to the present invention;

10 Figure 4 illustrates, in cross-section, the macrostructure of an alloy ingot produced by a conventional method.

Figure 5 illustrates in cross-section, the macrostructure of an alloy ingot produced by a method according to the present invention;

15 Figure 6 shows test pieces cut from the alloy ingot of Figure 5;

Figure 7 illustrates graphically the magnetic properties of the test pieces of Figure 6;

Figure 8 illustrates another form of mould for use with a method according to the present invention;

20 Figure 9 illustrates, in cross-section, the macrostructure of an alloy ingot produced by the method described in Example 7;

Figure 10 illustrates, graphically, the magnetic properties of a permanent magnet made from the alloy ingot of Figure 9;

25 Figure 11 illustrates graphically the relationship between saturated magnetisation and ageing of a permanent magnet made from

alloy ingot of Figure 9; and

Figure 12 illustrates two further moulds for producing permanent magnets in accordance with the present invention.

Generally, when molten metal is poured from a crucible
5 into a mould, solidification of the metal progresses inwardly
from the wall of the mould. This phenomenon is accounted for by
postulating that the embryo in contact with the mould wall has
a smaller energy barrier to become the nucleus of a crystal than
the embryo migrating within the molten metal. The crystals formed
10 on the mould wall continue to grow into the molten metal while
competing with the adjacent crystals. The region A shown in
Figure 1 is the outermost layer of an alloy ingot, where the
crystals are competing with each other to grow and this is called
the chilled layer or zone. Each crystal tends to grow
15 preferentially in a direction parallel to that of the heat gradient.
The crystals that grow parallel to the heat gradient tend to
prevent the growth of crystals in directions not parallel to the
heat gradient. The crystals grow towards the centre of the mould
and those crystals whose direction of growth is more coincident
20 with the direction of the heat gradient are allowed to survive
longer to the detriment of other crystals so that the number of
crystals gradually decreases. As a result, a columnar zone B
is formed. When the conditions are favourable the fronts of
columnar zones approaching each other from opposite sides of the mould
25 eventually collide bringing the solidification of the molten metal

to completion. Generally, however, an equiaxed structure zone C is formed inside the columnar zone as shown in Figure 1.

The cause for the formation of this equiaxed structure zone was not understood until recently. It has now been suggested that crystals formed at the mould wall or the cooled boundary surface of the molten metal liberate themselves to become floating crystals in the molten metal and these crystals give rise to the equiaxed structure zone. (A. Ohno, T. Motegi, and H. Soda: Trans. ISIJ, 11 (1971) 18).

A permanent magnet according to the present invention is made from a five-element alloy consisting of samarium (Sm), cobalt (Co), copper (Cu), iron (Fe) and any one or more of zirconium (Zr), titanium (Ti), hafnium (Hf), tantalum (Ta), niobium (Nb) and vanadium (V) and is a so-called precipitation-hardened magnet or a phase-separation magnet. This is because the magnetic hardening is caused by precipitation of a second phase in the matrix.

At present, roughly two methods are available for the production of commercial two-phase separation magnets. One such method is the sintering method. The sintering method induces the growth of particles during the process of sintering by liquid-phase or solid-phase atomic diffusion. Magnetic particles measuring $2\mu\text{m}$ to $3\mu\text{m}$ attain growth to $10\mu\text{m}$ to $50\mu\text{m}$ by sintering and recrystallization, for example. The sintering method, therefore, has a disadvantage that the inherent crystal structure

of the original alloy ingot cannot be retained and the composition changes. Among the component elements, the amount of rare earth metal samarium is reduced because of oxidation and vaporization. Producing a magnet from the optimum alloy composition does not
5 produce the prescribed magnetic properties without compensating for the loss of samarium. Further, the magnetic properties tend to vary considerably from batch to batch and within batches.

