

[54] **METHOD OF MAKING PERMANENT MAGNETS**

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[22] Filed: **Mar. 23, 1970**

[21] Appl. No.: **21,785**

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 538,985, Mar. 31, 1966, Pat. No. 3,502,584, and a continuation-in-part of Ser. No. 9,939, Feb. 9, 1970, abandoned.

[52] U.S. Cl. .... **204/10**, 148/31.57, 204/39, 252/62.55

[51] Int. Cl. .... **C22d 5/00**, C23b 5/00, B22f 3/00

[58] Field of Search ..... 204/10, 39; 252/62.55; 148/31.55, 31.57

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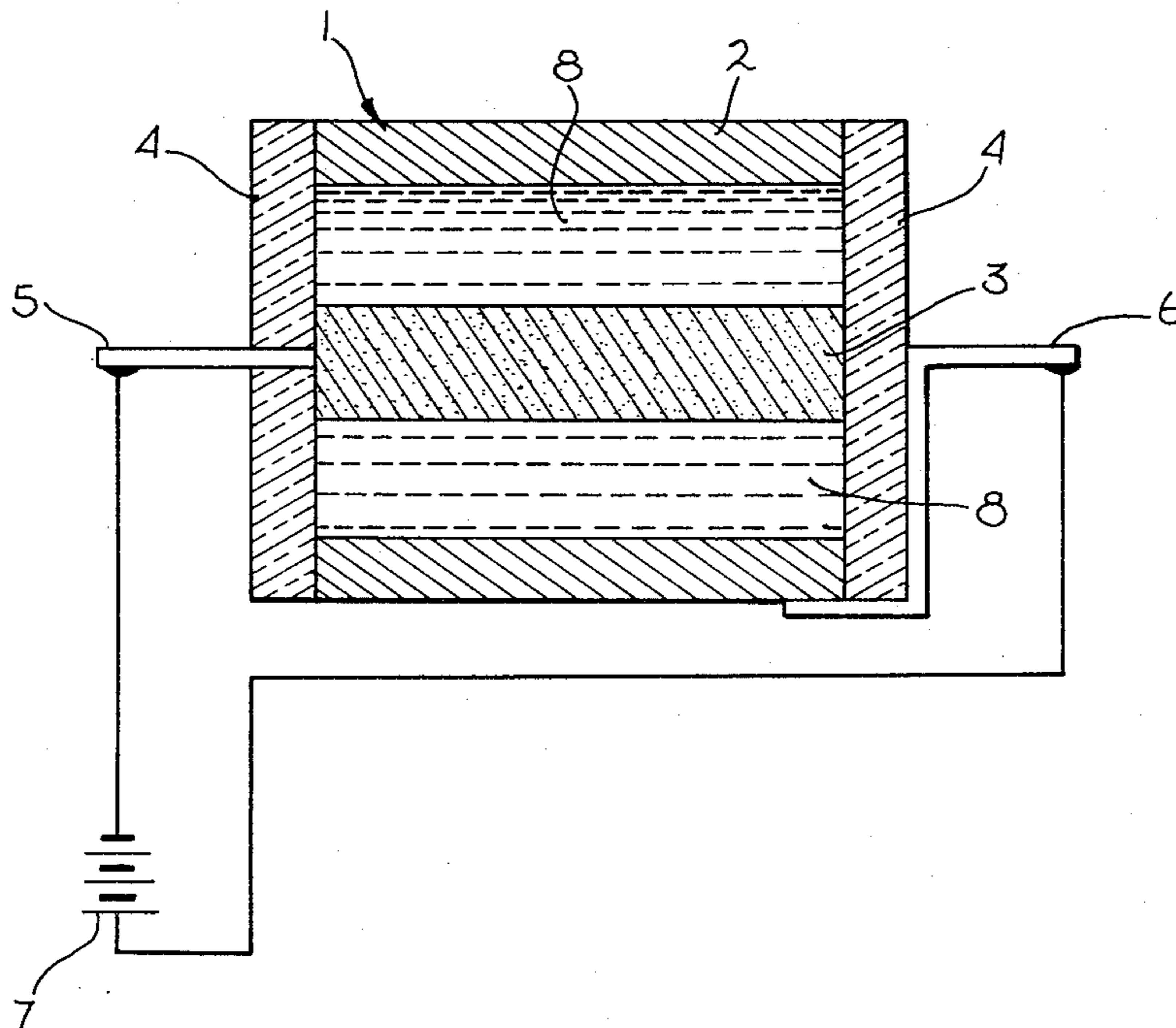
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[57] **ABSTRACT**

A method for making single phase or multiphase permanent magnets having high intrinsic coercivity, in which a molten state salt electrolysis technique is used to produce a variety of magnetic metallic or alloy particles, in controllable sizes. The magnetic particles thus produced are then bonded and formed into permanent magnets.

