

Nov. 28, 1967

R. M. BROWNELL ETAL

3,355,724

MAGNETIC MATERIAL AND DEVICES UTILIZING SAME

Filed Oct. 20, 1964

2 Sheets-Sheet 1

FIG. 1

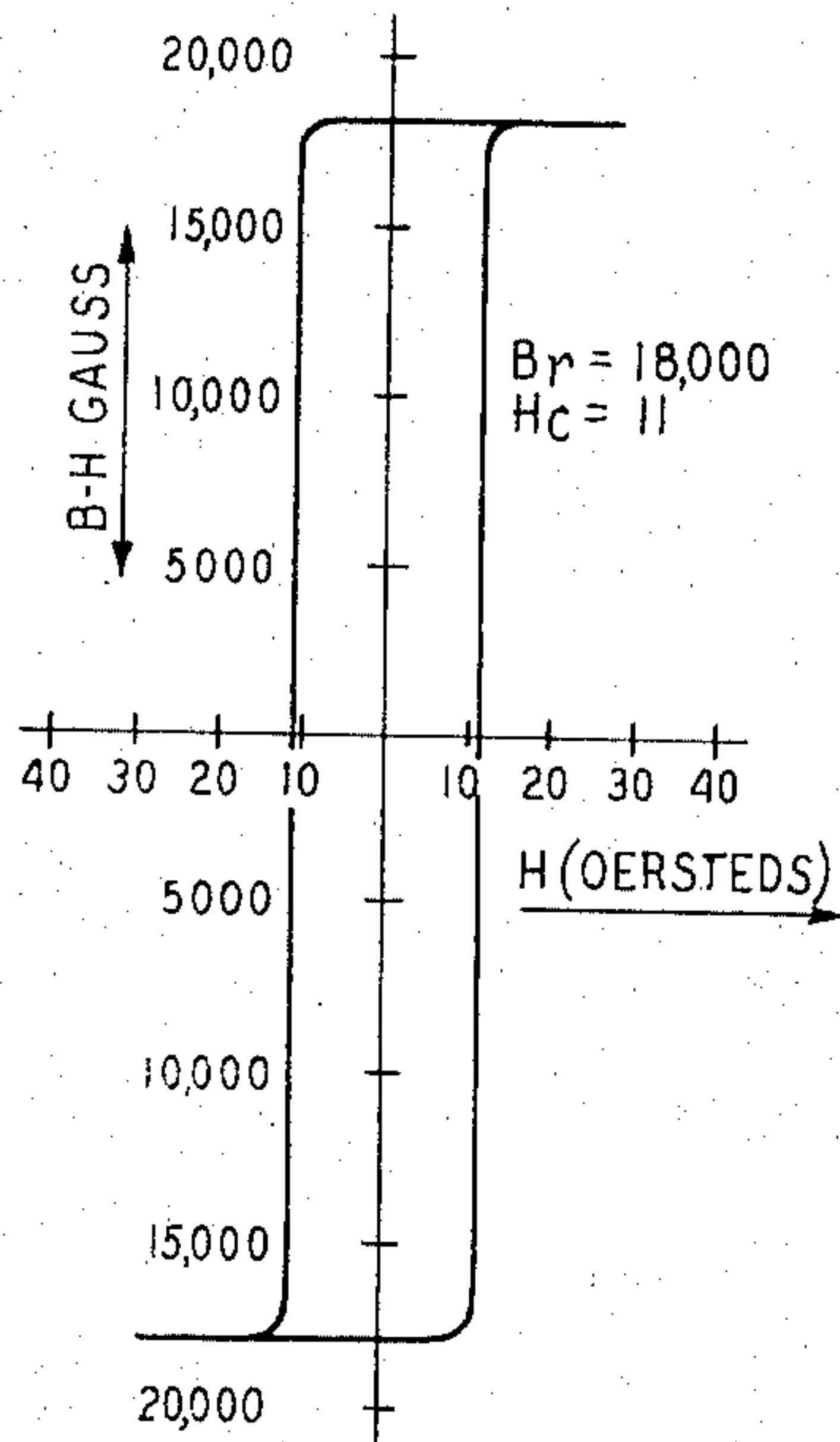


FIG. 2

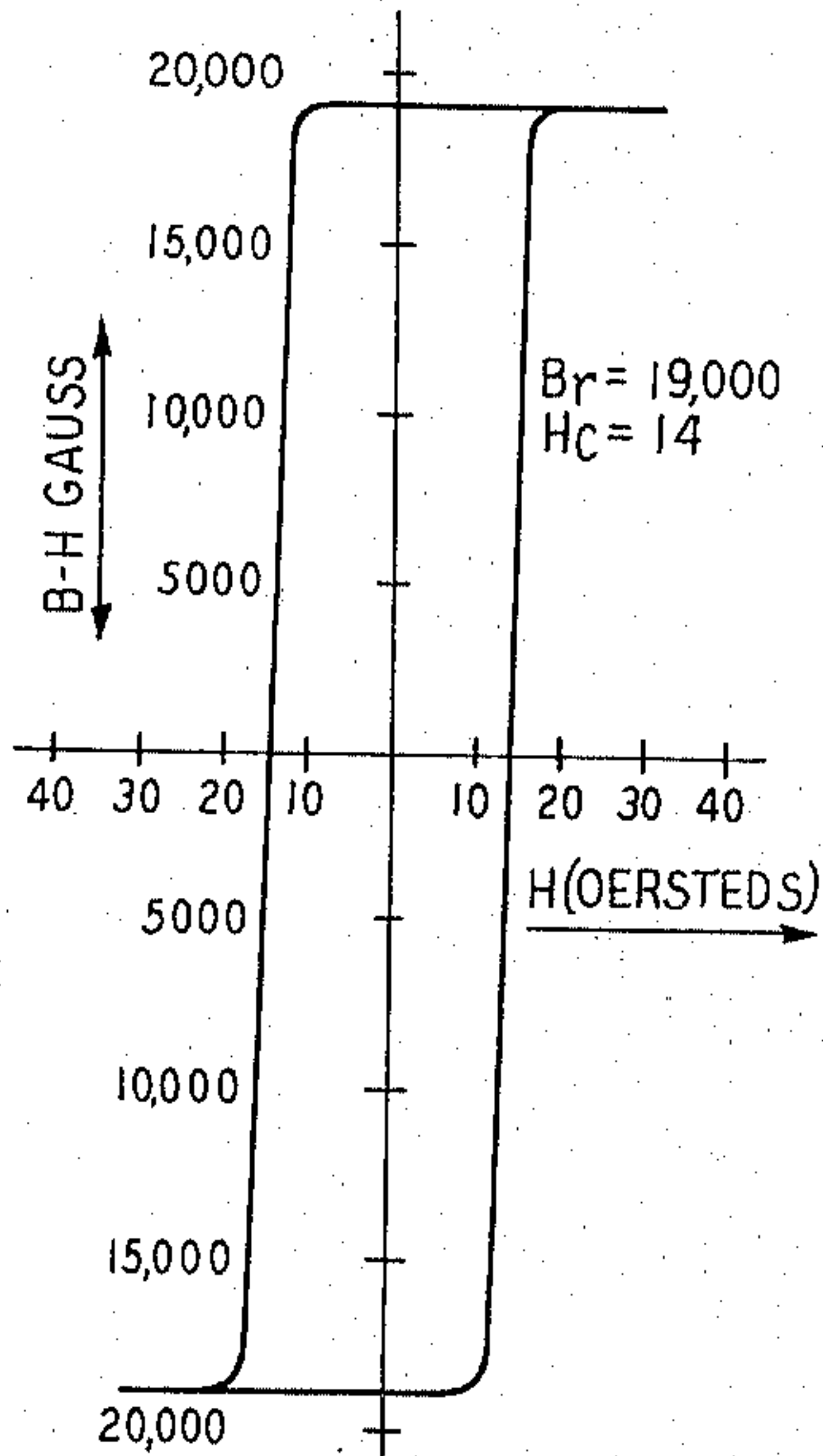