The other method for producing a two-phase separation magnet is used in the present invention where a resin-bound or metal-bound
10 magnet is obtained by subjecting an alloy ingot to a thermal treatment for magnetic hardening, pulverising the alloy ingot to produce a magnetic powder, and binding the powder with a resin or metal binder. A permanent magnet in accordance with the present invention is manufactured by such a method which is illustrated by
15 the flow diagram shown in Figure 2. This magnet is heavily affected by the cast structure unlike the magnet obtained by the sintering method. It has been ascertained that when an alloy composed of samarium, cobalt, copper, iron and any one or more of zirconium, titanium, hafnium, tantalum, niobium and vanadium is cast, its
20 macrostructure can be divided into three fractions, the first corresponding to an equiaxed structure, the second corresponding to a columnar crystal zone and the third corresponding to a chilled crystal zone. A permanent magnet made from the fraction of columnar crystals excels permanent magnets made from the other fractions in
25 all magnetic properties

including saturation magnetisation ($4\pi I_s$), coercive force (iH_c, bH_c), and squareness of hysteresis loop.

Since an alloy of columnar crystals has the crystals arranged in a given direction, a permanent magnet made of this alloy enjoys good monoaxial orientation of crystals. Because the production of a permanent magnet according to the present invention utilises the original crystalline structure of the ingot per se unlike the conventional method, the cast structure of the ingot must be considered. Further an alloy for a permanent magnet in accordance with the present invention produced by thermal treatment enjoys better structural homogeneity than that produced by any other method, probably because the alloy is composed predominantly of columnar crystals. Consequently, the alloy also exhibits better squareness of hysteresis loop. Moreover, the crystalline structure and configuration of the precipitations are improved to contribute towards enhancing the coercive force (iH_c) more than an alloy composed predominantly of equiaxed crystals.

In order to obtain a permanent magnet with good magnetic properties, therefore, it is important to adopt a method of manufacture which is capable of casting the alloy in such a manner that the chilled crystal zone in the immediate neighbourhood of the mould wall comprises columnar chilled crystals and the other part comprises columnar crystals. During the crystallisation of the alloy ingot, the proportion of columnar crystals can be increased by properly determining various conditions such as

temperature of the molten metal before casting, manner of casting, cooling rate of cast molten metal, and speed of solidification

It is desirable that a cast alloy ingot contains columnar crystals in a proportion of not less than 30% by volume. This proportion

5 preferably exceeds 50% by volume and even more preferably is greater than 70% by volume. In an alloy composition of a permanent magnet according to the present invention, the content of samarium is in the range of 21 to 28% by weight. If the samarium content is less than 21% by weight, the alloy permits growth of a Fe-Co

10 phase in addition to a $\text{Sm}_2\text{Co}_{17}$ phase. Consequently, the squareness of the hysteresis loop is degraded and the coercive force ($1H_c$) is extremely degraded. If the samarium content exceeds 28% by weight, then the proportion of SmCo_5 phase which deviates from the $\text{Sm}_2\text{Co}_{17}$ phase increases, the saturation magnetisation ($4\pi I_s$) decreases, and the energy product declines.

15 The copper content is required to exceed 3% by weight in order to permit desired acceleration of the hardening of the precipitate. If the copper content exceeds 10% by weight, however, the saturation magnetisation ($4\pi I_s$) and the squareness of the hysteresis loop are impaired. Thus, the upper limit for the copper content is fixed at 10%.

20 The iron occupies the cobalt site in $\text{Sm}_2\text{Co}_{17}$ crystals, improves the saturation magnetisation and lends itself to increasing the energy product. If the iron content exceeds 35% by weight, however, the $\text{Sm}_2\text{Co}_{17}$ crystals can no longer be retained and the

25

coercive force (iHc) is impaired. Thus the iron content has an upper limit of 35% by weight.

In the case where the content of element M, which stands for any one or more of zirconium, titanium, hafnium, tantalum, niobium or vanadium exceeds 5% by weight, the saturation magnetisation is extremely degraded. If the content of the element M is less than 0.5% by weight, the alloy fails to acquire the minimum 4000 Oe of coercive force indispensable to a permanent magnet. The element M, when incorporated in the alloy, is expected to disperse uniformly throughout the alloy ingot to improve the form of the precipitate and promote the fixation of nitrogen and make other contributions. With the range of from 0.5 to 5% by weight, the element M may be incorporated in the form of a sole element or in the form of a combination of two or more elements. In the latter case, the addition of the element M has the same or better effect in the improvement of magnetic properties compared to the addition of a single element. The remainder of the alloy composition is accounted for by cobalt.