**33 Claims, 3 Drawing Figures**



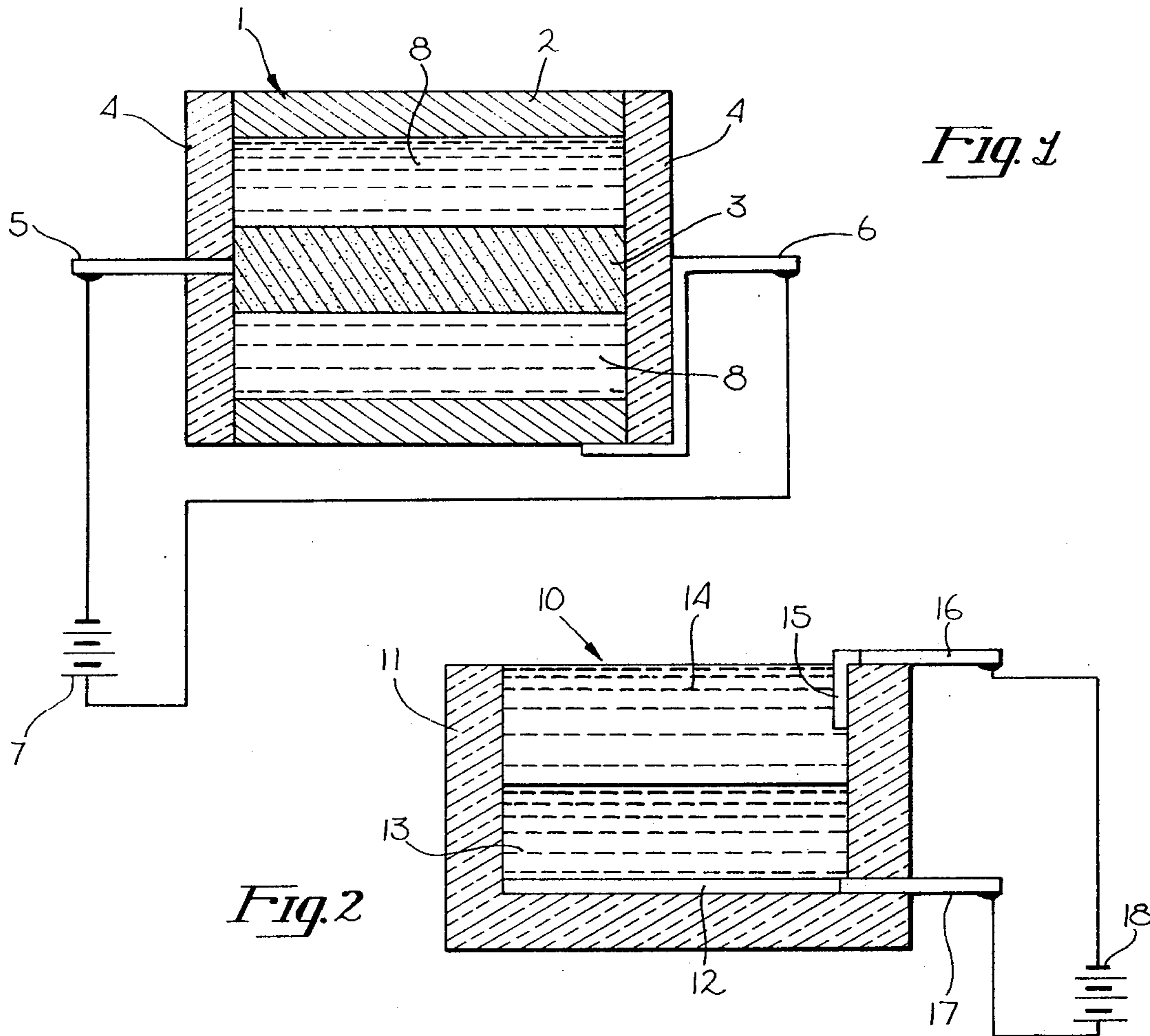


Fig. 2

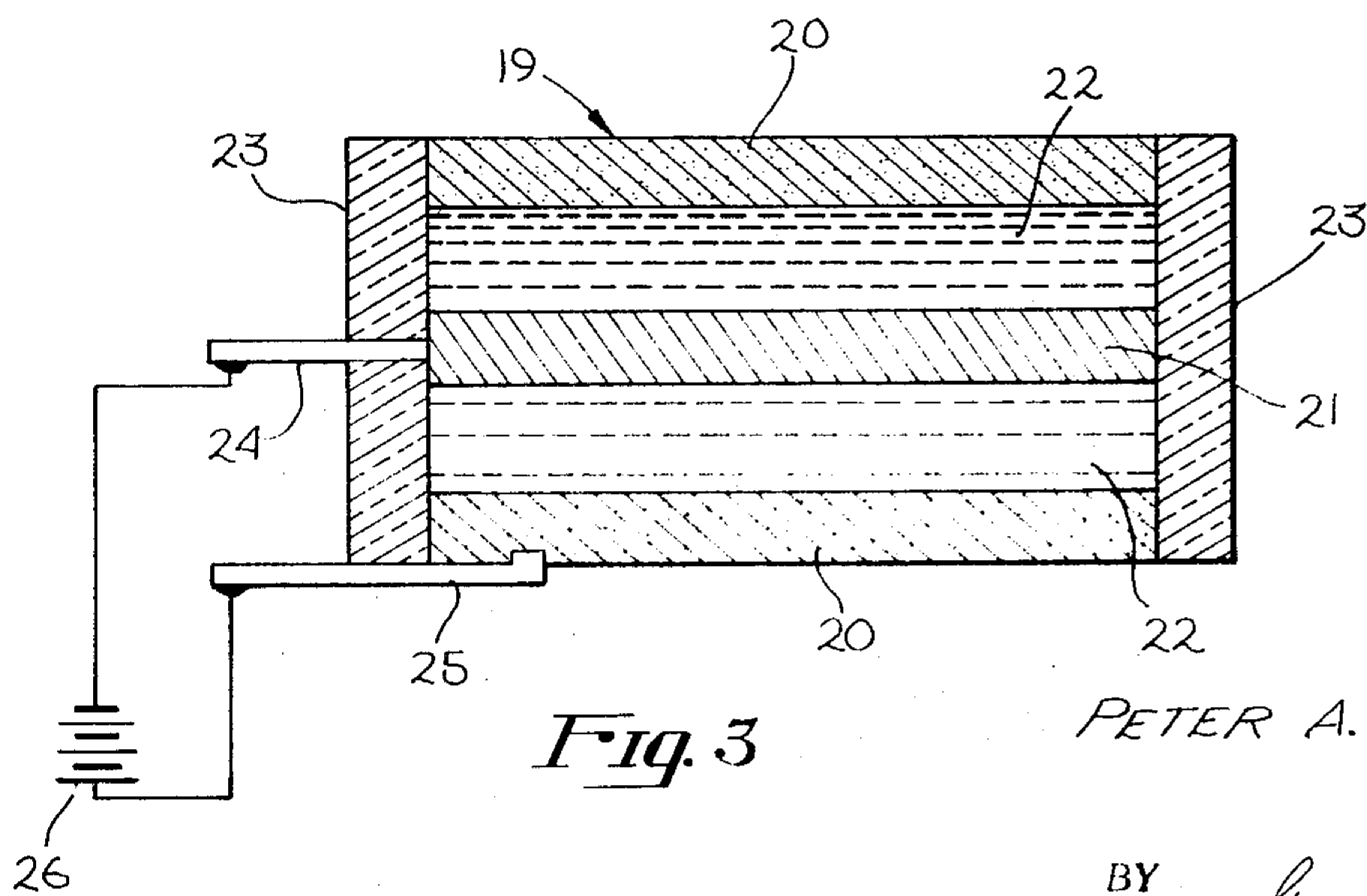


Fig. 3

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**METHOD OF MAKING PERMANENT MAGNETS**

