

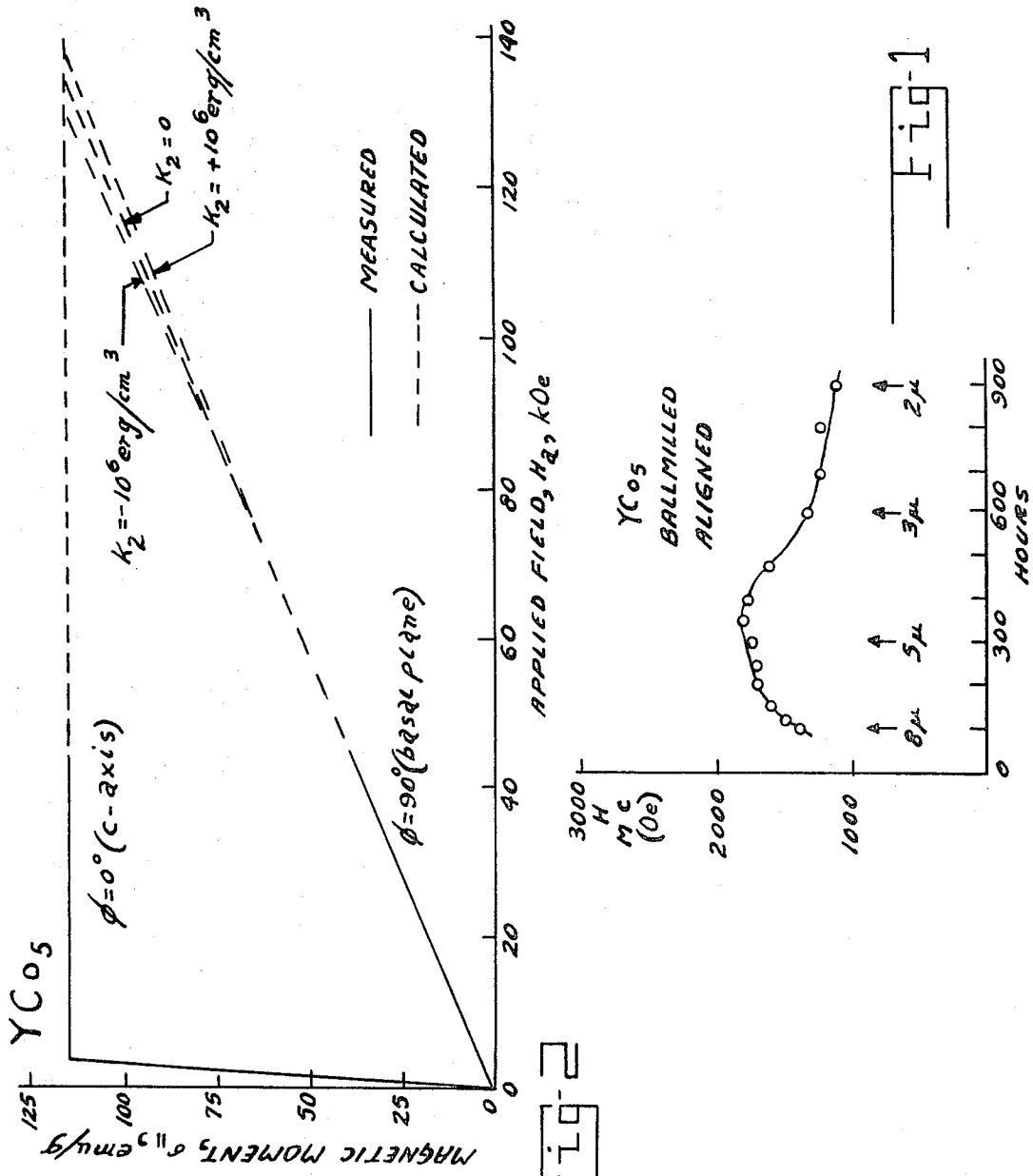
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PERMANENT MAGNETS

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1

3,540,945

## PERMANENT MAGNETS

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Original application June 5, 1967, Ser. No. 644,460, now Patent No. 3,424,578, dated Jan. 28, 1969. Divided and this application June 11, 1968, Ser. No. 748,889  
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U.S. Cl. 148—31.57

3 Claims

### ABSTRACT OF THE DISCLOSURE

A method of making permanent magnets comprising the steps of pulverizing an alloy consisting of (a) selected rare earth metals and (b) cobalt (or mixtures of Co with Fe and Mn) characterized by high crystal anisotropy in specific atomic percent ratios, mixing the pulverized alloy with a binding agent, subjecting said powder to a magnetic field of sufficient magnitude so as to align the alloy particles with their direction of easiest magnetization parallel to the applied magnetic field, and thereafter permanently bonding together the aligned powdered alloy, and the article resulting therefrom.

