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METHOD OF INCREASING THE SILICON CONTENT OF WROUGHT GRAIN ORIENTED SILICON STEEL
Filed Feb. 23, 1968 Sheet 1 of 3

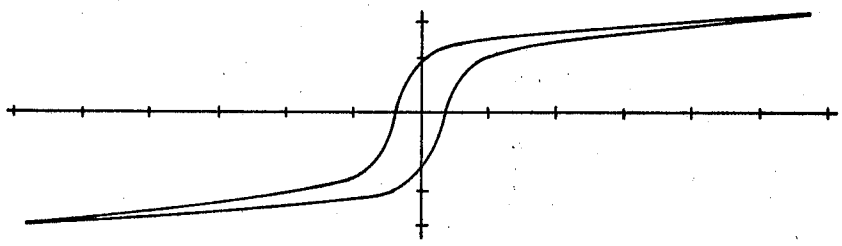


FIG.1

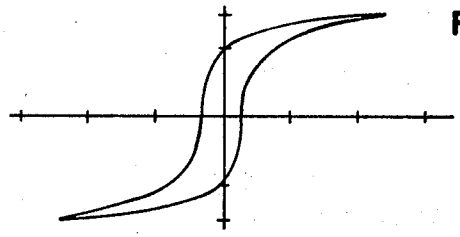


FIG.2

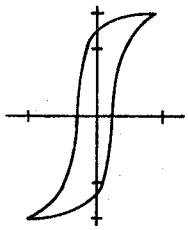