This is a continuation-in-part of my pending application Ser. No. 538,985, filed Mar. 31, 1966 and now U.S. Pat. No. 3,502,584, and of my co-pending application entitled "Permanent Magnetic Material and Method of Making Same," Ser. No. 9,939 filed Feb. 9, 1970 and now abandoned, which teaches the making of composite permanent magnetic material containing at least two different and distinguishable permanent magnetic materials in particulate form.

In this application the phrase "single phase magnetic material" refers to material which is a homogeneous metal or alloy, while "multiphase magnetic material" refers to composite magnetic material.

**BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present application relates generally to magnetic materials and more specifically to magnetic materials utilized in permanent magnets.

**2. Description of the Prior Art**

Permanent magnets which are presently known in the art are metals or alloys of a group which includes iron, nickel, cobalt, aluminum, titanium, vanadium, tungsten, molybdenum, manganese, bismuth, rare earth metals, etc., all of which are highly reactive metals. Therefore, the prior art teaches that cast permanent magnets have to be made primarily by vacuum melting and vacuum casting, to avoid oxidation of the metals or alloys. Sintered permanent magnets have also been made by sintering in vacuum or in a neutral or reducing atmosphere, for the same reason.

Magnetic materials have been classified as "soft" magnetic and "hard" or "permanent" magnetic material. It is known that the magnetic materials classified in the past as soft magnetic materials become hard or permanent magnetic materials if the magnetically isolated particles are so small that they contain only one magnetic domain. The classically named "permanent magnetic" materials are magnetic systems which have a relatively high intrinsic coercivity; e.g., more than 50 Oersteds even in a multidomain structure. However, the coercivity of these permanent magnets can be greatly increased if they are produced of magnetically isolated single domains. The role of intrinsic coercivity, obtainable by such means, is of great importance. If the coercivity, expressed in Oersteds, is about equal or greater than the saturation induction in Gauss, the remanence,  $B_r$ , is approximately equal to the saturation induction,  $B_s$ , and the magnetic energy product is the maximum which a magnetic material of that saturation induction can yield; specifically,  $B_r^2/4$  Gauss.Oersted.

As stated above, the presently known hard magnetic materials are made by casting or sintering in a protective atmosphere. Hence, the resulting permanent magnets in most cases do not have the maximum intrinsic coercivity obtainable by single domain systems and do not reach the maximum possible magnetic energy product defined above. It is known that cast bodies of metals or alloys cannot generally be ground to single domain size particles, such particles being approximately between 0.02 and 10 microns in size. Although small single domain metal particles can be produced by low temperature reduction, no alloys can be obtained at such low reduction temperatures (generally lower than 400° C). This is a significant limitation in the prior art since the best permanent magnetic systems are alloys. Metals or alloys of the iron, nickel, cobalt group can also be produced by wet electrolysis, employing a mercury cathode. These metals do not alloy with mercury, but the small metal or alloy particles remain suspended in it and can be separated by removing the mercury, e.g., by vacuum distillation. The production of permanent magnets by this method is limited to those metallic or alloy constituents which can be deposited by use of aqueous electrolytes. However, many constituents of modern magnets are too reactive to allow an electrolytic deposition of any aqueous solution.

The present invention overcomes these shortcomings of the prior art by enabling the production of a great variety of magnetic metals and alloys in single domain sizes. When such single domain magnetic particles are united to a permanent magnetic body, so as to secure the preservation of the particles as single domains, the resulting permanent magnet achieves the maximum possible permanent magnetic characteristics of the particular metals or alloys used. A preferred method of uniting magnetic particles into a permanent magnetic body while preserving them as single domain particles is taught by the disclosures in my pending application, Ser. No. 538,985, filed Mar. 31, 1966, and of my copending application entitled "Permanent Magnetic Material and Method of Making Same," Ser. No. 9,939, filed Feb. 9, 1970, which teaches the making of composite permanent magnetic material containing at least two different and distinguishable permanent magnetic materials in particulate form.

**SUMMARY OF THE INVENTION**

The present invention teaches a method of producing both a single phase permanent magnet which has a very high intrinsic coercivity, and a multiphase permanent magnet in which at least one phase has a very high intrinsic coercivity. The "very high intrinsic coercivity" referred to above includes coercivities within the range of about 500 to 50,000 Oersteds. The invention proposes electrolytic decomposition of the compounds which contain the constituents of the magnetic system, such compounds being in the form of molten salts and serving as electrolytes. Employing suitable protective measures, practically all the metals known can be produced by molten salt electrolysis; and, further, the co-deposition of several metals results, in most cases, in the production of desirable alloys. The liquid electrolyte may be any meltable inorganic, or metallo-organic compound of the desired magnetic constituents which, in liquid phase, does not harmfully react with the deposited metal or alloy particles. Further, it is known in the art that salts which are good electrical conductors may be employed in the electrolyte to increase the applicable cathode current density, and, thereby, increase the production rate of the magnetic particles. Such conductive salts are, for example, halides, nitrates, nitrites, sulfates, etc., of alkali metals. Still others conducting salt compounds will be mentioned in the examples below. The compounds of the magnetic constituents may be oxides, sulfides, halides, etc., which do not melt at the operating temperature of the cell, but which can be dissolved in the molten conductive salts. In addition, the electrolyte may contain certain complex salts; e.g., molybdenum can be deposited from molten sodium dimolybdate,  $\text{Na}_2\text{Mo}_2\text{O}_7$ , the melting point of which is 612° C.