This application is a division of our application, Ser. No. 644,460, filed June 5, 1967 and now Pat. No. 3,424,578.

### BACKGROUND OF THE INVENTION

#### Field of the invention

The present invention is predicated on the discovery that certain known intermetallic compounds possess high crystal anisotropy and when subjected to certain processing steps will form permanent magnets.

Representative of such compounds is yttrium pentacobaltide,  $\text{YCo}_5$ . It is to be understood that neither the discovery of  $\text{YCo}_5$  per se or its property of ferromagnetism is alleged but rather a specific process for treating  $\text{YCo}_5$  and related compounds to form a permanent magnet.

By way of further explanation and background, the terms "ferromagnet" and "permanent magnet" are by no means synonymous. The first term simply indicates the existence of an ordered arrangement of the atomic magnetic spin moments, a basic physical phenomenon also found in iron and in many other substances. A "permanent magnet," however, is a specific device for technological application. While a material has to be ferro- or ferrimagnetic to qualify for use in permanent magnets, the properties demanded of the latter are not inherent in any ferromagnetic material. The material must have a certain combination of basic properties which may be optimized by such measures as adding alloying elements or heat treating. Furthermore, rather complicated processing of the material is usually necessary to produce a "permanent magnet" with the best possible properties.

With the present invention, the basic property of  $\text{YCo}_5$ , for example, which the present inventors believe they were the first to recognize and measure, was its extremely large uniaxial crystal anisotropy. Only with the knowledge of this property and not on the basis of previously published values for Curie point, magnetization, etc., of  $\text{YCo}_5$  was it possible to predict and to develop process steps whereby permanent magnets could be made of  $\text{YCo}_5$ .

The technology set forth herein with respect to making permanent magnets from known ferromagnetic  $\text{YCo}_5$  represents a distinct and marked advance in the art even

2

as "Lodex" and "Alnico" magnets were of patentable merit. With regard to the "Lodex" magnets, pure iron, pure cobalt, and solid solution alloys of these elements have long been known to exist and to be ferromagnetic. However, the idea of using elongated single domain (ESD) particles for magnets, developed mainly in the last ten years, has resulted in a series of patents on "Lodex" magnets concerned with the basic principles and properties of such particles as well as details of particle and magnet preparation. In connection with "Alnico" magnets, ferromagnetic alloys of iron with cobalt and nickel have been known for many decades. Yet in the course of developing the family of alloys known as "Alnicos," various patents were issued covering first the use of such alloys processed in a certain manner for permanent magnets and later minor alterations in composition, heat treatment, sintering, etc., which resulted in better permanent magnets. With such precedents, it is believed that the unusually strong permanent magnets made from  $\text{YCo}_5$  by the process steps set forth herein are clearly of patentable merit.

#### Description of the prior art

The most pertinent prior art is probably represented by U.S. Pat. No. 3,102,002 to Wallace et al. who describe a group of ferromagnetic materials on compounds prepared from certain of the lanthanide elements and the transition metals of the first long period which have formulae corresponding to  $\text{AB}_5$  where A is a lanthanide element or yttrium and B is manganese, cobalt or iron. However, Wallace et al. only describe some basic crystallographic and magnetic properties of these compounds, including  $\text{YCo}_5$ . Furthermore, Wallace et al. make no specific statements about the merits of any of their listed compounds for permanent magnet application. Especially, no mention is made of the key property, "high crystal anisotropy," nor is there any reference to the necessity of making powders of the compounds.