FIG. 3

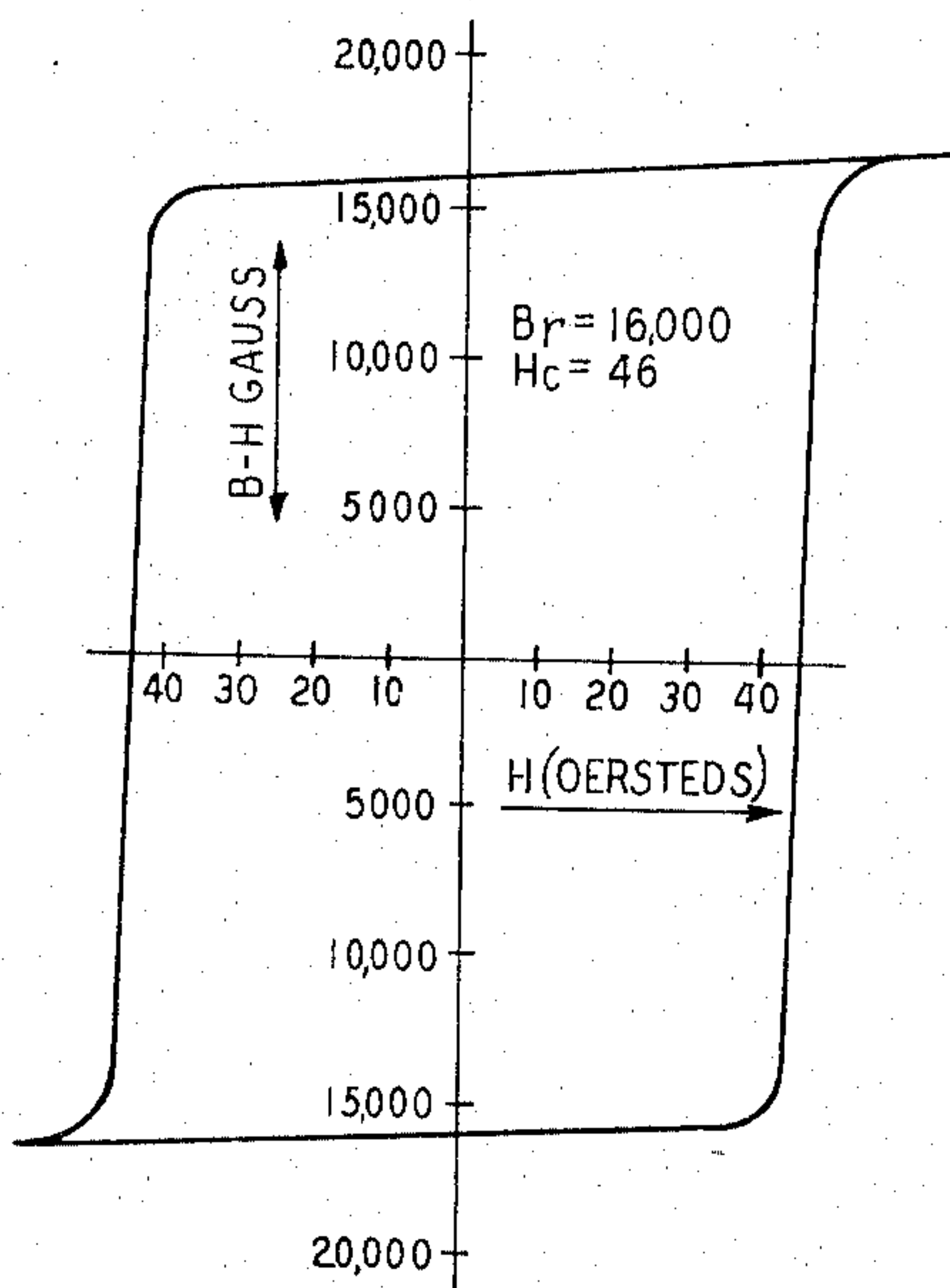
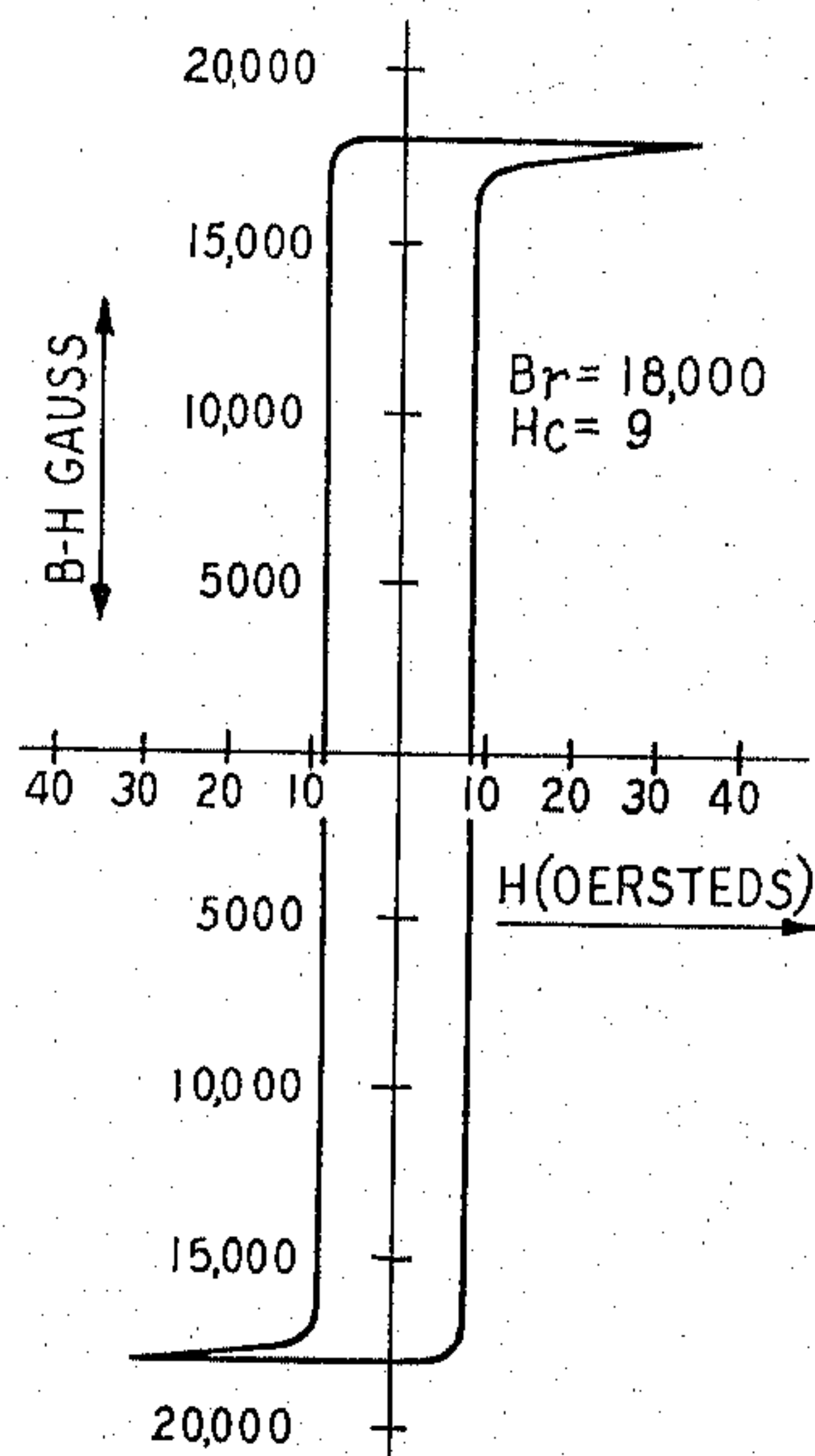