The invention discloses the production of such magnetic metals or alloys in controllable size particles. This is achieved by preventing the growth of the particles beyond a certain limit by removing them from the cathode in predetermined time intervals. The removal may occur by mechanical means or by coincidental generation of certain liquid metals or alloys which do not alloy with the magnetic particles, but which remove them from the cathode when produced. A third means of removing the magnetic particles from the cathode is to utilize a liquid cathode consisting of a metal or alloy whose propensity to alloy with the magnetic particles produced is at a tolerable level.

The molten salt electrolysis of the permanent magnetic materials disclosed herein may utilize any molten salt system which generally satisfies the following two conditions:

- a. the melting temperature should be lower than that at which adverse effects may occur to the deposited magnetic material, such adverse effects include excessive particle size growth, beyond the single domain size; and/or unwanted alloying or chemical reactions between the phases of a multiphase magnetic system; and,
- b. the salts remaining after the electrolysis should be removable from the deposited magnetic material without

adversely affecting said magnetic material. Thus, the chemicals selected for the dissolution of the salt remainders must be ones which do not attack the deposited magnetic particles; i.e., do not degrade their magnetic properties. Mild solvents of the employed salts are preferred, such as water, alcohol, glycerin, hydrocarbons, etc.

By reference to my pending application, Ser. No. 538,985, filed Mar. 31, 1966, and my copending application entitled "Permanent Magnetic Material and Method of Making Same" Ser. No. 9,939, filed Feb. 9, 1970, which teaches the making of composite permanent magnetic materials, this invention discloses the production of a composite permanent magnet containing at least two different and distinguishable permanent magnetic materials in particulate form, each of which material continues to possess approximately the same individual characteristics it has out of the combination; i.e., as separate particles. Optimum permanent magnetic characteristics can be obtained if the first material has a high saturation induction and the second material has a high intrinsic coercivity, although this patent application is not intended to be limited to such structures only.

The invention and its essential features will be better understood in the light of the description of the preferred embodiments and the drawings which follow.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a typical molten salt electrolytical cell utilizing a cylindrical anode.

FIG. 2 is a cross-sectional view of a typical molten salt electrolytical cell utilizing a liquid cathode.

FIG. 3 is a cross-sectional view of a typical molten salt electrolytical cell utilizing a cylindrical cathode.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Several preferred embodiments are described herein for implementing molten salt electrolysis. Each embodiment differs from the others in the particular method utilized to remove the deposited magnetic particles from the cathode at predetermined time intervals, thereby controlling particle size. In the described embodiments the molten salt electrolysis process takes place at melting temperatures which do not adversely affect the deposited magnetic particles; and further, after completion of the electrolysis process, the salts which remain are such that they can be removed from the magnetic material without adversely affecting it.

A preferred embodiment contemplates an electrolytical cell 1 such as depicted in FIG. 1. The electrolytical cell 1 is comprised of a cylindrical anode 2, which can be, for example, a rhodium plated heat resistant alloy; side plates 4 which completely cover and seal the ends of the cylinder 2, and which can be made of an insulating material resistant to the molten salt 8, such as aluminum oxide; a cathode 3, mounted between the centers of the side plates 4, which cathode can be, for example, a graphite rod with a particular surface texture selected, as disclosed below, to determine the shape of the magnetic particles removed from said cathode; an anode 5 which connects the cathode 3 to a conventional electrical power source 7, and which is installed through an orifice in one of the side plates 4 in such a manner as to prevent leakage of the molten salt 8 through such orifice; an electrode 6 connecting the anode 2 to the return side of the power source 7; and a molten salt electrolyte 8 contained within the interior of the enclosed cylinder 2. A conventional electrical power source 7 is connected to the electrodes 5 and 6 of the cell 1. If a conventional electric motor is mechanically coupled to the cell 1 by conventional techniques for power transmission (configuration not shown) the whole cell, including the cathode rod, can be rotated. When so rotated, the magnetic particles deposited on the cathode 3 are freed from the attracting influence of the cathode and, in most cases, will fall to the bottom of the cell 1. The rate of rotation is a function of the size of the electrolyte cell 1 and of the desired particle size.

Typically, the range of rotation rates is from 1 to 1,000 revolutions per minute. The removal process can be enhanced if the cathode 3 also is vibrated, e.g., at a frequency between 5 and 1,000,000 cycles per second. The configuration and power source for the controlled vibration of the cathode 3 can also be implemented by known techniques (not shown). In addition, the removal of the magnetic particles from the cathode 3 can be effected or further enhanced by the utilization of "magnetic jolts" at predetermined time intervals. Methods are known in the art for generating magnetic impulses in a desired direction. One method, for example, employs an electrical coil which is energized periodically by capacitive discharges. The magnetic particles are then collected in the molten salt 8 at the lower part of the cell 1. When the electrolytical process is completed, the magnetic particles can be reclaimed from the liquid or frozen salt. Several reclaiming methods are available, including decanting, and the removing of the salts by their dissolution in a solvent, such as, for example, water, the latter method being capable of accomplishment with no effect upon the magnetic particles. The thickness of the magnetic particles deposited can be accurately controlled by means of the rotational rate of the cell 1; the frequency and amplitude of the vibration of the cathode 3; the temperature of the molten salt 8; the current density on the cathode 3; and by the time intervals between the "magnetic jolts."

The above-described method produces flake shaped magnetic particles of controllable thickness. Often it is desirable to determine the approximate dimensions of the magnetic particles in length and width; for example, to produce approximately cubic or needle shaped particles. To achieve this object the present invention proposes the use of a cathode with a special surface texture comprising a fine mixture of conductive and non-conductive materials, both of which can withstand the molten electrolyte. One example of a cathode surface for production of cubic magnetic particles is a mixture of colloidal size graphite and colloidal size aluminum oxide, both sintered to the surface of a graphite cathode. If needle shaped magnetic particles are desired, the graphite particles in the abovedescribed mixture may be in the shape of very fine filaments; graphite particles so shaped are available in the art.

