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## METHOD OF MAKING PERMANENT MAGNET MATERIAL POWDERS HAVING SUPERIOR MAGNETIC CHARACTERISTICS

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4 Claims

### ABSTRACT OF THE DISCLOSURE

The grinding of bulk permanent magnet material to powder can result in a relatively low value of the maximum coercive force obtainable and can also limit the extent to which it is possible to align the powder particles in a binding medium to produce a composite permanent magnet material. By the present method involving immersion of such bulk material for a short time in a hydrochloric acid solution containing thiourea, powder particles are produced which have high coercive forces and excellent alignability characteristics.

The present invention relates generally to the art of making permanent magnets and is more particularly concerned with new magnetic material powders having unique characteristics and with a novel method of producing these powders.

It is generally recognized that the permanent magnet properties of bulk magnetic materials having large crystalline anisotropies can be enhanced by reducing them to powders. It is also common knowledge that such a powder can be aligned in a bonding medium by a magnetic field to produce a composite permanent magnet body having superior properties in the alignment direction. These advantages are, however, offset to a substantial degree in some instances when the particle size reduction is accomplished by grinding. Thus, both a comparatively low value of coercive force and a limitation upon the extent of alignment can outweigh the advantages to be gained by converting the bulk body to a powder and fabricating a composite finished article from the powder.

In accordance with the present invention, these detrimental effects of grinding can be avoided through an operation which can readily be carried out with consistently good results and with no substantial offsetting disadvantage. In essence, this operation or method of this invention centers in the key step of contacting bulk permanent magnet material with an aqueous mineral acid solution containing an organic compound corrosion inhibitor. Contact is relatively brief, as from 30 seconds to 30 minutes, and does not result in the dissolution of any significant amount of the bulk material, but the beneficial effect of a grinding step is obtained in that the bulk magnetic material is reduced to fine particle size.

This invention method thus is predicated upon my surprising discovery that under certain circumstances a brief chemical treatment can take the place of a grinding step or even a series of heavy grinding steps in reducing bulk permanent magnet material to fine powder form. It is also based upon my discovery that there are a number of alternative treating solutions which can be used for this purpose with uniformly good results and without any

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penalty of reduced yield of magnet material or other substantial disadvantage.

As a general proposition, the chemical treatment is carried out in accordance with this invention by contacting the bulk magnet material with a solution of hydrochloric acid, sulfuric acid or nitric acid diluted with water to intermediate or lower strength. Preferably, the magnet material is in the form of a coarse powder and is immersed in the acid solution and thereafter rinsed free of the solution. The solution content has as an essential ingredient a small amount of an organic corrosion-inhibitor such as thiourea, p-thiocresol or benzaldehyde.

Time, temperature, acid concentration and particle size of the permanent magnet material to be treated are inter-related factors in this method. I have found, however, that the practical operating ranges of these variables are so broad that the necessity for precise control of the method can readily be avoided. Except for threshold conditions of time, temperature, concentration and bulk material size, none of the operating conditions or combination of these conditions is highly critical, making the difference between operability and inoperability. Rather, there is a practical range of each variable in relation to the others which lies between the somewhat arbitrary limits of the economies of the method of this invention. This bulk material in the form of coarse powder is more rapidly and efficiently treated to produce a given amount of desired fine particle powder product than bulk material in the form of somewhat larger pieces can be, assuming the other conditions of the operation are the same. Similarly, the process is accelerated by increasing the temperature of the treating solution and the yield of desired product is increased within limits by prolonging the treatment period. Acid concentration exerts only a small influence on the product quality so far as has been observed as long as acid is present in an amount from 0.25 percent to 20 percent.

In accordance with my preference, the treating solution during use will be about room temperature, although it can be any temperature at which the solution exists in the liquid state so that the bulk magnet material may be immersed in it for the required time of treatment. The period of immersion may likewise be varied from a minimum of 30 seconds to 30 minutes or more with my preference being from one to ten minutes. Longer times may lead to diminishing product yields, particularly if the treating solution temperature is in the range approaching the solution boiling point temperature. On the other hand, periods shorter than 30 seconds are not sufficient for the production of good product yields even when solution temperature is high and the bulk material is a coarse powder.

For practical purposes, I prefer that the bulk magnet material to be treated by this new method be of particle size less than 100 microns and suitably less than 25 microns. I have found that permanent magnet materials can be ground to such sizes without significantly impairing the desired properties of the powder product ultimately obtained by subjecting these ground materials to the present invention method. Thus, apparently it is in the final stages of reduction by grinding that these materials are detrimentally affected and it is this undesirable effect which is avoided by my chemical treatment step.