FIG.3

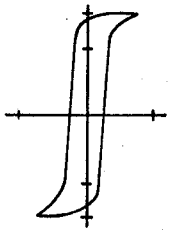


FIG.4

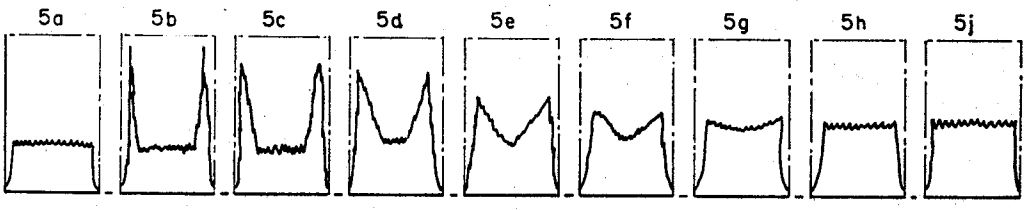


FIG.5

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FIG. 8

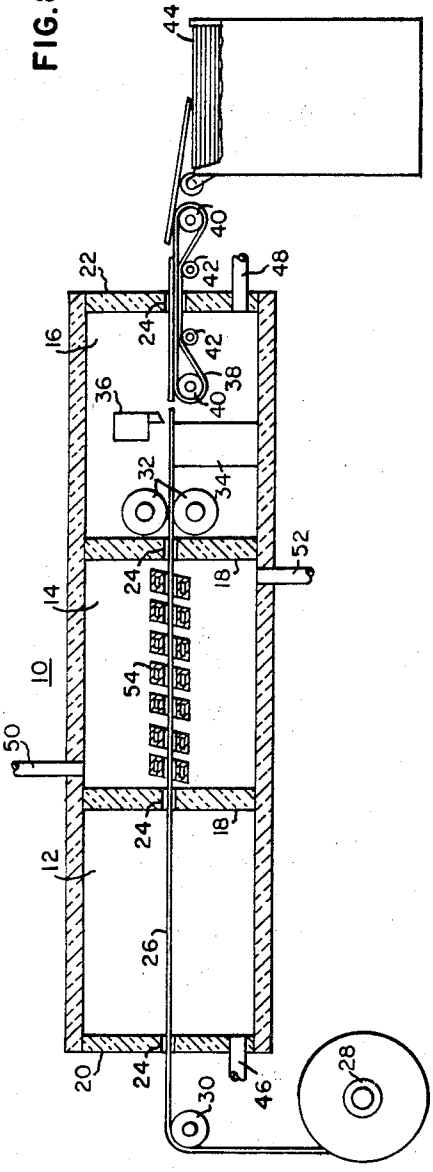


FIG. 7

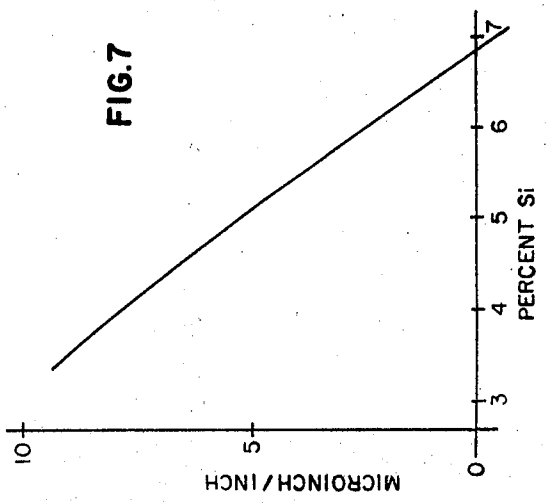
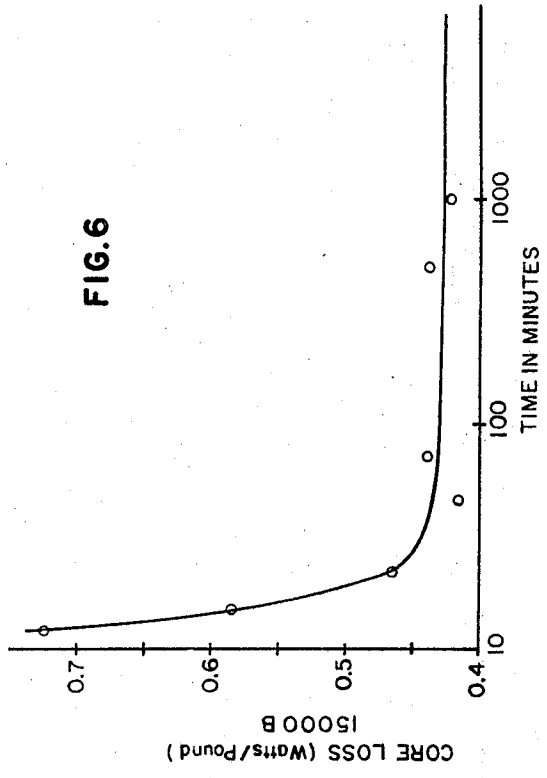