FIG. 4



R. M. BROWNELL
H. L. B. GOULD
D. H. WENNY, JR.
INVENTORS
BY

George S. Indig
ATTORNEY

Nov. 28, 1967

R. M. BROWNELL ETAL

3,355,724

MAGNETIC MATERIAL AND DEVICES UTILIZING SAME

Filed Oct. 20, 1964

2 Sheets-Sheet 2

FIG. 5

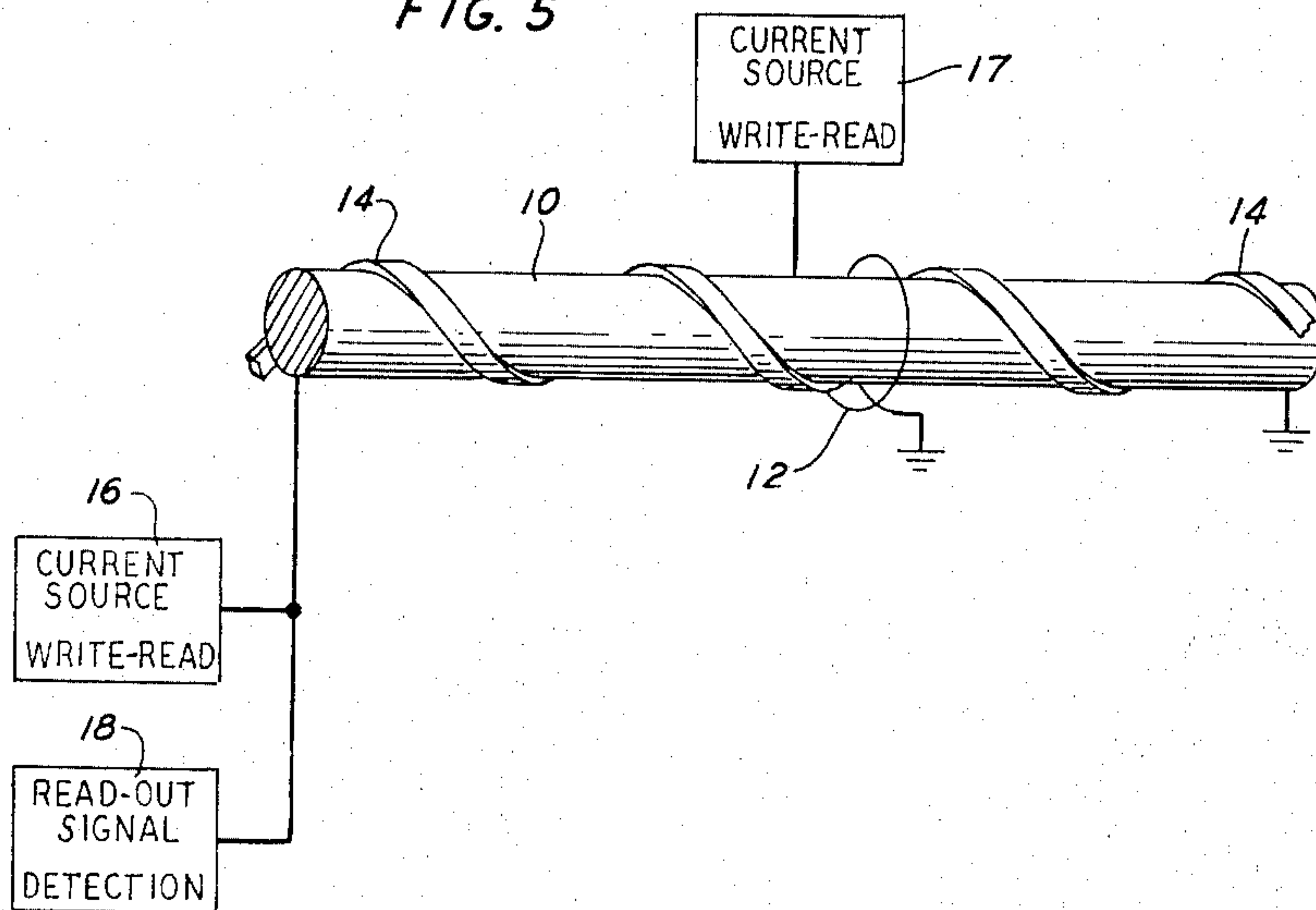
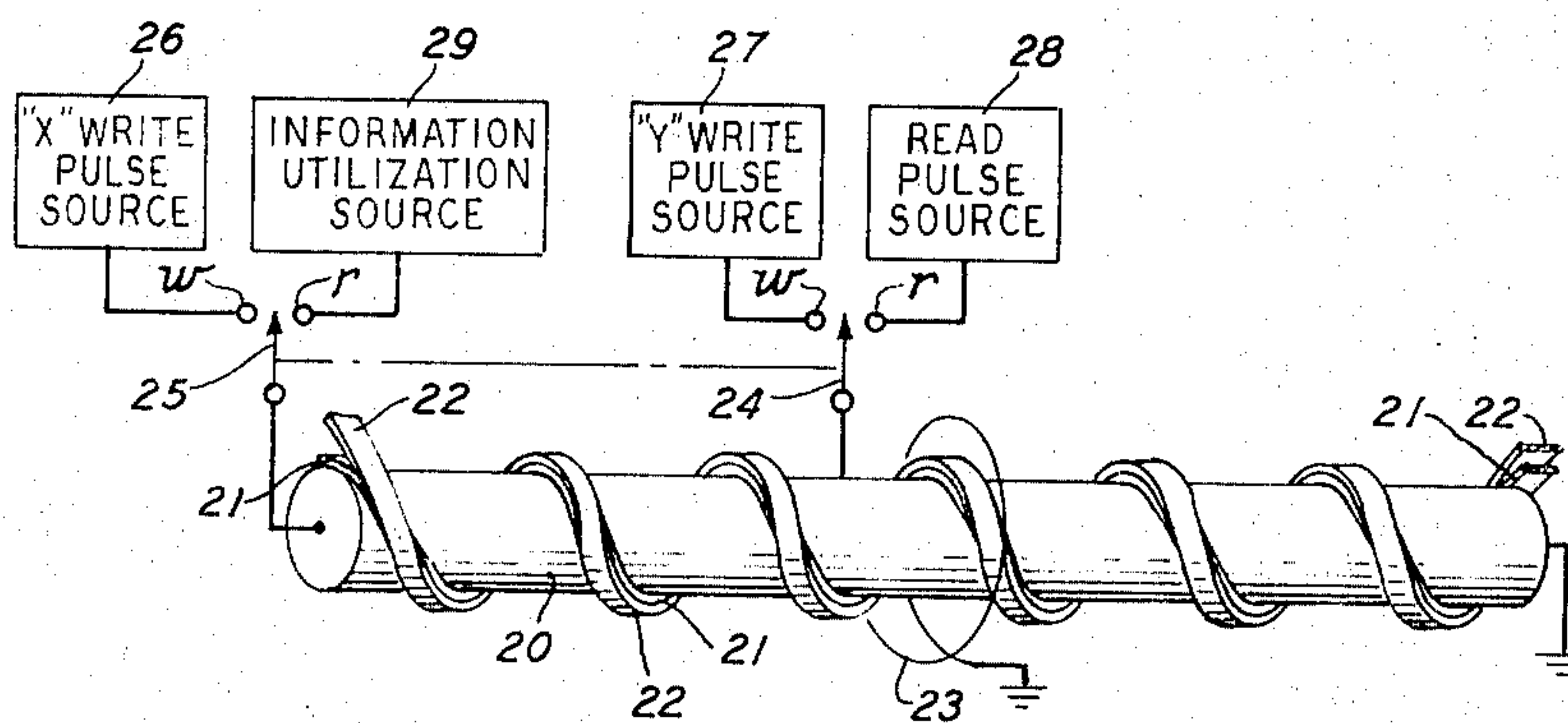