This present method has been found in actual practice to be particularly beneficial in the treatment of cobalt-base permanent magnet materials including  $\text{Co}_5\text{Y}$ ,  $\text{Co}_5\text{Sm}$

and Co<sub>5</sub>Ce. The results obtained by applying the method to materials of this kind are summarized in Table I:

ments in a protective atmosphere of argon. The resulting ingot was very brittle. A piece weighing approximately

TABLE I

Material	Coercive force of initial -25 micron powder, oersteds <sup>1</sup>	Composition of aqueous solution	Time in solution, minutes	Coercive force of treated material, oersteds <sup>1</sup>
Co <sub>5</sub> Y.....	525	20% HCl+.2% thiourea.....	1	1,780
			3	3,200
			5	5,400
			15	4,700
Co <sub>5</sub> Sm.....	3,100	.....do.....	2	6,850
Co <sub>5</sub> Sm.....	<sup>2</sup> 6,000	.....do.....	1	<sup>2</sup> 8,400
Co <sub>5</sub> (cerium-rich misch metal). Co <sub>5</sub> Sm.....	1,400	.....do.....	1	2,000
	4,350	5% HCl+.05% thiourea.....	1	5,450
			2	7,800
Co <sub>5</sub> Y.....	660	20% HCl+.2% thiourea.....	10	6,750
Co <sub>5</sub> Y.....	635	20% HCl+.2% benzaldehyde.....	5	1,080
Co <sub>5</sub> Y.....	635	20% HCl+.04% thiourea.....	15	4,850
Co <sub>5</sub> Y.....	635	20% HCl+.1% thiourea.....	15	4,500
Co <sub>5</sub> Y.....	635	20% HCl saturated with p-thiocresol.....	25	3,270
Co <sub>5</sub> Y.....	635	5% H <sub>2</sub> SO <sub>4</sub> +.1% thiourea.....	10	2,800
Co <sub>5</sub> Y.....	402	10% HNO <sub>3</sub> +.2% thiourea.....	5	1,500

<sup>1</sup> All coercive force values measured after magnetization in field H<sub>m</sub>=21,000 oersteds unless otherwise indicated.  
<sup>2</sup> H<sub>m</sub>=29,000 oe.

The powder products set out in Table I are new in the art in that the several cobalt-base permanent magnet materials have never before existed in the form of powders having the combination of magnetic properties, and especially the very high coercive forces, possessed by these novel products. They are also new in that they have X-ray diffraction patterns which in respect to line width are essentially identical to those of the bulk or unground starting material from which they are obtained. These materials owe these unique properties to the novel method of their production which also serves to characterize and distinguish them from permanent magnet material powders of the prior art.

While I do not intend any limitation upon the appended claims, it is my belief and theory that the results obtained in applying this method to permanent magnet materials as exemplified in Table I can be explained on the basis that the particles which are produced by grinding to final size have locked-in stresses resulting from cold-working strains which impair desirable magnetic characteristics of these materials. The fact that this impairment is more marked in powders produced by heavy grinding is consistent with this hypothesis and the discovery underlying the present invention method is further substantial proof. Additional substantiation of the theory consists in the facts that while the lines of the X-ray diffraction pattern of the initial bulk material and the product obtained by this process are essentially of the same sharpness and width, the lines of the X-ray diffraction pattern of the product produced by grinding the same initial material are invariably considerably broader and blurred. Thus, the substitution of a chemical treatment for the final grinding step or phase results in further comminution of the bulk material (as a coarse powder) to final size without cold working the material and without impairing its desirable magnetic properties. Accordingly, I contemplate very broadly and generally as my invention and contribution to the art the concept of subjecting powder particles of permanent magnet materials to a chemical treatment which results in further size reduction of these particles to the same or similar extent as is accomplished in accordance with the acid solution contacting step described elsewhere herein with resulting superior magnetic characteristics in the final product.

To further illustrate and describe this invention method to those skilled in the art, the following are examples of processing operations as I have actually carried them out:

EXAMPLE I

Co<sub>5</sub>Y was prepared by arc-melting together the ele-

½ gram was ground with a mortar and pestle for a few seconds. The resulting powder was washed with water through a coarse fritted glass filter, using suction, yielding several milligrams of -25 micron powder. This was rinsed with acetone and allowed to dry. A portion of it was removed for magnetic testing. This portion was mounted in a glass sample holder in molten paraffin. A magnetic field of about 1000 oersteds was applied as the paraffin solidified. The sample holder was then placed in a vibrating-sample magnetometer. The coercive force measured in this instrument after applying a magnetizing field of 21,000 oersteds was 660 oersteds. The rest of the sample was placed in a dish with 10 ml. of a solution of 20% HCl+.02% thiourea. This was placed on a magnetic stirrer in order to agitate the particles in the solution. After 10 minutes the particles were rinsed with water and then with acetone and allowed to dry. They were then mounted in paraffin and tested as above. The coercive force was 6750 oersteds.