### SUMMARY OF THE INVENTION

The present invention consists essentially of a novel method of preparing a permanent magnetic material and the product resulting therefrom which is characterized by a high saturation magnetization, a reasonably high Curie temperature of several hundred degrees C., and high coercive force. The permanent magnets made by the present method are made from particles with magnetocrystalline anisotropy instead of shape anisotropy, and thereby avoid a number of disadvantages noted of the latter. The outstanding advantage of the permanent magnet material made by the present method is its potential energy product which is 29.2 mg. oe. (1 mg. oe. =  $10^6$  gauss $\times$ oersted) for 100 percent packing of perfectly aligned, single-domain particles and 16.4 mg. oe. for 75 percent density packing. This compares with (a) 9.5 mg. oe. for a platinum and cobalt alloy which is the maximum energy product known for a commercial magnet, (b) 12.5 mg. oe. for the best laboratory magnet of "Alnico," and (c) 6.5 mg. oe. for the commercial "Lodex" (ESD) magnets.

The permanent magnets of the present invention find application in communication equipment, control devices, navigational instruments, auxiliary power generators, etc. Specific examples include instruments which are based on the galvanometer principle, small electrical motors and generators, microwave tubes (in magnetrons and as focusing magnets in traveling wave tubes), biasing magnets for relays, microphones and telephones, and loudspeakers. The use of magnets in motors to replace the conventional stator windings is rapidly gaining acceptance and, while until recently only very small rotating electrical machines were built this way, permanent

magnets are now invading the medium-power motor field. New concepts for equipment to be used on board of air—or spacecraft are presently under study which require strong, large-volume, steady magnetic fields such as magnetohydrodynamic energy converters, devices which would direct the flow of hot plasma or of radiation particles around a space vehicle, and magneto-plasma-dynamic engines for space vehicles. While present designs are mostly based on the use of electromagnets, permanent magnets of appreciably larger energy density than presently available combined with good high-temperature performance would simplify designs considerably and reduce the equipment weight.

#### BRIEF DESCRIPTION OF THE DRAWING

In the accompanying drawing:

FIG. 1 is a graph showing the intrinsic coercive force of powders produced by ballmilling plotted as a function of grinding time and particle diameter.

FIG. 2 is a graph showing the magnetization curves of a spherical single crystal of  $\text{YCo}_5$  measured in the easy and hard directions; and

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is predicated upon the discovery that permanent magnet materials or alloys having a potential energy product which surpasses available permanent magnet material by a factor of over 2.5 can be prepared from (1) a rare earth metallic component selected from the group consisting of yttrium, scandium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium including mixtures thereof and (2) a second metallic component selected from the group consisting of cobalt, manganese and iron including mixtures thereof. This discovery in turn is dependent upon the recognition and measurement for the first time of the extremely large uniaxial crystal anisotropy of the aforementioned materials as typified by  $\text{YCo}_5$  coupled with certain process steps. The manner in which the magneto-crystalline anisotropy of  $\text{YCo}_5$  is measured is set forth in an article entitled "Magneto-crystalline Anisotropy of Some Rare-Earth-Cobalt Compounds" published in the Journal of Applied Physics, March 1967. The ratio of rare earth metal employed to the second metallic component is 11 to 22 atomic percent rare earth metal to 78 to 89 atomic percent of Co, Fe or Mn.

In general, the permanent magnet materials of the present invention are prepared by melting together the desired amounts of the two general components, such as Y and Co, under a protective noble gas atmosphere or under a vacuum. This step may be effected by arc melting on a cold copper hearth, induction melting in pure alumina crucibles, or containerless levitation melting so as to avoid crucible contamination. The resulting alloy, such as  $\text{YCo}_5$ , can be formed in ~30 gram buttons and then crushed and thereafter ground in a ball mill or a vibratory mill. By way of example, after 24 hours ball-milling time, all particles will be smaller than 53 microns, with further milling particles having a diameter as small as .3 to 3 microns can be obtained and effectively used in the present process. (See FIG. 1.) Vibration milling was found to be considerably faster, yielding 1 to 5 $\mu$ -size particles in periods of ½ to 10 hours with charges of  $\text{YCo}_5$  varying from 1 to 25 grams. However, it should be noted that these particles are relatively large compared to the 100 to 1000 A. diameters of the particles required for shape anisotropy particles of comparable coercive force.

