

## UNITED STATES PATENT OFFICE

2,239,144

## PERMANENT MAGNET

Reginald S. Dean and Charles W. Davis, Washing-  
ton, D. C., assignors to Chicago Development  
Company, Chicago, Ill.

No Drawing. Application July 11, 1938,  
Serial No. 218,634

3 Claims. (Cl. 175-21)

Our invention relates to permanent magnets, and our present application is a continuation-in-part of our co-pending application Serial No. 711,820, filed February 17, 1934 now Patent No. 2,132,404.

In our prior co-pending application, we disclose methods of producing magnetic materials in a state of high coercive force. As one example of the general method disclosed in that application, we disclose the preparation of permanent magnets by the electrolysis of a magnetic metal, iron, into a mercury cathode, the removal of the mercury by distillation, and the compacting of the resulting material into a permanent magnet.

In addition to the objects set forth in our prior application, our present object is to provide improved methods for preparing such magnets to produce materials of enhanced magnetic properties, and magnets having increased usefulness in the industries in which permanent magnets are employed.

In accordance with our invention, we produce improved materials for the production of permanent magnets by dispersing a magnetic material, such as iron, with or without a non-magnetic material, such as aluminum, in a body of mercury, remove the mercury by suitable means, and compact the resulting highly pulverulent material into a suitable form.

The production of high coercive force in magnetic materials is facilitated greatly by producing them under conditions where crystal growth is greatly inhibited if not completely prevented. This is accomplished by electrolysis into a surface of mercury which interrupts the deposition of metal atoms and in the case of the metals iron, nickel, cobalt, manganese and chromium produces a dispersion of very fine metal particles in the mercury. The preferred condition of electrolysis to accomplish this purpose is deposition into a moving surface of mercury. Such motion may be one of flow or vibration. The removal of the mercury may be accomplished entirely by distillation as in the known art; we prefer, however, to remove as much mercury as possible from the dispersion in the cold. This may be accomplished by forcing the amalgam through a filter plate having fine perforations. Such a plate retains most of the metal in the form of a solid mass containing from 25-50% of metal depending upon the pressure used in filtering. We have found that an iron plate drilled with small holes makes an entirely satisfactory filter. The relatively solid material so obtained lends itself readily to mechanical feeding into an appropriate still and

after the removal of the mercury by distillation the resulting porous pellet is ready to go into a die for compacting into the form of a magnet.

In another form of our invention, the amalgam is concentrated by magnetic means. The amalgam as formed by electrolysis is passed through a magnetic field so that the magnetic material is attracted and the mercury or dilute amalgam passes through the field. The concentrated amalgam is then mechanically removed from the field and distilled. Various types of apparatus known in the art of magnetic separation may be adapted to this separation. The type used to separate magnetic particles from clay slips is especially useful provided the removable magnet poles are of such form that the solid amalgam can be readily removed.

In still another form of our invention, centrifugal force is used to concentrate the amalgam. The centrifuge may be of the bowl type or tubes may be used so as to obtain the concentrated amalgam in a form ready for distillation.

With any type of preliminary mercury removal, two units may be used so that a continuous flow through the electrolyte cell may be maintained, the volume of amalgam being kept constant by adding mercury from a reservoir which collects the condensate from the still.

The electrolyte cell itself may take various forms, but, in general, comprises a suitably modified Castner or Acker cell. The simplest form is a wooden trough with a relatively shallow layer of mercury, e. g. an inch deep in the bottom of the cell, and a number of anodes suspended above the mercury in the electrolyte. The mercury may either flow continuously or be changed intermittently. We have found it advantageous to continuously renew the surface by agitation or vibration.

In another form of electrolyte cell the electrolysis takes place in an upward direction, that is, from an electrolyte below to the under surface of a layer of mercury supported above by means of a suitable porous medium. The iron being lighter than the mercury rises in it as fast as deposited and leaves the lower mercury surface free of iron. This action may be strengthened by the application of a suitably placed magnet, which pulls the iron to the upper surface of the mercury layer.

A continuous operation based on these principles operates as follows: electrodeposition proceeds without interruption while the magnetic metal together with a certain amount of mercury is picked up by the magnet and is removed

for treatment to separate the magnetic metal and recover the mercury, the latter being added to the mercury as required.

When the magnetic material is iron, we prefer to use an electrolyte ferrous ammonium sulfate or ferrous sulfate (but a solution of many soluble iron salts may be used), and a pure iron anode. Although impure iron may be employed, to maintain a high current efficiency, a high purity of the anode is advisable. Electrolytic iron or the material known as Svea iron has proven satisfactory. The current density is not critical but we prefer to use about 10 amps. per sq. dm. The product obtained in this way has a coercive force of 125-150 and an induction depending upon the pressure. In the following table we give an example of the relation of Br to the pressure of compacting. These results are for iron magnets  $\frac{1}{2}$ " dia. by 1" long, and are merely illustrative.