In another preferred version of the present invention, an electrolytical system is devised in which other metals or alloys are deposited in addition to the desired magnetic particles. The former metals or alloys, however, do not alloy with the desired magnetic metal or alloy, but serve to remove them from the cathode as they are produced.

It is known that some members of the group of so-called alkali metals, namely, lithium, potassium, rubidium, sodium, do not alloy at all, or alloy only in a very minute amount, with iron, nickel, chromium, titanium, vanadium, tungsten, zirconium, tantalum, niobium, hafnium, beryllium, manganese, aluminum, copper, etc., and their alloys. If the voltage of the electrolytical cell 1 is high enough to deposit simultaneously alkali metals or alkali metal alloys together with the magnetic constituents, the separation of the magnetic particles from the cathode is achieved by the generation of a different liquid phase. The melting points of potassium, rubidium, and sodium are below 100° C; the melting points of some alkali metal alloys are below room temperature. Hence, the codeposited alkali metals or alloys immediately melt in the cell 1. The liquid alkali metal phase surrounds the deposited magnetic metal or alloy particles which are simultaneously deposited. However, the alkali metals or alloys do not alloy with the magnetic particles. By this process the alkali liquid phase separates the magnetic particles from each other and removes them from the cathode 3. Once removed from the cathode 3, the magnetic particles fall to the bottom of the cell 1.

Certain constituent metals in the electrolyte 8 do form alloys with some of alkali metals (or their alloys). These constituent metals include bismuth, antimony, tin, zinc, and silver. Nevertheless, if alloys containing any of the above constituents are deposited simultaneously with the deposition of alkali metals (or their alloys), the constituent metal, in many

cases, will alloy with the permanent magnetic particles present, rather than with the alkali metals as a result of minimum energy laws. The alloys formed in this way, even though containing bismuth, zinc or silver, for example, are no longer attached by the alkali metal (or their alloys).

In yet another preferred version of the present invention an electrolytical cell 10, as depicted in FIG. 2, is contemplated. The cell 10 is comprised of an open container 11, made of an electrically insulating material, such as beryllium oxide, which is resistant to the molten salt electrolyte 13, and to the molten cathode 14; an anode 12, disposed at the bottom of the container 11, which anode may be, for example, a platinum plated tungsten sheet; a molten cathode 14, such as, for example, an alkali metal or alloy which has a lighter density than the molten salt electrolyte 13, and which, therefore, floats above said electrolyte; a graphite plate 15 which is electrically in contact with the molten cathode 14; an electrode 16 which connects the plate 15 and, therefore, the molten cathode 14, to a conventional electrical power source 18; and an electrode 17 which connects the anode 12 to the return side of the power source 18, and which is installed through an orifice in the container 11 in such a manner as to prevent leakage of the electrolyte 13 through such orifice. A conventional electrical power source 18 is connected to the electrodes 16 and 17 of the electrolytical cell 10.

In this embodiment, the magnetic particles generated by the electrolysis process are deposited into the molten cathode 14 where they at first float. The molten cathode 14 does not form alloys with the magnetic particles. Because the specific density of the magnetic particles is higher than that of both the molten cathode 14 and the molten salt electrolyte 13, they gradually sink toward the bottom of the container 11. After the completion of the electrolysis, the permanent magnetic particles are removed from the molten electrolyte 13 by any one of several known methods including decanting, dissolution of the salt, etc. The following factors influence the average size of the magnetic particles deposited in the molten cathode 14; the voltage of the power source 18; the temperature of the cell 10; and the length of time during which the magnetic particles dwell in the molten cathode 14. The said voltage also effects the "dwell time" of the magnetic particles. More specifically, a higher voltage causes the deposited magnetic particles to move farther up in the molten cathode 14; since removal of the magnetic particles from the molten cathode 14 is by gravitational force, the particles are in the cathode 14 for a greater time before they emerge into the electrolyte 13 where they cease to grow. In addition, the rate of removal of the magnetic particles can be greatly increased, and controlled, by means of a vertical magnetic field generated by conventional techniques. Control of the removal rate is achieved by regulation of the strength of said magnetic field.

In still another preferred version of the present invention a particulate magnetic metal or alloy is first distributed in a rotating electrolytical cell 19 similar to the one shown in FIG. 3. Such a cell 19 is especially suitable for applications requiring the coating of one type of magnetic material with another; for example, for coating a magnetic material having a high saturation induction with one having a high intrinsic coercivity.

The electrolytical cell 19 is comprised of a cylindrical cathode 20, which, for example, can be made of graphite; side plates 23 which completely cover and seal the ends of the cylindrical cathode 20, and which can be made of an insulating material resistant to the molten salt electrolyte 22, such as aluminum oxide; an anode 21, mounted between the centers of the side plates 23, which anode can be a graphite rod, for example; an electrode 24 which connects the anode 21 to a conventional electrical power source 26, and which is installed through an orifice in one of the side plates 23 in such a manner as to prevent leakage of the molten salt 22 through such orifice; an electrode 25 connecting the cathode 20 to the return side of the power source 26; and a molten salt electrolyte 22 contained within the interior of the enclosed

cylinder 20. A conventional electrical power source 26 is connected to the electrodes 24 and 25 of the cell 19. If a conventional electric motor is mechanically coupled to the cell 19 by conventional techniques for power transmission (configuration not shown) the whole cell 19 can be rotated. Likewise, a power source can be coupled to the cathode 20 to effect the vibration of said cathode. The configuration and power sources for the controlled vibration of the cathode 20 and the rotation of the entire cell 19 can be implemented by known techniques, and are not shown.