Thereafter the particles of the alloy are bonded together which may be effected by several methods. Use of an organic resin or plastic binder, such as an epoxy resin, is simple and will yield magnets that are sturdy,

easy to shape, and corrosion resistant. They will not be usable at temperatures much above room temperature. High temperature capability may be achieved by sintering or hot-pressing the powder without a binder, or with an inorganic binder such as boron nitride or a metal power. In either case, a magnetic field of at least several kilo-oersteds must be applied before or during the consolidation if oriented magnets with optimum magnetic properties are desired. By way of example, the finely divided particles of  $\text{YCo}_5$  have been formed into magnets by the following three different methods: (1) The powder was mixed with molten paraffin and the mixture permitted to solidify in a magnetic field of ~14 koe.; (2) The powder was compacted to a density of ~60 volume percent by means of a hydraulic press in a field of ~6 koe. and the resulting magnet soaked in a polystyrene solution and subsequently dried; (3) The powder was stirred into a quick-setting epoxy resin which hardened while the magnet was in a homogeneous 20 koe. field.

The basic principles and considerations of the properties of permanent magnets of this kind were discussed previously in the publication by K. Strant and C. Hoffer, "YCo<sub>5</sub> A Promising New Permanent Magnet Material," AFML-TR-65-446, Air Force Materials Laboratory, Wright-Patterson Air Force Base, May 1966. These authors determined the magnetocrystalline anisotropy constants of  $\text{YCo}_5$  at room temperature from magnetization vs. field curves measured on a spherical single crystal of ~1 mm. diameter in the direction of the c-axis and normal to it. These curves are shown in FIG. 2.  $\text{YCo}_5$  was found to have a single "easy" magnetic direction, the c-axis, and no detectable anisotropy in the basal plane in which the crystal is hardest to magnetize. The maximum applied external field of ~45 koe. was far insufficient to saturate the crystal in a direction in the basal plane. A straight line extrapolation off the M vs. H curve for the basal plane yields a saturation field  $H_A \approx 132$  koe. (also called "anisotropy field"). Based on this extrapolation one can calculate the extremely high anisotropy constant.

$$K = 5.7 \times 10^7 \text{ erg/cm}^3$$

The following examples are submitted to illustrate further the invention and not to limit the invention.

#### EXAMPLE I

The metals yttrium (Y) and cobalt (Co), both commercial products of 99.9% nominal purity, were mixed in the weight ratio of 1 to 3.31 (atomic ratio 1:5). Pea-size lumps or chips from machining on a lathe were used. In the latter case, it was found advantageous to precompact the charge to prevent loss of chips during melting. The charges of 5 to 10 grams were melted in a levitation furnace (USAF Technical Documentary Report No. ML-TDR-64-90, "A Levitation Melting Apparatus for the Preparation of Ultrapure Samples of Reactive Materials" by John C. Olson, April 1964) and then cast and cooled rapidly by dropping the melt into a cold, thin-walled porcelain crucible of 5 cm.<sup>3</sup> capacity. Temperatures of over 1600° C. were reached during melting, a protective atmosphere of purified argon gas of typically ~7 p.s.i.a. pressure was employed to prevent reaction of the yttrium with oxygen or nitrogen of the air. The resulting ingots were wrapped in tantalum foil, fused into evacuated quartz bulbs, and annealed at a temperature of ~1000° C. for 100 hours. This treatment typically resulted in homogeneous alloys and metallographic sections appeared completely single-phase and coarse-grained. The ingots were then crushed in a hardened-steel mortar until the grains passed through a 60 mesh sieve.

Fifty (50) grams of this coarse powder together with 100 cm.<sup>3</sup> of hexane were placed in an alumina milling jar (5" ID x 5" long) with 12 cylindrical alumina pieces (3/4" OD x 1" long) and "ballmilled" for 50 hours.

The resulting slurry was removed from the jar, dried by letting the hexane evaporate at room temperature, and portions of the powder consolidated into magnets in the following different ways:

(a) 8 grams were placed in a  $\frac{1}{2}$ " diameter cylindrical brass die to be compressed between two hardened carbon-steel pistons inserted axially. An axial magnetic field was applied with a solenoid surrounding the die. The field was repeatedly turned on and off before pressure was applied, and was then maintained during compacting in an attempt to align the powder particles with their magnetic easy axes parallel to one another. Because the moving pistons also served as pole caps, the field acting on the sample during compression varied from an initial  $\sim 6000$  oersted to  $\sim 9,000$  oe. A pressure of 51,000 p.s.i. was applied. A cylindrical magnet resulted which had a density of 4.5 g./cm.<sup>3</sup> (60% of massive YCo<sub>5</sub>) and a powdery surface and the following magnetic properties:  $B_r=3680$  g.,  $MH_c=1180$  oe.,  $BH_c=930$  oe.,  $(BH)_{max}=1.1 \times 10^6$  Goe.