Pressure #/sq. in.	Br (gauss)
20,000	3,300
50,000	4,500
150,000	7,500
200,000	8,900
250,000	9,300

In the case of cobalt produced in the same way, the anode may be electrolytic cobalt deposited from cobalt ammonium sulphate on platinum and the electrolyte being cobalt ammonium sulfate or some other suitable dissolved salt of cobalt. We have found that both Hc and Br are unexpectedly large, Hc being 400-500 oersteds and Br varying in accordance with the following table, the size of the magnets being as before  $\frac{1}{2}$ " by 1" long.

Pressure #/sq. in.	Br (gauss)
20,000	5,000
50,000	5,800
150,000	9,000
200,000	10,500
250,000	11,000

We have also found that the normally non-ferromagnetic metal manganese can be produced in a ferromagnetic form having high coercive force by this process. A manganese sulphate solution containing ammonium sulphate may be used for electrolyte with an anode of electrolytic manganese. The resulting amalgam is pressed to remove as much mercury as possible and the excess mercury distilled at 400-600 degrees C. In our development work, we found that this distillation temperature seemed to be necessary to produce a permanent magnet. As an alternative the mercury may be distilled off at a lower temperature and the resulting metal heated in vacuo or nitrogen to 400-600 degrees C. The following table gives the relation between the magnetic properties of permanent magnets made by compacting metallic manganese made in accordance with the above process at 250,000 lbs./sq. in. and the temperature of distillation or subsequent heating.

Temperature	Coercive force	Br
300	450	1.5
400	350	300
450	300	2000
500	250	3000
600	100	1500

The magnets may be made of many other metals and alloys which are either initially magnetic or become so by heat treatment by the use of our invention.

5 An especially interesting alloy is that of iron, nickel and aluminum. This alloy is produced by first depositing aluminum into mercury by electrolysis in a solution of aluminum bromide in acetone, using a platinum anode. The acetone is then removed and an electrolyte containing ferrous and nickel sulfate in water substituted. An anode of iron-nickel alloy containing iron and nickel in the proportions desired is used. The mercury is removed from the amalgam produced by one of the methods herein described and the resulting alloy compacted into a magnet at 250,000 lbs. per sq. in. The magnetic properties with varying iron nickel and aluminum percentages and various heat treatments are given in the following table:

	Nickel	Al	Hc	Br
	Percent	Percent		
1	15	5	410	6500
1a			400	9500
2	20	13	580	5200
2a			550	9700
3	40	20	350	4100
3a			300	8500

30 (1a, 2a, and 3a heated to 1000 degrees C. for 1 minute and quenched)

The number of other combinations of metals which may be used in our process for the production of permanent magnets is almost unlimited. We have successfully used copper manganese aluminum, silver manganese aluminum, iron platinum, iron neodymium, iron tungsten, iron molybdenum, iron molybdenum cobalt, manganese antimony and many other combinations. Some of these require heat treatment for best results but most are satisfactory in the compressed form.

We have found that the crystal growth of metals produced by the processes heretofore described may be even further inhibited and material of still greater coercive force obtained by the addition of certain substances to the amalgam before electrolysis or after electrolysis but previous to distillation. We have found a great variety of substances to be beneficial in this respect but prefer to use substances which are more readily oxidized than iron so that during any exposure to air they will be oxidized to form a coating which inhibits crystal growth and at the same time protects the iron particles. Zinc and aluminum are particularly useful for this purpose. In certain cases it is desirable to use as a coating substance a metal that is resistant to this action of air such as chromium.

As an example of this part of our invention, we find that if zinc sulphate is added to the electrolyte from which iron is being precipitated into mercury in such proportion that the resulting amalgam contains 2% as much zinc as iron and the amalgam distilled in vacuo at 250 degrees C., the magnet made by compacting the resulting metal into a cylinder  $\frac{1}{2}$ " diam. by 1" long at 250,000 lbs./sq. in. has Hc=475, Br=9500. These results are merely illustrative since it is advisable in some instances to markedly increase the proportion of zinc, as will be disclosed hereinafter.

70 In another instance aluminum amalgam prepared by treating aluminum bromide with sodium amalgam was added to iron amalgam in such amount that the aluminum comprised .5% of the iron. The mercury was removed by distillation at 250 degrees C. in vacuum and the resulting

metal compacted into a cylindrical magnet at 250,000 lbs. sq. in. It has the following properties  $H_c=483$ ,  $B_r=9650$ .