The impurities which inevitably creep into the alloy from the raw materials used and during the manufacture of the alloy desirably should not account for a proportion of more than 0.5% by weight.

The important points which govern the magnetic properties of an alloy for a permanent magnet in accordance with the present invention after the step of pulverisation are enumerated below:

(1) The magnetic powder is produced by using a suitable machine such as, for example, a jet mill, a ball mill, a hammer crusher or a top mill, with all possible efforts being made for preventing oxidization during pulverisation. It is desirable that the magnetic powder has an average particle size of not more than 50 μ m. Preferably, this average particle size falls in the range of from 10 to 20 μ m. The particle size distribution is such that the largest particle diameter is not more than 100 μ m. Otherwise, the orientation in the magnetic field is impaired and the residual magnetic flux density (Br) exerts a bad influence. Also, the die used for pressing the powder to form the permanent magnet is heavily worn so that the magnet may not be shaped accurately.

(2) As concerns the binder, either an organic polymer or a metal can be used. Examples of organic binders which can be used advantageously include thermoplastic and thermosetting resins such as epoxy resins, EVA (ethylene vinyl acetate), rubber, polyesters and nylon. Resin in an amount roughly in the range of 1.0 to 15% by weight, the magnetic powder accounting for the balance to make up 100% by weight, are mixed. The resultant mixture is moulded or compacted into a given shape in a magnetic field and thermally solidified.

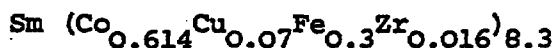
If the binder is a metal, a metal or alloy having a melting point of not more than 400°C should be used. The metal binder is mixed with the magnetic powder or applied to the surface of

the particles of the magnetic powder by plating. Metals which can be used advantageously include zinc (melting point 419.5°C), cadmium (melting point 320.9°C), indium (melting point 156.6°C), tin (melting point 231.9°C), lead (melting point 327.3°C) and bismuth (melting point 271°C). Their alloys may also be used. The plating of the metal binder to the surface of the particles of the magnetic powder is accomplished by a non-electrolytic nickel plating or vacuum deposition technique, such as a sputtering technique, ion plating technique, CVD technique or PVD technique.

Now the present invention will be described in detail below with reference to the following Examples.

EXAMPLE 1

In an atmosphere of argon, 1 kg of an alloy composition consisting of 23.54% by weight of samarium, 5.78% by weight of copper, 21.77% by weight of iron, 1.9% by weight of zirconium and a balance of cobalt to make up 100% by weight and represented by the constitutional formula



was melted and cast in a mould illustrated in Figure 3.

First a conventional casting method was used, the molten metal temperature being 1460°C and the casting speed being 1 kg/10 seconds to suit rather slow casting. The cooling was by air. The mould was made of a material of Grade S15C, and consisted of matched dies 1, 2. Reference numeral 3 in Figure 3 denotes the portion in which the alloy was cast. An ingot

measuring 35 mm x 35 mm x 80 mm was produced.

Figure 4 is a cross-section of the macrostructure of the ingot obtained by this conventional method, the mould being indicated by the reference numeral 4. In Figure 4 there is shown a columnar crystal zone B and an equiaxed crystal zone C. The equiaxed crystal zone C accounted for 60 to 70% by volume and the columnar crystal zone B for a fairly small proportion.

In the method of making a permanent magnet according to the present invention the alloy composition referred to above was melted with high-frequency energy in an atmosphere of argon and the molten alloy cast in the same mould shown in Figure 3. The molten metal temperature during casting was 1580°C and the casting speed was about 3 to 5 seconds/kg. Thus the alloy which had a melting point of 1260°C was cast at a molten metal temperature 320°C or higher than the melting point. Consequently, the amount of solidification nuclei possibly produced after introduction of the molten alloy in the mould can be decreased and the growth of columnar crystals promoted.