(b) 10 g. of the powder were intimately mixed with 2.5 cm.<sup>3</sup> of a clear lacquer (Plastiklear No. 225, an acrylic ester resin in colloidal solution containing  $\sim 12\%$  by weight solids, manufactured by the Illinois Bronze Powder Company, Chicago, Ill.), using a porcelain mortar and pestal. The mixture was dried completely in a stream of warm air of  $\sim 50^\circ$  C. and re-powdered in the mortar. The powder was then compacted as described before, except that 1" diameter dies and pistons were used and the field varied from 11,000 to 15,000 oe.

The product was a disc magnet,  $\sim \frac{1}{8}$ " thick and 62% dense (massive YCo<sub>5</sub>=100%) which is mechanically much stronger than the magnet made without a binder. The properties measured in the alignment (=pressing) direction normal to the disc face are  $B_r=3500$  g.,  $MH_c=960$  oe.,  $BH_c=750$  oe.,  $(HB)_{max}=0.7$  MGoe.

(c) In an attempt to use an inorganic binder which would not interfere with use of the magnet at elevated temperatures, 10 g., of YCo<sub>5</sub> powder were mixed with 2.0 g. of 325 mesh boron nitride powder in the porcelain mortar. The mixture was compressed as in (a). The compact had mechanical strength and cohesion superior to those of the binder-free magnet, but not as good as those of the acrylic-plastic bonded one, with magnetic data inferior to both.

#### EXAMPLE II

In contrast to the procedure of Example I, the YCo<sub>5</sub> alloy was prepared by fusing the alloying constituents Y and Co in an arc melting furnace having a water-cooled copper hearth and a non-consumable tungsten electrode. Melting was done under a protective atmosphere of either pure argon gas or an argon-helium mixture, the charges weighing between 30 and 60 grams. Each charge was melted and resolidified three to four times to assure good mixing, the "buttons" were turned over between meltings. The ingot usually broke into several pieces under the thermal stress. They were vacuum-annealed for five days at  $1100^\circ$  C. The material prepared in this manner was again crushed to a coarse powder in the steel mortar. 100 g. of powder were ballmilled as described in Example I, but more pieces of grinding medium were used (20 alumina cylinders) and 100 cm.<sup>3</sup> of hexane were initially added. Samples of powder were taken from the jar at regular time intervals for coercive force measurements, and hexane was replenished as needed to maintain the same consistency of the thin slurry.

Specimens for coercive force measurements were made by mixing a small amount (200–300 mg.) of the dried powder with ca. 5 times its weight of an epoxy resin (Allaco Twenty/Twenty), then putting the thick liquid in a 0.4" I.D. x 0.6" cylindrical mold of Teflon, and letting the epoxy harden at a temperature of  $\sim 70^\circ$  C. while a magnet field of  $\sim 15,000$  oe. was applied to orient the particles in axial direction. Measurements of the in-

trinsic coercive force in this direction as a function of milling time and estimated average particle size are summarized in FIG. 2. A maximum value of  $MH_c=1850$  oe. for  $\sim 5\mu$  particles is followed by a drop-off on prolonged milling which is attributed to plastic deformation of the particles which destroys the favorable magnetic symmetry. It is expected that this undesirable "overmilling effect" can be overcome when the powders are vacuum-annealed at temperatures between  $300^\circ$  and  $600^\circ$  C., or if they are prepared by a technique which avoids plastic deformation such as grinding below room temperature, but for powders prepared by ballmilling at room temperature coercive forces appear to be limited by it.