FIG. 6



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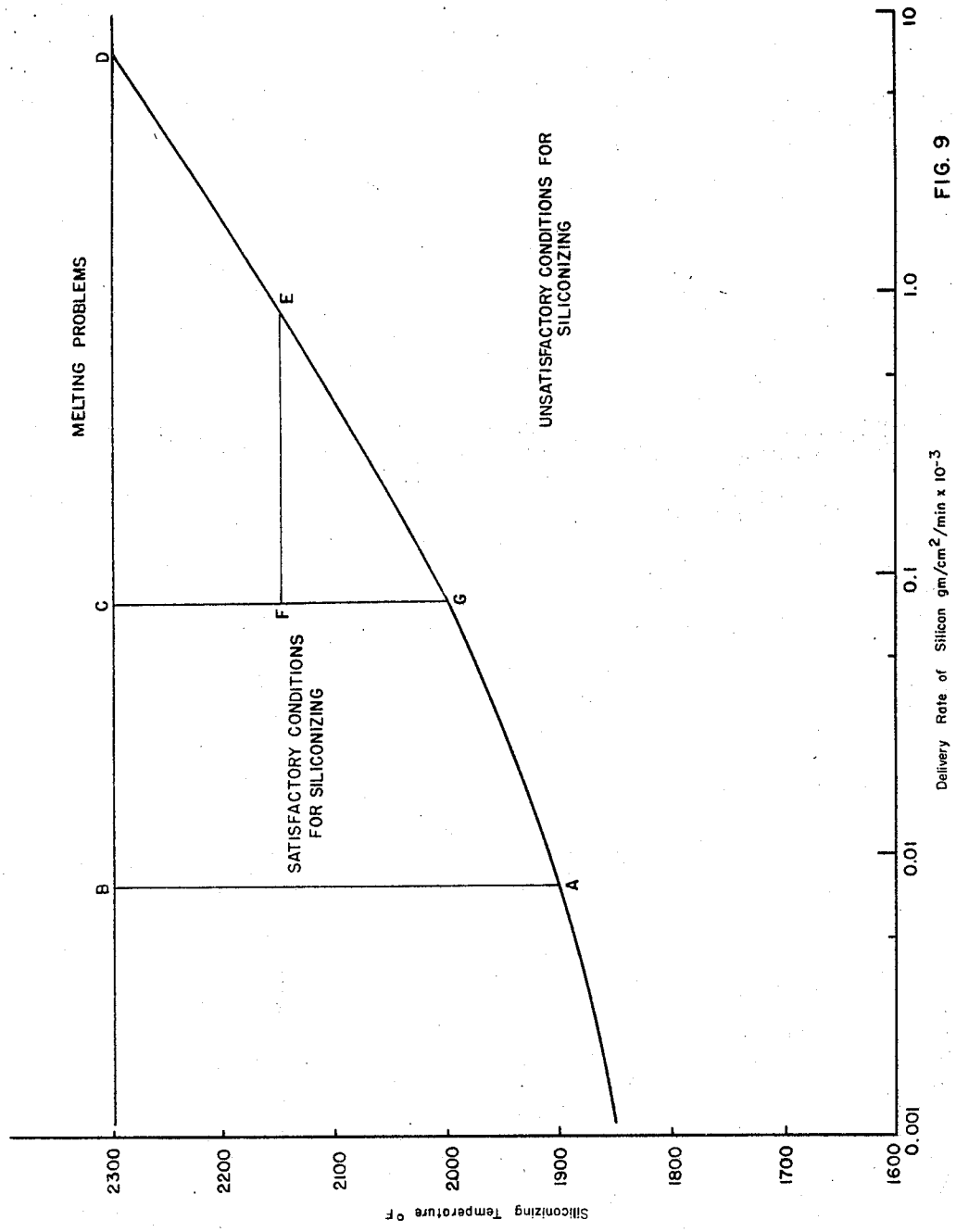


FIG. 9

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3,423,253

METHOD OF INCREASING THE SILICON CONTENT OF WROUGHT GRAIN ORIENTED SILICON STEEL

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Continuation-in-part of application Ser. No. 422,718, Dec. 31, 1964. This application Feb. 23, 1968, Ser. No. 712,324

U.S. Cl. 148—110 14 Claims

Int. Cl. H01f 1/04

ABSTRACT OF THE DISCLOSURE

In the manufacture of wrought silicon steel containing in excess of 4% silicon, the steps comprising, reacting at an elevated temperature finish gauge silicon steel containing less than about 4.0% silicon with a siliconizing atmosphere containing a mixture of a non-reactive gas and between about 0.01% and 23% by volume of a non-reactive gas saturated with a thermally decomposable silicon compound, regulating the mean delivery rate of the siliconizing atmosphere and the elevated temperature at which reaction is effected so that both the mean delivery rate and the elevated temperature fall within the area defined by the lines connecting points ABCDEGA in FIG. 9 of the drawings, and thereafter heat treating the reacted steel. The heat treatment may be carried out in a magnetic field and the thermally decomposable silicon compound can be silicon tetrachloride.

This invention relates to a method of improving the magnetic characteristics of wrought silicon steel products, and in particular to a method of increasing the silicon content of wrought, grain oriented silicon steel, and is a continuation-in-part of application Ser. No. 422,718, filed Dec. 31, 1964, and now abandoned.

Some of the effects of silicon on iron have been known for some time, and have been commercially embodied in the so-called silicon steels which possess a desirable combination of magnetic characteristics. When properly processed, iron containing about 3.25% silicon can be manufactured into the form of a wrought product which, through proper heat treatment, will be characterized by a preferred orientation. The magnetic characteristics of this 3.25% silicon-containing iron having a preferred orientation include high resistivity, low core loss and high permeability when measured in a given direction. Wrought silicon steel products possessing these characteristics are widely employed in the production of power transformers and the like, to provide distinct advantages over power transformers employing, for example, a soft iron core.