The alloy ingot thus obtained was then subjected to the process set out in Figure 2, consisting of the steps: thermal treatment; pulverisation to form a magnetic powder; incorporation of a binder into the magnetic powder; compression of the mixture of magnetic powder and binder in a magnetic field; compression moulding; curing; and B-H measurement to test magnetic properties. For the thermal treatment step, 200 g of the alloy ingot was used.

A central portion in the length direction of the alloy ingot was heated at $1150 \pm 2^\circ\text{C}$ for 20 hours and then cooled to normal room temperature at a rate of 20°C to $25^\circ\text{C}/\text{minute}$. Subsequently, in an argon atmosphere, the ingot was heated at $800 \pm 3^\circ\text{C}$ for 24 hours and then quenched at a rate of 15°C to $20^\circ\text{C}/\text{minute}$.

Figure 5 shows the macrostructure of the alloy ingot produced by this method.

After magnetic curing, the ingot was cut in intervals of 4 mm measured from the mould wall 4 as illustrated in Figure 6 to produce test pieces. The test pieces were serially numbered 5, 6, 7, 8 from the mould wall towards the centre of the ingot. Thus the test piece 8 fell at the centre of the cross-section of the alloy ingot. Each test piece was pulverised to a magnetic powder having an average particle size of $12\mu\text{m}$. In a mortar, the magnetic powder was mixed with 1.9% by weight of a one-component type epoxy binder and compressed in a magnetic field. The strength of the magnetic field was 15 to 18 KG and the maximum compression pressure was $5 \text{ tons}/\text{cm}^2$. The compression produced a cylindrical test piece 15 mm in diameter and 5 mm in length. The test piece was cured at 150°C for 3 hours and the B-H curve measured on a DC self-recording magnetic flux meter. The magnetic properties thus determined are shown graphically in Figure 7. In the columnar zone and the equiaxed structure zone, the magnetic properties were found to be clearly different from each other. The symbol "Mix" indicated in Figure 7 represents data which was

obtained from a test piece prepared by pulverising the remaining half of the ingot of Figure 6 and treating the resultant powder in the same procedure as that described above. The portion of columnar zone accounted for 20 to 30% by weight of the whole ingot obtained by the conventional method and for 70 to 80% of the whole ingot obtained by a method of making a permanent magnet according to the present invention. It will be appreciated that the magnetic properties were improved in proportion to the percentage of the macrostructure of the ingot which consisted of columnar crystals.

EXAMPLE 2

Under the same conditions as those in the method according to the present invention described in Example 1, 1 kg of an alloy composition was melted and cast in the same mould at a molten temperature of 1590°C. The alloy composition was represented by the constitutional formula:



The conditions of manufacturing a permanent magnet from this alloy ingot were the same as those used in the method according to the present invention described in Example 1. The properties of the permanent magnet obtained were as follows:

Br (KG)	-	8.56
bHc (KOe)	-	6.75
iHc (KOe)	-	10.1
(B.H) max.	-	15.9 MGOe
Density	-	7.16 g/cm ³

In this alloy ingot, the columnar zone accounted for 75% by volume of the whole of the ingot.

EXAMPLE 3

By following the procedure of the method according to the present invention described in Example 1, a permanent magnet was produced from an alloy having the composition shown below. The magnetic properties of the permanent magnet are also shown below:

	Sm (Co _{0.6} Cu _{0.08} Fe _{0.3} Hf _{0.02})	8.26
	Br (KG)	- 8.68
	bHc (KOe)	- 7.00
	iHc (KOe)	- 9.8
10	(B.H) max.	- 16.15 MGOe
	Density	- 7.20 g/cm ³

In this alloy, the columnar zone accounted for 80% by volume of the whole.