#### EXAMPLE III

An alloy was made of 28.3 weight percent yttrium-rich mischmetal (Y-MM) and 71.7 weight percent Co by arc melting as in Example II and vacuum annealing for 160 hours at  $1000^\circ$  C. The resultant material was  $\sim 95\%$  single-phase and brittle. It was mortar-crushed to  $-60$  mesh size, a small amount of the powder was imbedded in epoxy resin and this binder was allowed to harden in a magnetic field as described in Example II. Magnetization curves were measured on this aligned powder sample for the alignment direction and normal to it, using a maximum field of 45 koe. The magnetization curves resemble those of the YCo<sub>5</sub> single crystal (see FIG. 1). The following room temperature data were determined from the measurements on this alloy:

Saturation induction,  $B_s \approx 9,500$  g.  
Anisotropy field strength,  $H_A \approx 142$  koe.  
Anisotropy constant,  $K_1 + K_2 \approx 5.4 \times 10^7$  erg./cm.<sup>3</sup>  
Density,  $d = 8.06$  g./cm.<sup>3</sup>

From these results the conclusion is drawn that (Y-MM)Co<sub>5</sub>, as a fine particle permanent magnet material, behaves basically like YCo<sub>5</sub>. The upper limit for the energy product is  $(BH)_{max} = (B_s/12)^2 = 22.5 \times 10^6$  g. oe. The advantage of using the mischmetal instead of pure yttrium is a substantial reduction in the raw material cost with only a small sacrifice in magnet performance.

A typical analysis of Y-rich mischmetal (Y-MM) supplied by the Research Chemical Corporation, Phoenix Ariz., was as follows:

Element:	Approx. weight percent
Y	57
La	4
Ce	8
Pr	0.5
Nd	3
Sm	3
Gd	3
Dy	4
Ho	1
Er	4
Yb	4
Ca	7

In addition, there were also traces of other rare earths and other elements.

It is to be understood that the above mixtures are simply illustrative of the application of the basic principles of the present invention. By way of example other plastic or resinous materials can be employed as binders in addition to the aforementioned "Plastiklear" No. 225 and "Allaco Twenty/Twenty." In general the requirements for a binder to be used in dense magnets in the manner outlined above (Example Ib) are as follows:

The application form must be a true solution or a colloidal suspension of particles having an average size below  $\sim 0.1\mu$ . The application viscosity must be 100 centipoise (cps.). Preferably on the order of 1 cp. The boiling point of the solvent should be under  $150^\circ$  C., preferably near  $50^\circ$  C.; the coating left on the particles after evaporation of the solvent must bond them into a solid body under

pressures of less than 50,000 p.s.i. at temperatures below 70° C.; the resulting plastic must have very low absorption for water from the atmosphere.

Another satisfactory commercial product of the same general type as Plastiklear No. 225, is GC Koloid-Clear Acrylic, which like Plastiklear is available in the form of an aerosol container made by the GC Electronics Company, Rockford, Ill. This is a colloidal solution of methyl methacrylate in butyl acetate, 40% solids.

On the other hand, a resin to be effective as a binder or matrix for coercive force specimens (see Example II above) should have the following general properties:

A chemically hardening two-liquid system without a filler material having a low application viscosity (<5,000 cp. at 25° C.) and a pot life longer than 15 minutes. It must cure into a hard solid (rather than a rubber-like substance) in no more than 2 hours at room temperature, no more than 30 minutes from the atmosphere.

In addition to Allaco Twenty/Twenty, another commercial product which gives satisfactory results as a binder or matrix for coercive force specimens is Allaco Crystal-Clear also made by Allaco Products, Incorporated, 238 Main Street, Cambridge, Mass.

What we claim is:

1. A permanent magnet having as the active magnetic component an alloy in particle form consisting of component A selected from the group of rare earths consisting of Y, Y-rich mischmetal, Ce, Pr and Sm, and a second component B selected from the group consisting of:

(a) Co alone, and

(b) Co plus at least one metal selected from the group consisting of Mn and Fe,

in the ratio of 11 to 22 atomic percent for component A and 78 to 89 atomic percent for component B.

2. A permanent magnet having as the active magnetic component an alloy in particle form consisting of yttrium and cobalt in the ratio of 11 to 22 atomic percent for said yttrium and 78 to 89 atomic percent for said cobalt.

3. A permanent magnet having as the active magnetic component an alloy in particle form consisting of an yttrium-rich mischmetal and cobalt in the ratio of 11 to 22 atomic percent for an yttrium-rich mischmetal and 78 to 89 atomic percent for said cobalt.

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