FIG. 6



1

3,355,724

MAGNETIC MATERIAL AND DEVICES UTILIZING SAME

Richard M. Brownell, Bethlehem, Pa., Harold L. B. Gould, Kinnelon Borough, and Daniel H. Wenny, Jr.,
Morris Township, Morris County, N.J., assignors to
Bell Telephone Laboratories, Incorporated, New York,
N.Y., a corporation of New York

Filed Oct. 20, 1964, Ser. No. 405,203

6 Claims. (Cl. 340—174)

This invention relates to processes for making square loop magnetic alloy materials, to the materials themselves, and to devices containing such materials.

There is a broad technology based on the use of ferromagnetic materials having remanent magnetization, that is, materials which remain magnetized after the removal of an external field. Such a characteristic permits the retention of accessible information in switches and memory elements without the need for a continuing external field. Devices of this nature are of many designs and include core memories, twistors, tensors, waffle irons, "laddies," and many others. Various device designs give rise to different required coercivity, saturation, remanence, etc. All of these devices, however, require remanent magnetization.

An accepted measure of the remanent magnetization is the value at the intercept of the B-H D-C hysteresis loop characteristic of the material of concern with the ordinate between the first and second quadrants. In order to reach this remanent value, it is first necessary to magnetically saturate the material, that is, to apply an external field sufficient to produce a flux with a value equal to the maximum attained in the first quadrant. The ratio of remanent magnetization, B_R , to saturation magnetization, B_S is often referred to as the "squareness ratio" of the material.

It is well known that squareness ratio is of importance in other design considerations. For example, many composite memory devices operate on the coincident current principle. Such elements are operated by use of two associated current windings, which in either the read or write function may each carry currents of a magnitude of the order of half that required to produce a field necessary to magnetically saturate the element. Such elements are switched only when both associated windings are carrying their designated half currents. The more skewed the hysteresis loop, that is, the lower the value of the squareness ratio, the greater the possibility of a half current producing "partial switching." By reason of this condition, a disturb current may, when reinforcing a half current, be adequate to produce switching. Disturb currents increase for closer spacing of elements. It therefore follows that improved squareness ratio may permit closer packing of memory elements.

A large class of the magnetic devices in use today is designed to take advantage of the magnetic properties offered by metallic alloy compositions. Such compositions, which may take the form of cast sections, wire or tape configurations, are generally iron alloys, often containing nickel, as in the permalloys. A recently added member of this class of materials is an iron alloy of cobalt, nominally fifty parts of each of these constituents. This material, as processed in accordance with a particularly critical series of steps, is characterized by a hysteresis loop having both an unusually high degree of remanence and an acceptable squareness ratio. Many of these materials are possessed of hysteresis loop characteristics suitable for certain device applications and, at least as important, are physically of such nature that they can be fabricated into the desired wire or tape forms.

While these materials are suitably incorporated in presently manufactured devices, continued emergence of new

2

designs is bringing about a broad range of magnetic characteristic requirements which is not immediately available. The state of the art at this time is such that each newly developed magnetic material showing acceptable hysteresis loop characteristics is immediately of interest by reason of its new range of coercivities or saturations or remanent magnetizations or any other characteristics differing from those of the already available materials.

In accordance with this invention, it has been discovered that a particular type of cold working of a specific high-cobalt compositional range in the cobalt-iron alloy system results in a material having good hysteresis loop squareness ratios. Other characteristics are intermediate of the soft and hard materials now in use. Fundamentally, the compositions here of concern are from 85–95 weight percent cobalt, remainder iron, to which the usual alloying ingredients may be added for the various reasons associated with such additives. The square loop characteristic upon which this invention is based results only upon cold working necessarily taking the form of cold drawing as round wire. Conditions must be such as to result in an area reduction of at least 95 percent as calculated from the ratio A_1-A_2/A_1 , where A_1 and A_2 are, respectively, the cross-sectional area of the body before and after drawing.