Silver, copper, tin, lead and cadmium may be used in place of zinc or aluminum with somewhat less satisfactory results. When the intermediate step of filtering the amalgam is used the added material must be proportioned so that the material finally distilled will contain .25-5% of the added material.

In another method of practicing our invention the amalgam of iron is shaken with a solution of anhydrous  $CrCl_3$  in acetone. In this way the iron particles are coated with metallic chromium and are thus prevented from undergoing crystal growth. An aqueous solution of copper sulphate may be used but with somewhat inferior results.

The general features of our invention are believed to be clear from the preceding description. We wish it to be understood, however, that that we may depart considerably from the specific methods described, while still following the essential teachings of our invention.

As magnetic materials we may employ any substances or combination of substances having suitable paramagnetic properties and coercive force normally present when our basic method is employed, or developed therein, for example, by heat treatment. We may employ therewith, any one or combination of non-magnetic materials, such as zinc, aluminum and the like. These added substances serve important and diverse functions, notwithstanding the fact that suitable magnets may be prepared following our method, even though the non-magnetic materials be not employed. The development of our invention emanated, at least in part, from the concept that high coercive force would result from the presence of two phases, even though one phase might not be magnetic, and that a phase could comprise that condition which exists at a grain boundary. Hence, by producing an extremely fine subdivision of the magnetic material, resulting in the formation of particles of sub-microscopic size, high coercive force results even though a substantially pure iron or cobalt product results.

Extremely finely divided metal has the disadvantage of being pyrophoric, and unless carefully handled may ignite in air, thus introducing problems of handling which might well be eliminated if equal results could otherwise be secured. The proper use of a proportion of a metal such as zinc or aluminum renders the final powderlike product non-pyrophoric and simplifies handling. When extremely high pressures are employed in pressing the powder, grain growth may occur, and because of the somewhat more uniform results obtained when a proportion of non-magnetic material is employed, we believe that such material may function also to inhibit grain growth.

It is important that the pressing operation be carried out so as to develop a minimum of heat since a combination of heat and pressure is conducive to grain growth and therefore defeats the purpose of our invention. This may be accomplished by slow application of the pressure and by having the die parts very cold. We have found that cooling the material and die parts with  $CO_2$  snow is very effective.

The non-magnetic material may be introduced in several ways and the proportion may be varied. A suitable method is to dissolve the metal, when soluble, as in the case of zinc, in the mercury be-

fore the iron amalgam is produced. As an example of proportions, we have employed up to 25% of zinc in a product otherwise consisting solely of pure iron, and have produced very good magnets. There seems no reason why, for some purposes the proportions should not be further increased, although in general, it appears that proportions of the order of 10% of zinc are preferable in most instances. Reference to the use of zinc in the discussion of the non-magnetic constituent is merely illustrative, since, as previously noted, such metals as chromium, aluminum, lead, cadmium, tin, silver and copper may be employed, singly or in combination with other metals.

Earlier in this specification we disclosed the step of heating manganese to develop increased residual induction, and gave a table showing the relation between temperature of treatment, and magnetic properties expressed in terms of  $H_c$  and  $B_r$ . It was shown that temperatures ranging from 400 degrees to 600 degrees were employable to develop residual induction, but that the coercive force falls off rapidly before the maximum in induction is obtained. The use of zinc and the like as described hereinabove serves to maintain coercive force near its maximum until the maximum induction is reached. Thus we have been able to produce manganese with small amounts of added zinc by heating to approximately 500 degrees wherein the resulting material has a coercive force of 425 and a remanance of 3000.

We append hereto a specific example of a process in which the main features of our invention are utilized.

One hundred pounds of previously prepared zinc amalgam containing 1 lb. of zinc are made a cathode of a cell containing a 10% solution of ferric ammonium sulphate. Anodes of pure iron having a total area of 20 sq. dec. are suspended in the electrolyte. The mercury is so arranged as to have surface in contact with the electrolyte of 15 sq. dec. Electrolysis is carried out at 100 amperes, i. e., at about 6.8 amperes per sq. dec. of anode surface, until 10 lbs. of iron have been deposited in the mercury. Approximately 50 to 60 hours are required under the conditions given.

The product obtained is a slushy amalgam of iron, zinc and mercury. This product is then heated to 260 degrees C. in a vessel through which a stream of  $H_2$  is continuously passed. The mercury comes off rapidly at first, but later the evolution is slower as the concentration of mercury reaches the vanishing point. The time required for distillation depends on the conditions.