As noted above this electrolytical cell 19 is especially suitable for the production of a double phase magnetic system in which a second magnetic material is coated on powders of a first magnetic metal or alloy. The powders of said first magnetic metal or alloy are distributed in the cell 19 and come in electrical contact with the cathode 20 due to the force of gravity. As the cell 19 rotates, all the surfaces of the first magnetic material (powder) are exposed to the effects of the electrolysis. As a result, the second magnetic material uniformly deposits on the surfaces of the powders of the first magnetic metal or alloy. At the same time particles of the second magnetic material are also generated and deposited on the portions of the cathode 20 which are free of the first metal or alloy powder. The rotation and/or vibration of the cathode 20 insures that the coated magnetic particles are kept separated. In addition, "magnetic jolts" can be utilized to stir up the particles, thereby improving the uniformity of the coating.

When the electrolytical process is completed, the magnetic particles can be reclaimed from the liquid or frozen salt by conventional techniques such as decanting, or dissolution in a solvent like, e.g., water, which removes completely the salts without any effect upon the magnetic particles.

The thickness of the magnetic coating deposited can be accurately controlled by means of the rotational rate of the cell 19; the frequency and amplitude of the cathode 20 vibration; the temperature of the molten salt 22; the current density on the cathode 20; the time intervals between "magnetic jolts"; and by the total duration of the electrolysis. These factors can be varied so that the coating, i.e., the second magnetic phase has one single magnetic domain. This provides maximum intrinsic coercivity for the composite system. The structure of such a magnetic system, wherein the high intrinsic coercivity material completely surrounds the lower coercivity magnetic material, eliminates the possibility of internal magnetic leakage.

Several examples illustrating the generation of permanent magnetic metallic or alloy particles in controllable sizes using the invented method are described below:

#### EXAMPLE I

The electrolyte 8 consists of 30 percent by weight of nickel iodide,  $\text{NiI}_2$ , and 70 percent by weight of sodium iodide,  $\text{NaI}$ . The operating temperature is  $750^\circ\text{C}$ ; the applied voltage 8.5 volts D.C. An electrolytical cell 1 similar to that of FIG. 1 is rotated at a rate of 150 revolutions per minute and, at the same time, the cathode 3 is vibrated with a frequency of 5,000 cycles per second. The surface of the cathode 3 is a mixture of conductive and insulating areas, both having an average linear dimension of approximately 800 Angstroms. The deposited nickel particles have an average particles size of 800 Angstroms.

#### EXAMPLE II

The electrolyte 8 consists of 50 percent by weight cobalt (II) chloride,  $\text{CoCl}_2$ , and 50 percent by weight potassium chloride,  $\text{KCl}$ . Both the cathode 3 and the anode 2 are made of graphite. The voltage is relatively high, 30 volts D.C., in order to codeposit cobalt and potassium which do not alloy. The operating temperature is  $800^\circ\text{C}$ . After the electrolysis is completed and the deposit removed, the latter is placed in a vessel and heated in a vacuum to  $120^\circ\text{C}$ , in order to melt the potassium particles. The vessel in which said deposit is heated

is made of a non-magnetic material. Consequently, when a strong magnetic field is applied at the bottom of said vessel, the magnetic particles collect there. The major part of the liquid potassium, which has a density of only one tenth that of cobalt, is then decanted. The remaining particles of potassium can be washed out with water in a nitrogen atmosphere. The average size of the cobalt particles is 500 Angstroms.

#### EXAMPLE III

The electrolyte 13 consists of 25 percent by weight iron (II) chloride,  $\text{FeCl}_2$ , 25 percent by weight cobalt (II) chloride,  $\text{CoCl}_2$ , and 50 percent by weight potassium chloride,  $\text{KCl}$ . The operating temperature is  $800^\circ\text{C}$ . The liquid cathode 14 as shown in FIG. 2 is molten potassium. The working voltage is 30 volts, which is high enough to codeposit potassium as well as the iron-cobalt (magnetic) particles. The average size of the iron-cobalt particles deposited in the molten potassium is approximately 200 Angstroms.

#### EXAMPLE IV

A mixture of 255 grams manganese (II) fluoride,  $\text{MnF}_2$ , and 745 grams bismuth (III) fluoride,  $\text{BiF}_3$ , is heated to  $900^\circ\text{C}$  as a fused electrolyte 8. The cathode 3 is carbon, with a surface pattern of alternating conducting and insulating areas of 0.2 microns in each linear dimension; the anode 2 is stainless steel plated with platinum. The cathode 3 is vibrated with a frequency of 12,000 per second. The produced bismuth-manganese particles have an average particle size of approximately 0.2 microns, and their intrinsic coercivity is greater than 20,000 Oersteds.

#### EXAMPLE V

The melting point of potassium dichloriodide,  $\text{KICl}_2$ , is relatively low, approximately  $60^\circ\text{C}$ . Into a 1,000 gram "melt" of potassium dichloriodide the following compounds are dissolved: 300 grams cobalt (II) chloride,  $\text{CoCl}_2$ , and 250 grams cerium chloride,  $\text{CeCl}_3$ . The temperature of the electrolyte 8 is kept at  $200^\circ\text{C}$ . The voltage is 30 volts D.C. in order to cause the co-deposition of potassium. The potassium does not alloy with the produced magnetic particles of cobalt-cerium,  $\text{Co}_3\text{Ce}$ , but it causes the removal of said particles from the cathode 3. Magnets made of these particles have an intrinsic coercivity of 20,000 Oersteds and an energy product of  $14 \times 10^6$  Gauss.Oersteds, if the particles are magnetically oriented.