As will become evident from this description, tape configurations may be formed without loss of properties only by flattening the reduced round wire, for example, by rolling or hammering, providing the area reduction resulting from such flattening step is less than 50 percent, as determined by the same ratio. The flattened section so produced constitutes a significant embodiment herein. While the effects of this critical cold working are lost by any anneal of such temperature or duration as to result in any substantial strain relief, it is permissible to incorporate a final stabilizing anneal which, as understood by those skilled in the art, may result in heating over a temperature range of up to about 600 degrees centigrade for times of the order of a few seconds.

The nominal composition of the alloy herein is 90 percent cobalt, remainder iron. Exceeding a cobalt content of 95 weight percent impairs the workability of the material so that the requisite cold drawing cannot be carried out. The minimum indicated content of 85 weight percent may be exceeded, however with a concomitant decrease in squareness ratio. Of course, squareness ratio is dependent upon the degree of cold drawing as well as on composition, so that sufficient reduction to appreciably greater than 95 percent area reduction may result in squareness ratios of better than 90 percent for alloys containing as little as about 82 percent cobalt. Nevertheless, the indicated minimum of 85 percent, in providing a result in a squareness ratio of 0.95 or better for reductions of as little as 95 percent, constitutes a preferred limit for these purposes.

Materials of this invention typically show squareness ratios of from 0.90 on up to better than 0.99, remanent magnetizations typically of the order of from 15,000 to 20,000 gauss, and coercivities of from 5 to 15 oersteds. Such properties are not produced in these materials by forms of cold working other than drawing, by minimal reductions less than noted, or by hot working.

Addition of alloying ingredients other than minor amounts of the usual additives impairs the excellent hysteresis loop characteristics. Tolerable additives, all based on weight percent of total composition, are up to 2 percent, usually about 1/2 or 1 percent of Mn, but alternatively Be, Mg, Ca, Al, etc., to control sulfur, and oxygen. Unintentional ingredients include carbon, up to about 1/4 of 1 percent, beyond which workability is impaired, silicon, up to about 2 percent, larger amounts again impairing workability (molybdenum, vanadium, niobium, chromi-

um, titanium, tantalum and tungsten up to about 6 percent), and phosphorus and sulfur, to about $\frac{1}{10}$ of 1 percent, both of these materials causing embrittlement in larger quantities. Since certain of these ingredients may serve to increase resistivity or to bring about some other desired characteristic change, they may be added intentionally.

A suitable processing schedule expressed in general terms is set forth below. Specific conditions as applied to specific compositions are reported in the examples.

As would be expected, the critical processing conditions are those subsequent to dead anneal. Since cold drawing as round wire to the cross-sectional area reduction noted is absolutely mandatory in the practice of this invention and is, in fact, the only critical processing (so long as subsequent processing steps which may impair the results which obtain on drawing are avoided), prior operations are of significance only in obtaining a configuration in size which is expeditiously drawn. In terms of available cold-drawing equipment at this time, this indicates a cross-section of the order of from 0.060 inch to 0.0005 inch. These two limits are determined by capabilities of available equipment, and the need to produce an area reduction of 95 percent. Of course, equipment for drawing larger diameter wire may become available in the future, as may more refined apparatus capable of attaining smaller drawn sizes. The suitability of processing conditions are to be limited only by a need to obtain a minimum of 95 percent cross-sectional area reduction in cold drawing.

In the experimental results reported herein, starting bodies were generally produced by casting, the cast ingot being of the order of $\frac{3}{4}$ inch diameter by 8 inches long. Other crystallizing techniques, such as zone melting or the Bridgeman method or crystal pulling, are suitable.

The casting was then hot worked by swaging or rolling to a diameter of the order of $\frac{1}{4}$ inch. Hot working to produce a wire form, whether by either of the techniques mentioned or by any alternative procedure, as by forging, is expediently carried to a minimum diameter of the order of $\frac{1}{4}$ of an inch.

Again, primarily as an expedient to reduce die wear during subsequent drawing, surface defects were removed by grinding. Alternative techniques include pickling, blasting, etc.

The hot worked wire form was then subjected to a dead anneal. Requisite conditions for dead annealing in this alloy system are well known. In general, heating within the range of from 750° C. to 1000° C. for from one hour to fifteen minutes is necessary. Deviation may be made from these limits where the bulk of the body so indicates. Fine wire forms may be annealed more quickly; large reels may require greater duration. In the work reported in this description, a one-hour anneal at a temperature of about 975° C. was found suitable. Annealing was carried out in a protective atmosphere of hydrogen, nitrogen, argon, helium or forming gas (mixture of nitrogen and hydrogen). Use of a protective atmosphere is recommended to minimize the embrittling effect of oxygen inclusion.

The crucial step of cold working was then carried out. The criticality of this procedure has been indicated. As will be noted from the examples, cold drawing was continued until a diameter of 10 mils or smaller resulted. Area reductions ranged from 95 percent to 99 percent and greater.

In one of the examples, the cold drawn round wire was roll flattened. It has been noted that such final procedure to produce a desired tape configuration is permissible so long as an area reduction of 50 percent or greater does not result. It will be noted from the example that a reduction by flattening of the order of 5 percent did not significantly impair the squareness ratio.

Finally, a stabilizing anneal not to exceed ten seconds at a temperature in the range of from 500° C. to 600° C.

may be carried out. Further annealing tends to remove the strain produced during cold drawing and impairs the squareness ratio.

Reference is made to the drawings in the examples and the descriptive matter which follows:

FIGS. 1 through 4, on coordinates of magnetization, B, in units of gauss on the ordinate, and applied field, H, in oersteds on the abscissa, are D-C hysteresis loops for the compositions and procedures described in detail in Examples 1 through 4, respectively;

FIG. 5 is a perspective view of a magnetic memory device utilizing an element constructed of a material of this invention; and

FIG. 6 is a perspective view of a different type of memory device, again utilizing an element of a material of this invention.