EXAMPLE 4

By following the procedure of the method according to the present invention described in Example 1, a permanent magnet was produced from an alloy having the composition shown below: The magnetic properties of the permanent magnet are also shown:

	Sm (Co _{0.604} Cu _{0.08} Fe _{0.3} Ta _{0.016})	8.3
	Br (KG)	- 8.60
	bHc (KOe)	- 6.95
	iHc (KOe)	- 10.9
	(B.H) max.	- 16.0 MGOe
20	Density	- 7.06 g/cm ³

In this alloy, the columnar zone accounted for 70% by volume of the whole.

EXAMPLE 5

By following the procedure of the method according to the present invention described in Example 1, a permanent magnet was produced from an alloy of a composition shown below. The magnetic properties are also shown:

Sm (Co _{0.604} Cu _{0.08} Fe _{0.3} Zr _{0.01} Hf _{0.006})	8.3
Br (KG)	- 8.68
bHc (KOe)	- 7.00
iHc (KOe)	- 11.0
(B.H) max.	- 16.2 MGOe
Density	- 7.10 g/cm ³

In this alloy, the columnar zone accounted for 72% by volume of the whole. In this Example zirconium and hafnium are used in combination. The magnetic properties of the resultant permanent magnet are as favourable as those of the permanent magnet obtained in Example 1.

EXAMPLE 6

By following the procedure of the method according to the present invention described in Example 1, a permanent magnet was produced from an alloy of a composition shown below. The magnetic properties are also shown:

Sm (Co _{0.602} Cu _{0.08} Fe _{0.3} V _{0.018})	8.25
Br (KG)	- 8.50
bHc (KOe)	- 6.65
iHc (KOe)	- 10.1
(B.H) max.	- 15.6 MGOe
Density	- 7.15 g/cc

In this alloy, the columnar zone accounted for about 70% by volume as a whole.

EXAMPLE 7

1 kg of an alloy whose composition is shown in the column "Alloy 1" of Table 1 was melted in an alumina crucible by use of a high-frequency furnace. The molten alloy was cast at a temperature of 1600°C in a metal mould of iron of a construction shown in Figure 8. The mould had a wall thickness of 10 mm. The alloy ingot produced had a macrostructure shown in Figure 9.

TABLE 1

	Alloy 1	Alloy 2	Alloy 3
Sm	23.12	26.59	21.54
Co	51.15	47.06	52.20
Cu	6.57	9.44	6.70
Fe	15.87	15.21	16.19
Zr	3.30	1.69	3.37

(In % by weight (wt%))

In Figure 9 the chilled zone is indicated as A', the columnar zone as B' and the equiaxed zone as C'. Test pieces were cut out of the zones A', B', and C' of the ingot of "Alloy 2". Each of the test pieces in solid solution was treated at a proper temperature in the range of 1140°C to 1180°C and then was subjected to a treatment for ageing at 800°C. Thus each test piece was magnetically hardened. Each test piece was then pulverised into a magnetic powder which was kneaded with 2.1% by weight of an epoxy

type organic binder. The resultant mixture was compressed in a press in a magnetic field. The compressed mixture was heated at 150°C for 2 hours to cure the resin. The permanent magnet so produced was cylindrical measuring 15 mm in diameter and 6t mm in length. The relationship between the magnetic properties of the permanent magnet so obtained and the macrostructure of the alloy is shown in Figure 10. Figure 10 shows the relationship between the coercive force (iHc) and the ageing time at 800°C. Figure 11 shows the relationship between the saturated magnetisation and ageing time. As will be seen from Figures 10 and 11, the columnar zone exhibits better magnetic properties than the other zones.

EXAMPLE 8

Alloys of the compositions shown in columns "Alloy 2" and "Alloy 3" in Table 1 were melted by the same method as in Example 7. The molten alloys were cast each at a temperature of 1600°C in an iron mould shown in Figure 12. In Figure 12, (b) denotes a mould having a copper pipe wound thereon so as to be cooled by circulating water and (a) denotes a mould which is air-cooled.