#### EXAMPLE VI

An example of a low melting point organic fused salt is ethyl pyridium bromide, the melting point of which is  $112^\circ\text{C}$ . Into a 3,000 gram "melt" of ethyl pyridium bromide, the following quantities of metal chlorides are dissolved: 476 grams of iron (II) chloride,  $\text{FeCl}_2$ , 225 grams cobalt (II) chloride,  $\text{CoCl}_2$ , 150 grams aluminum chloride,  $\text{AlCl}_3$ , 131 grams nickel (II) chloride,  $\text{NiCl}_2$ , and 18 grams copper (I) chloride,  $\text{CuCl}$ . The temperature of the "melt" is kept at approximately  $140^\circ\text{C}$ . The applied voltage is 10 volts. The cathode 3 is a graphite rod, whose surface is a mixture of alternating conductive and insulating squares having a linear dimension of 0.5 micron. Such a structure can be easily produced by a photoetching process, since the operating temperature is low. The insulating material on the cathode 3 can be, e.g., epoxy. During the electrolysis process magnetic material coats the surface of the cathode 3. When the thickness reaches 0.5 microns, the electrolysis is interrupted. The thickness can be determined by measuring the elapsed time of the electrolysis, since the magnetic particle growth rate on the cathode 3 is a known function of the cathode current density and the operating temperature. Following interruption of the process, the cathode 3 is removed from the cell 1, and the magnetic particles are physically brushed off. The resulting particles have a composition close to that of Alnico V and an average particle size of 0.5

microns. Their intrinsic coercivity is greater than 1,000 Oersteds; and the energy product of sintered magnets made of these particles can be  $7 \times (10)^6$  Gauss.Oersted if the particles are oriented in a magnetic field.

#### EXAMPLE VII

Alloy powders consisting of 50 percent by weight iron and 50 percent by weight of cobalt, of an average particle size of 1 micron, are distributed in a rotating cell 19 similar to that one shown in FIG. 3. The particles come to rest on the lower part of the cathode 20. The electrolyte 22 consists of 31 percent by weight cobalt (II) bromide,  $\text{CoBr}_2$ , 9 percent by weight samarium (II) bromide,  $\text{SmBr}_2$ , and 60 percent by weight sodium bromide,  $\text{NaBr}$ . The operating temperature is  $800^\circ\text{C}$ . The cylindrical cell 19 is rotated at a rate of 300 revolutions per minute. The iron-cobalt particles, being in electrical contact with the rotating cathode 20, become coated with a cobalt-samarium alloy, and at the same time, cobalt-samarium alloy particles are also deposited on the free parts of the cathode 20. The cathode 20 is vibrated with a frequency of 500 cycles per second, to free both kinds of particles from said cathode.

Rare-earth-cobalt magnets, as a group, have among the highest known values of intrinsic coercivity relative to other magnetic compounds. This is true even in bulk form where the intrinsic coercivity of some rare-earth-cobalt compounds can be as high as 25,000 Oersteds. Much higher values can be achieved when particles of these magnets are in the single domain size.

The composite particles produced in this way have a structure in which the high coercivity material completely surrounds the low coercivity material, and, hence, no internal magnetic leakage can occur through the low coercivity material. Consequently, the intrinsic coercivity of the composite material is approximately identical with that of the coating material, i.e., the cobalt-samarium alloy, and of the individual cobalt-samarium particles, reclaimed from the cathode 20. The saturation induction of the iron-cobalt alloy particles is 24,500 Gauss. Hence, the saturation induction of a composition of 60 percent by weight iron-cobalt particles and 40 percent by weight samarium-cobalt coating and samarium-cobalt particles is approximately 18,000 Gauss. Since the intrinsic coercivity of the cobalt-samarium alloy is higher than that value, the remanence of the composite system is also approximately 18,000 Gauss. Such a magnetic system, with an intrinsic coercivity of 25,000 Oersted, yields a magnetic energy product of more than  $60 \times (10)^6$  Gauss.Oersted.

#### EXAMPLE VIII

The iron-cobalt particles of Example VII are coated with a bismuth-manganese alloy. The electrolyte 22 consists of 45 percent by weight bismuth trioxide,  $\text{Bi}_2\text{O}_3$ , 15 percent by weight manganese dichloride,  $\text{MnCl}_2$ , and 40 percent by weight potassium chloride,  $\text{KCl}$ . Operational temperature is  $900^\circ\text{C}$ . The ratio between the iron-cobalt and bismuth-manganese alloys is 50-50%. The intrinsic coercivity of the resulting system is 20,000 Oersted; the remanence is 15,000 Gauss; the magnet energy produce is  $40 \times (10)^6$  Gauss.Oersted.

#### EXAMPLE IX

The melting point of the mixture of 46.5 mol % lithium fluoride,  $\text{LiF}$ , 11.5 mol % sodium fluoride,  $\text{NaF}$ , and 42 mol % potassium fluoride,  $\text{KF}$ , is  $454^\circ\text{C}$ . Into a 3,000 gram "melt" of the above-described mixture, 1,000 grams of salts are dissolved in the following ratios: 50 mol % cobalt (II) chloride,  $\text{CoCl}_2$ , 33.3 mol % copper (I) chloride,  $\text{CuCl}$ , and 16.7 mol % cerium chloride,  $\text{CeCl}_3$ . The temperature of the electrolyte 22 is kept at  $550^\circ\text{C}$ . Cobalt powders with an average particle size of 3 microns are distributed within the cell 19. The voltage applied is 12 volts D.C. The plating is completed when the average coating thickness of the cobalt-copper-cerium alloy on the cobalt particles is 1 micron. The approximate ratio of cobalt to cobalt-copper-cerium is 68 percent to 32 percent.

The maximum energy product of the hot pressed magnets is  $40 \times (10)^6$  Gauss.Oersted.