EXAMPLE II

The experiment of Example I was repeated with induction-melted Co<sub>5</sub>Sm being substituted for Co<sub>5</sub>Y. All the conditions and operations were as stated in Example I except that the powder particles were in contact with the acid solution for only two minutes. The coercive force of the resulting powder product was measured to be 6850 oersteds, as reported in Table I.

EXAMPLE III

A product nominally Co<sub>5</sub>Ce was prepared by arc-melting together cobalt and cerium-rich misch metal in a protective atmosphere of argon. Following the procedure stated in Example I except that the acid solution contact period was limited to one minute, a powder product was obtained which had a coercive force of 2000 oersteds, as reported in Table I.

EXAMPLE IV

In still another experiment, a Co<sub>5</sub>Ce powder product having a coercive force of 2020 oersteds was prepared from a -20 micron powder fraction obtained from the Example III ingot. The -20 micron starting material powder was found by the Example I technique to have a coercive force of 1125 oersteds. The acid treating solution in this instance was 0.25% HCl and 0.4% thiourea (balance water as in all these examples and in all instances reported in Table I). The solution contact period in this case, however, was five minutes.

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## EXAMPLE V

Another experiment like that of Example IV was performed to test the effect of an aqueous 5% HCl treating solution containing 0.4% thiourea. Thus, all other conditions were as stated in Example IV. The ultimate powder product had a coercive force of 1690 oersteds.

## EXAMPLE VI

Still another experiment to test the effect of varying the acid concentration in the aqueous treating solution was performed using  $\text{Co}_5\text{Ce}$  produced and prepared as a -20 micron powder as set forth in Examples IV and V. In this instance, however, the aqueous treating solution had an HCl content of 1.0% and a thiourea content of 0.4%. With all other conditions being the same as those stated in Examples IV and V, a final product powder was obtained which was measured to have a coercive force of 1750 oersteds.

Wherever percentages or proportions are stated in this specification and the appended claims, reference is made to the volume basis rather than the weight basis.

Having thus described this invention in such full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains to make and use the same, and having set forth the best mode contemplated of carrying out this invention, I state that the subject matter which I regard as being my invention is particularly pointed out and distinctly claimed in what is claimed, it being understood that equivalents or modifications of, or substitutions for, parts of the specifically described embodiments of the invention may be made without departing from the scope of the invention as set forth in what is claimed.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. In the method of producing a permanent magnet of a cobalt rare earth compound having the formula  $\text{Co}_5\text{R}$  where R is selected from the group consisting of yttrium, cerium and samarium by mechanically reducing the cobalt-rare earth compound to a coarse powder having a particle size of less than 100 microns, the improve-

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ment consisting in treating the reduced powder particles to substantially increase their coercive force by washing the powder particles for at least 30 seconds with an aqueous acid solution containing from 0.25 percent to 20 percent of a mineral acid and from 0.04 percent to 2 percent of an organic corrosion inhibitor, said washing treatment being carried out at a temperature at which the mineral acid solution remains in a liquid state.

2. The method of claim 1 in which the bulk magnet material is  $\text{Co}_5\text{Y}$  in the form of coarse minus 25 micron powder and the contacting step consists in submerging the  $\text{Co}_5\text{Y}$  bulk material in a 5 percent  $\text{H}_2\text{SO}_4$  solution containing 0.1 percent thiourea.

3. The method of claim 1 in which the bulk magnet material is  $\text{Co}_5\text{Sm}$  in the form of coarse minus 25 micron powder and the contacting step consists in submerging said  $\text{Co}_5\text{Sm}$  powder for 5 minutes in a 20 percent hydrochloric acid solution containing 0.2 percent thiourea.

4. The method of claim 1 in which the bulk magnet material is  $\text{Co}_5\text{Ce}$  in the form of coarse minus 25 micron powder and the contacting step consists in submerging the said  $\text{Co}_5\text{Ce}$  powder for one minute in a 20 percent hydrochloric acid solution containing 0.2 percent thiourea.

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