The two moulds of Figure 12 were identical in size, shape and material, except for the cooling device used. The alloy compositions indicated in columns "Alloy 1" and "Alloy 3" in Table 1 were melted by the same method as in Example 7. Two ingots were obtained. In addition, one ingot was produced by cooling the molten metal directly in the crucible. Observation of the structure of

the above-mentioned three alloy ingots involving different cooling speeds revealed that the ingots of "Alloy 1" and "Alloy 3", obtained by water cooling, were formed substantially wholly of chilled crystals, whereas those obtained by air cooling contained more than 90% by volume of columnar crystals and those cooled within the crucible were formed of coarsened equiaxed crystals. The three kinds of ingots of "Alloy 1" and "Alloy 3", in solid solution, were heat treated under the optimum conditions between 1140°C and 1180°C and subsequently aged at 800°C for 2 hours and then at 700°C for 4 hours. Then, by following the procedure of Example 7, resin-bound permanent magnets were produced from the alloy ingots. These were tested for magnetic properties. The results are shown in Tables 2 and 3. Table 2 shows the results for "Alloy 1" and Table 3 for those of "Alloy 3". The constitutional formulae of the alloy compositions of "Alloy 1", "Alloy 2" and "Alloy 3" are shown below:

Alloy 1 - $\text{Sm}(\text{Co}_{0.67}\text{Cu}_{0.08}\text{Fe}_{0.22}\text{Zr}_{0.028})_{8.40}$

Alloy 2 - $\text{Sm}(\text{Co}_{0.645}\text{Cu}_{0.12}\text{Fe}_{0.22}\text{Zr}_{0.015})_{7.0}$

Alloy 3 - $\text{Sm}(\text{Co}_{0.67}\text{Cu}_{0.08}\text{Fe}_{0.22}\text{Zr}_{0.028})_{9.20}$

TABLE 2

Method of cooling	Br (G)	bHc (O _g)	(BH) max (MGO _g)
Water cooling	6800	2100	6.5
Air cooling	7600	5500	13.7
Cooling in crucible	7500	1800	6.0

TABLE 3

Method of Cooling	Br (G)	bHc (O ₂)	(BH)max (MGO ₂)
Water cooling	7050	1050	4.2
Air cooling	8100	5400	14.5
Cooling in crucible	7800	950	3.8

It will be seen from Tables 2 and 3 that the ingots obtained from "Alloy 1" and "Alloy 3", the air-cooled ingots, had a columnar structure exhibiting the best magnetic properties.

As described in detail above, the present invention resides in converting the cast structure of an alloy into a columnar structure and causing such columnar structure to account for preferably at least 50% by volume of the whole. This enables the magnetic properties of the powder-bound magnet obtained and consisting of predominantly Sm₂Co₁₇ crystals to be enhanced and, at the same time, permits the alloy itself to be mass-produced in the form of large ingots weighing 5 kg, 20 kg, 50 kg or 100 kg, for example.



- 20 -

CLAIMS

1. A permanent magnet made from a powdered alloy composed of samarium, cobalt, copper, iron and any one or more of zirconium, titanium, hafnium, tantalum, niobium and vanadium and formed predominantly of $\text{Sm}_2\text{Co}_{17}$ crystals with a predominantly columnar macrostructure.
2. A permanent magnet as claimed in claim 1 comprising 21% to 28% by weight of samarium, 3% to 10% by weight of copper, 14% to 35% by weight of iron and 0.5% to 5% by weight of any one or more of zirconium, titanium, hafnium, tantalum, niobium and vanadium, the balance being cobalt.
3. A permanent magnet substantially as herein described with reference to the Examples.
4. A method of making a permanent magnet as claimed in any preceding claim comprising the steps of subjecting the alloy to a heat treatment for magnetic alloy hardening, forming a magnetic powder from the heat treated alloy having an average particle size of not more than $50\mu\text{m}$, mixing the magnetic powder with a binder, and compacting the mixture so formed into a desired shape under the influence of a magnetic field.
5. A method as claimed in claim 4 in which the binder is an organic resin or a metal or metal alloy.
6. A method of making a permanent magnet as claimed in claim 4 and substantially as herein described.

The text of the specification has been reproduced by photocopying the applicants original typescript. It may contain a few amendments which are difficult to read. The original typescript containing these amendments may be inspected on the premises of the Patent Office