FIGS. 1 through 4 correspond with the materials resulting from the procedures of Examples 1 through 4 in that order.

Example 1

A melt was prepared of the following materials:

Cobalt—1448 grams, or 89.9 weight percent
Iron—152 grams, or 9.5 weight percent
Manganese—8 grams, or .5 weight percent
Aluminum—2 grams, or .1 weight percent.

The materials were reacted at a temperature of approximately 1550° C. The resulting melt was held at temperature for about two minutes to ensure thorough mixing and solution of ingredients and was then poured into a mold and solidified to make an ingot about three-quarters' inch in diameter and eight inches in length. The ingot was heated to a temperature of 1200° C. for hot working to a diameter of one-quarter inch. Attainment of this diameter required about fifteen steps, with reheating between steps as required. The resulting one-quarter inch diameter bar was examined and surface defects were removed by machining. It was then annealed for thirty minutes at 950° C. in a protective atmosphere of hydrogen. Cold reduction to one-sixteenth inch diameter resulted from swaging or wire drawing, with dead anneals at one-eighth and one-sixteenth inch diameters. A further reduction of the wire was accomplished by drawing through dies to a diameter of two mils. The wire was dead annealed by heating from 950° C. to 1000° C. in a protective atmosphere to relieve strains resulting from work hardening at 0.025 and 0.015 inch diameters. Final reduction from .015 inch to .002 inch was carried out cold without subsequent anneal. This final step represented a reduction of 98.3 percent. The hysteresis loop of FIG. 1 resulted from D-C measurements made on the resulting material at a peak magnetizing force of

$$H=125\pm 5$$

oersteds. As is seen from this figure, the residual induction or remanence, B_R , is about 18,000 gauss. The coercive force, H_c , is about 12 oersteds, and the squareness ratio B_R/B_{sat} , is about 0.95.

Example 2

The procedure of Example 1 was repeated, utilizing the following amounts of the indicated materials:

Cobalt—1592 grams, or 88.3 weight percent
Iron—200 grams, or 11.1 weight percent
Manganese—8 grams, or 0.5 weight percent
Aluminum—2 grams, or 0.1 weight percent.

After processing as indicated in Example 1, the composition had the D-C magnetic characteristics indicated on FIG. 2. The residual induction, B_R , was about 18,200 gauss, the coercive force, H_c , was about 13 oersteds, and the squareness ratio, B_R/B_{sat} , was again about 0.95.

Example 3

The procedure of Example 1 was repeated, however utilizing the following amounts of the indicated materials:

Cobalt—1520 grams, or 95 weight percent

Iron—72 grams, or 4.5 weight percent

Manganese—8 grams, or 0.5 weight percent.

Processing was as in Example 1, however with an intermediate anneal at a diameter of 10 mils for three seconds at 950° C. in an atmosphere of hydrogen. Considering the anneal at 10 mils to be strain relieving, a minimum area reduction of 96 percent resulted upon subsequent cold drawing to two mils. The additional anneal was introduced to overcome embrittlement, probably resulting from the formation of the brittle epsilon phase of cobalt from cold worked gamma phase. The resulting characteristics are those of FIG. 3. As is seen from this figure, the residual induction, B_R , is about 16,000 gauss, the coercive force, H_c , is about 46 oersteds, and the squareness ratio, B_R/B_{sat} , is about 0.94.

Example 4

The composition of Example 1 was processed to two-mil wire by the procedure described in that example and was then cold roll flattened to a ribbon 0.5 mil to 6.0 mils in cross-section. The magnetic characteristics of the resulting ribbon are shown in FIG. 4. A comparison of FIGS. 4 and 1 reveals that flattening has appreciably affected only the coercive force, H_c , this value having been reduced from about 12 oersteds for the round wire to about nine oersteds for the ribbon.

The experiments described in Examples 1 through four were selected to represent related compositions and processing procedures. These examples are not intended to in any way restrict the general requirements which have been set forth.

The device of FIG. 5 is a memory element known as the twistor. This device, which depends upon the direction of remanent magnetization of a length of magnetic wire or tape (a memory bit) for information, is fully described in United States Patent 3,083,353, issued March 26, 1963 to A. H. Bobeck. This device includes a metallic conductor 10, about which there is disposed a helical winding 14 of a wire or tape configuration of a composition herein. The possible directions of the flux may be in either direction in the helical winding 14. One end of the conductor 10 is connected to a current source 16, and the other end is connected to ground. A series of external insulated windings represented by 12, one end of each of which is connected to ground, the other end being connected to a current source 17, are inductively coupled to the conductor 10. Initially, all the bits, that is, sections, of winding 14 corresponding with windings 12, are magnetized in a given direction, with such direction representing, for example, a binary zero. To switch any given bit, it is necessary to generate a current sufficient to produce a magnetomotive force, H , to produce an opposite flux direction. When a current pulse producing a magnetomotive force of the magnitude $H/2$ is applied from the source 16 simultaneously with a current pulse again producing a magnetomotive force of the magnitude $H/2$ from a given source 17, the total magnetomotive force is sufficient to switch the flux state of the associated length of winding 14, so producing a binary 1. In accordance with the principles of coincident current memory elements generally, either of the current pulses applied from the sources 16 and 17 alone is insufficient to accomplish the magnetic switching.

Information stored in the winding 14 is read out by reversing the polarity of the currents applied from the sources 16 and 17, the simultaneous reverse current pulses again causing switching in the direction of magnetization in the helical winding if an information bit has been previously stored in the manner described above. No switching occurs for any bit magnetized in the zero direction.