The materials formed by the invented methods disclosed herein may then be formed into permanent magnets. Preferred embodiments and examples relating to the formation of solid permanent magnetic bodies are discussed in my pending application, Ser. No. 538,985, filed Mar. 31, 1966, and in my copending application entitled "Permanent Magnetic Material and Method of Making Same" Ser. No. 9,939 filed Feb. 9, 1970, which teaches the making of composite permanent magnetic material containing at least two different and distinguishable permanent magnetic materials in particulate form. In particular, my pending application, Ser. No. 538,985 teaches in Example III the forming of composite permanent magnetic material utilizing, in part, particles of a ferromagnetic iron-cobalt alloy. The present invention discloses in Example III a method for producing the iron-cobalt particles required for the above-referenced forming of permanent magnets. Iron-cobalt particles are also used in Examples VII and VIII disclosed in my pending application, Ser. No. 538,985 (although for applications other than the forming of permanent magnets). In my copending application entitled, "Permanent Magnetic Material and Method of Making Same," Ser. No. 9,939, filed Feb. 9, 1970, which teaches the making of composite permanent magnetic material containing at least two different and distinguishable permanent magnetic materials in particulate form, Examples I, III, and IV disclose methods of forming permanent magnetic material using, in part, either particles of iron-cobalt (Example I) or particles of cobalt-samarium (Example III) or both (Example IV). The present invention teaches in its Example III a method for producing particles of iron-cobalt alloy; and in Example VII a method for producing particles of cobalt-samarium.

The forming of solid permanent magnetic bodies, with or without magnetic orientation, may be achieved by other methods which do not adversely alter the magnetic properties of the particles used. Similarly, the basic principles disclosed above for the generation of permanent magnetic particles, of controllable sizes, are susceptible of numerous other applications which will be apparent to persons skilled in the art.

Therefore, the specific examples given and cited hereinabove are to be considered as only illustrative of some preferred embodiments and/or methods of utilizing the present invention; and the invention is not intended to be limited thereto.

I claim:

1. A method of making controllable size permanent magnetic particles comprising the steps of:
  - a. providing an electrolytic cell having first and second electrodes;
  - b. providing in said cell a molten salt electrolyte having therein a compound containing a material for the desired permanent magnetic particles;
  - c. providing a given voltage to said electrolytic cell causing the deposition of the desired magnetic particles on said first electrode;
  - d. removing said magnetic particles from said first electrode at predetermined time intervals, whereby the time interval for removal is a determining factor as to the size and intrinsic coercivity of said magnetic particles.
2. The method of claim 1 in which said first electrode is a cathode, said second electrode is an anode.
3. The method of claim 1 in which said magnetic particles have a size within the range of about 0.02 to 10 microns.
4. The method of claim 1 in which said magnetic particles have intrinsic coercivities within the range of 500 to 50,000 Oersteds.
5. The method of claim 1 in which the content of the electrolytic cell is exposed to intermittent magnetic pulses to aid in removing the magnetic particles from said first electrode and in controlling the particle size.
6. The method of claim 1 in which the melting temperature of the electrolyte is lower than the temperature which will adversely affect the deposited magnetic particles.

7. The method of claim 1 in which the salts remaining after the completion of the electrolysis are salts from which said magnetic particles can be recovered without adverse effects.

8. The method of claim 1 in which the magnetic particles are removed by applying magnetic pulses while simultaneously said first electrode is vibrated and said electrolytic cell is rotated, causing the magnetic particles to be removed from said first electrode into said salt electrolyte, and then removing said particles from said electrolyte.

9. The method of claim 1 in which the surface of the cathode has a texture of alternating conductive and insulating areas.

10. The method of claim 9 in which the conductive areas have an approximately square shape.

11. The method of claim 9 in which the conductive areas have the shape of needles.

12. The method of claim 9 in which the material of the conductive areas is graphite.

13. The method of claim 1 in which the magnetic particles are removed by rotating said electrolytic cell causing the magnetic particles to fall from said first electrode into said molten salt electrolyte and then recovering said particles from said electrolyte.

14. The method of claim 13 in which said electrolyte cell is rotated at rates between 1 and 1,000 revolutions per minute.

15. The method of claim 13 in which said particles are recovered from said molten salt electrolyte by decanting.

16. The method of claim 13 in which said particles are recovered from said molten salt by relative dissolution.

17. The method of claim 13 in which particles of a magnetic metal are placed in physical and electrical contact with said first electrode, resulting in the coating of said metallic particles by the permanent magnetic material being deposited on said first electrode.

18. The method of claim 17 in which said permanent magnetic coatings on said magnetic metal particles are single domains.

19. The method of claim 13 in which particles of a magnetic alloy are placed in physical and electrical contact with said first electrode, resulting in the coating of said alloy particles by the permanent magnetic material being deposited on said first electrode.

20. The method of claim 19 in which at least 90 percent by weight of the constituents of said magnetic alloy are iron and cobalt.

21. The method of claim 20 in which said permanent magnetic coatings on said magnetic alloy particles are single domains.

22. The method of claim 1 in which said first electrode is vibrated to aid in removing the magnetic particles from said first electrode and in controlling the particle size.

23. The method of claim 22 in which said first electrode is vibrated between 5 and 1,000,000 cycles per second.

24. The method of claim 1 in which said voltage is applied sufficiently high to cause the deposition of another metal in addition to the deposition of said magnetic particles, where such other metal does not alloy with said magnetic particles but causes the removal of said magnetic particles from said first electrode.

25. The method of claim 24 in which said other metal deposited is an alkali metal.

26. The method of claim 1 in which said voltage is applied sufficiently high to cause the deposition of another alloy in addition to the deposition of said magnetic particles, where such other alloy does not alloy with said magnetic particles but causes the removal of said magnetic particles from said first electrode.

27. The method of claim 26 in which said other alloy deposited is an alloy alkali metals.

28. The method of claim 1 in which the magnetic particles are removed by simultaneously rotating the cell and vibrating said first electrode, causing the magnetic particles to be removed from said first electrode into said salt electrolyte, and then recovering said particles from said electrolyte.

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29. The method of claim 28 in which said particles are recovered from said molten salt electrolyte by decanting.

30. The method of claim 28 in which said particles are recovered from said molten salt electrolyte by selective dissolution.

31. The method of claim 2 in which said cathode is a molten metal whose specific density is lighter than that of said molten

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salt electrolyte and of said magnetic particles.

32. The method of claim 31 in which said molten cathode is an alkali metal.

5 33. The method of claim 31 in which said molten cathode is an alkali alloy.

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