The product resulting from this treatment is a pulverulent mass, consisting of extremely fine size particles coated or interspersed with zinc, about 8 to 10% of the latter being present.

This product is non-pyrophoric, and can readily be pressed into the form of a permanent magnet. When compacted at a pressure of ten thousand pounds per square inch, it produces a mechanically strong body magnetizable to produce a permanent magnet. When pressed, a coercive force of the order of 400 oersteds is present. The magnetic induction depends on the shape of the piece and the pressure employed. With appropriate shape for measurement, we have found a remanent magnetism of 9500 gauss.

The methods described hereinabove all relate to the use of mercury for the purpose of producing the requisite subdivision of the magnetic ma-

terial. However, we may produce this form of material in other ways. For example, finely divided iron may be produced by any of various ways known in the art; such as low temperature reduction of precipitated iron oxide (Reference: Transactions of the A. S. M., December, 1937, page 1011), the dispersion of iron in water by the Bredig method, and the spraying of iron into water from the Shoop metal spray or similar mechanism. Such finely divided iron (or other magnetic material), when compressed without further treatment, usually undergoes crystal growth to such an extent as to be unfit for practical commercial use in the practice of our invention. However, by suitable treatment of this finely divided iron such as by the use of a solution of metal salts (e. g. copper sulphate or silver nitrate), we precipitate on each particle a thin layer of another metal, thus preventing crystal growth when the particles are compressed to form a permanent magnet.

As an example of this method, we produce iron by the production of precipitated iron oxide and treat it for five minutes in a solution containing .1% copper sulphate. The resulting material is washed free from copper sulphate, dried, and compressed to form a magnet having a coercive force of 350 and a remanence of 8300.

In another form of our invention, we produce particles of finely divided magnetic materials by reactions taking place in a suitable slag. For example, we produce a low melting glass containing lime, silica, and boric oxide, and add to this a small amount of sodium peroxide. Very finely divided nickel silicide ( $\text{NiSi}_2$ ) is then sprinkled into this molten mixture. The silicon is immediately oxidized, leaving finely divided nickel. In order to reduce the amount of slag in this material, we grind the mixture so that it will pass a 200-mesh screen, and then separate a magnetic portion of such slag by the use of a magnetic separation, such, for example, as described in our parent application. This material, when compressed into a cylinder, gives a coercive force of the order of 500 and a remanence of 5800.

In another form of our invention, an alloy of iron with some readily oxidizable material such as aluminum is sprayed into water, giving finely divided iron particles coated with alumina. Such particles, when compacted, give a coercive force of 400 and a remanence of 8000.

In still another form of our invention, pure iron is sprayed from a Shoop gun into a slag to produce a dispersion of iron in slag and a magnetic separation made to reduce the amount of slag. We have produced material in this way having a coercive force of 300 and a remanence of 7500.

We have also found that a number of materials which are only paramagnetic or slightly ferromagnetic become increasingly so on fine subdivision, their coercive force being at the same time increased. It will be clear that our invention encompasses the preparation of magnetic bodies from these materials as well as materials definitely ferromagnetic in their compact state. We have already cited the increase in remanence of cobalt brought about by producing it from an amalgam. A similar increase in magnetic induction may be brought about in cobalt by mixing the material reduced from the oxide at low temperatures with an inert substance as tungsten carbide. We have also used stainless steel of the austenitic type for the practice of our invention. This material in the form of wire is substantially nonmagnetic. By spraying this material into water from a suitable gun a finely divided material was obtained which had a coercive force of 300 and a remanence of 5000.

The terms employed in the appended claims are used in their ordinary sense as the context indicates, and such claims properly define the scope of our invention.

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

1. The process of producing a permanent magnet which comprises forming an amalgam of a magnetic material with mercury, removing substantially all of the mercury, and subjecting the resulting finely divided magnetic material to a pressure of over 150,000 pounds per square inch to produce a mechanically strong, firmly compacted, permanent magnet material of high coercive force and of adequate chemical stability.

2. The process of producing permanent magnets which includes the steps of depositing a magnetic material into a mercury cathode by electrolysis, depositing in said mercury another metal in an amount comprising between about .25% and 25% of the magnetic material, removing substantially all of the mercury whereby to provide finely divided particles of magnetic material coated with said other metal, thereby to inhibit oxidation and crystal growth of said particles of magnetic material and produce a chemically stable material, and compacting said stable material comprising said coated particles into suitable shape for use as a permanent magnet.

3. A permanent magnet composed of fine particles of iron and zinc intermingled and pressed into the form of a self-sustaining body, having a coercive force of over 200.

REGINALD S. DEAN.  
CHARLES W. DAVIS.