When the magnetic state of the winding 14 is switched during the read function, a change in potential results. This change may be detected by suitable detection means 18 as an output pulse superimposed upon the switching current pulse.

Since the effect of the read function in the device of FIG. 5 is to return the state of magnetization to that corresponding with the binary zero, the active reading is necessarily "destructive" since, subsequent to reading, all bits manifest a zero direction of magnetization. Where it is desired to operate such a device as a "nondestructive" memory, such may be accomplished, for example, by additional magnetic fields associated with each bit, each field being of a value sufficient to overcome the coercivity of the material of winding 14. In devices now in use, this is provided by a series of permanent magnets having remanent magnetizations of the requisite value. Where it is desired to have a "permanent" memory which is electrically alterable, such may be accomplished by "piggybacking" a harder magnetic winding about the softer winding 14 of the device of FIG. 5. This second piggyback winding has a remanent magnetization of the necessary value. Such a piggyback may be operated in the fashion of the device of FIG. 5 simply by using current pulses in the write function sufficient to produce the requisite coincident magnetomotive force. Interrogation is accomplished by using a pulse of opposite polarity of a magnitude sufficient to reverse the sense of magnetization only of the softer winding.

The device of FIG. 6 is a piggyback twistor. The particular element depicted utilizes a conductor 19, about which there is disposed a first helical winding of a tape 21 of a magnetic material and an overlay helical winding 22 of a different magnetic material. The material of winding 22 may be of a composition as processed in accordance with this invention. The material of winding 21 is a softer material having a loop characteristic and manifesting a saturation magnetization equal to or less than that of the remanent magnetization of the material of winding 22. Suitable material for winding 21 is one of the compositions of the permalloy system, for example of a composition and as produced in accordance with United States Patent 3,086,280, issued April 23, 1963 to W. B. Gibbs, C. V. Wahl, and D. H. Wenny, Jr. The principle of operation of a piggyback twistor is set forth in United States Patent 3,067,408, issued Dec. 4, 1962 to W. A. Barrett, Jr.

As in the device of FIG. 5, the write and read functions are accomplished in coincident fashion, the magnetomotive force being supplied with wiper switches 24 and 25 in the w or write position from current sources 26 and 27, the first of which produces a current by means of lead 25 through conductor 20 which, at its other extremity is connected to ground and the second of which produces the other half current through lead 24 which is connected to winding 23, the other end of which is also grounded. The read function for the device depicted is accomplished by use of current sources 28 and 29, which, with function switches 24 and 25 in the r or read position, together produce a pulse of sufficient magnitude to switch the direction of any bit of low coercive force material of winding 21.

The devices of FIGS. 5 and 6 are exemplary only, the material of this invention being suitable for use in any device which, by reason of its design, can take advantage of the wire or tape form, to the production of which this invention is necessarily limited. Many other devices beneficially incorporating compositions of this invention are known. Various of these are described in United States Patent 2,736,880. Such devices may utilize open as well as closed flux paths which may have associated with them printed as well as wire or even waveguide conductive paths and may even effect partial switching by passage of the current through the magnetic material itself. The suitability of the materials of this invention to all

7

such devices is understood by persons skilled in the art.

What is claimed is:

1. Device comprising an element defining at least one magnetically remanent flux path including a material consisting essentially of from 85 to 95 weight percent cobalt, remainder iron, produced by cold-drawing as round wire, such drawing resulting in an area reduction of at least 95 percent as determined by the ratio

$$\frac{A_1 - A_2}{A_1}$$

where A_1 and A_2 are the cross-sectional area of the wire before and after drawing, in which the said wire is utilized substantially in its as-worked state, such path having associated therewith at least two electrical paths.

2. Device of claim 1 in which the said flux path is a helical winding about a conductor, the said conductor constituting one of the said electrical paths and in which there is disposed about the said helical winding a plurality of separate insulated windings, each constituting a second electrical path with respect to an associated portion of the said helical winding.

3. Device of claim 1 in which there is an additional helical winding adjacent the said helical winding, the said additional helical winding being constructed of a magnetic material having a coercive force and saturation magnetization and being so positioned that the remanent magnetization of the material of the said additional helical winding is sufficient to magnetize the said helical winding.

4. Device of claim 1 in which the ferromagnetic wire

8

is partially annealed subsequent to drawing at a temperature of up to about 600° C.

5. Device of claim 1 in which the alloy additionally contains up to 6 weight percent vanadium based on the total composition.

6. Device of claim 1 in which the said wire is flattened so as to produce an area reduction of up to 50 percent by cold working.

References Cited

UNITED STATES PATENTS

1,932,308	10/1933	Freeland	148—31.55
3,067,408	12/1962	Barrett	340—174
3,108,912	10/1963	Frischmann	148—31.55
3,134,965	5/1964	Meier	340—174

OTHER REFERENCES

Bozorth R. M., *Ferromagnetism*, Van Nostrand Co., 1951, Princeton, N.J., QC 753 B69 C.5, pp. 193—199 and 873.

20 "Cobalt," Cobalt Information Center, Columbus, Ohio, No. 3, June 1959, TA 480C6C6, p. 23.

"Cobalt," Cobalt Information Center, Columbus, Ohio, No. 4, September 1959, TA480C6C6, pp. 30—32.

25 Metal Handbook, Metals Handbook Committee, The American Society for Metals, 1948, Cleveland, Ohio, TA 412.A3 cop. 2, pp. 591—592.

TERRELL W. FEARS, *Primary Examiner*.

30 IRVING L. SRAGOW, *Examiner*.

M. S. GITTES, *Assistant Examiner*.