The literature is replete with the descriptions of processes for producing grain oriented silicon steel, which processes usually involve at least two cold reductions to obtain material of the desired thickness, an intermediate anneal which is interposed between the cold reductions, and a final, high temperature box anneal in a protective atmosphere in order to develop a secondary grain growth which permits grains having the preferred orientations to grow at the expense of those grains which do not have a preferred orientation. This grain orientation has been variously described employing the Miller Indices, and two of such orientations have been described in the art as cube-on-edge and cube-on-face.

Limitations on the prior art practices have resulted from the fact that where the silicon content is increased to beyond about 4%, a serious loss in the ductility of the resulting materials is noted. While higher silicon contents

are effective for reducing the magnetostriction, increasing the resistivity, lowering the core loss and increasing the permeability, nonetheless it is extremely difficult to produce wrought products having such outstanding magnetic characteristics because of the exceedingly gross brittleness exhibited by the steel with silicon contents in excess of 4%. The gross brittleness has resulted in the utilization of elaborate processes including hot-cold reductions of limited drafts interspersed with frequent heat treatments in order to obtain a wrought product having in excess of 4% silicon therein.

The method of the present invention makes possible the attaining of improved magnetic characteristics in a wrought silicon steel product.

An object of the present invention is to provide a method for increasing the silicon content of wrought silicon steel.

Another object of the present invention is to provide a wrought silicon product having improved magnetic characteristics.

Another, more specific object of the present invention is to provide a product, and a method for producing said product, which product is a wrought silicon steel containing in excess of about 4% silicon therein and which is characterized by having excellent core loss and magnetostriction properties.

These and other objects of this invention will become apparent to those skilled in the art when taken in conjunction with the following description and the drawings in which:

FIGURE 1 is a plot of the AC hysteresis loop of a wrought, grain oriented silicon steel produced in accordance with this invention in which the starting material having a silicon content of 3.25% was treated at 2150° F. for a total time period of 15 minutes to produce a product containing more than 5% silicon;

FIG. 2 is an AC hysteresis loop of the material of FIG. 1 after a further heat treatment consisting of annealing at 2100° F. for a time period of about 3 minutes;

FIG. 3 is an AC hysteresis loop of the material of FIG. 1 after annealing at 2100° F. for a time period of about 10 minutes;

FIG. 4 is an AC hysteresis loop of the material of FIG. 1 after annealing for a period of 35 minutes at 2100° F.;

FIG. 5 is a series of X-ray microprobe traces of the cross section of wrought, grain oriented silicon steel and demonstrates the effect of the time component at 2150° F. on the distribution of silicon through the cross section of the steel during treatment in an atmosphere capable of enriching the total silicon content from 3.25% to 5.5%, at the following specified times:

5*a*	Starting material.
5*b*	After one minute.
5*c*	After two minutes.
5*d*	After three minutes.
5*e*	After five minutes.
5*f*	After 7½ minutes.
5*g*	After 15 minutes.
5*h*	After 30 minutes.
5*j*	After 60 minutes.

FIG. 6 is a plot of the core loss versus time for homogenizing at a temperature of 2100° F. of a steel processed in accordance with this invention to contain in excess of 5% silicon;

FIG. 7 is a plot of the effect of silicon on the cross-grain magnetostriction of materials processed by the method of the present invention;

FIG. 8 is a schematic drawing illustrating a zoned furnace suitable for use in practicing the present invention, and

FIG. 9 is a plot of the temperature-mean delivery rate relationship for producing satisfactory material.

In its broader aspects, the method of the present invention contemplates employing a starting material which includes a wrought silicon steel containing from about 2.5% to less than about 4% silicon and thereafter subjecting this material to a siliconizing treatment whereby the wrought silicon steel product is reacted at a predetermined temperature range in a silicon-containing atmosphere to provide for the deposition and diffusion of silicon into the wrought silicon steel product followed by a heat treatment either as a separate or integral step to remove any concentration gradients, said heat treatment being applied either with or without an externally applied magnetic field in order to obtain a silicon steel product having outstanding magnetic characteristics.

While the method of the present invention may be most advantageously applied to silicon steels having a preferred orientation, it is also applicable to steels which have been processed to finish gauge whether or not the same will ultimately exhibit a preferred orientation. In this respect the texture annealing may be combined with the method of the present invention, thereby providing obvious additional economies.

At the outset it should be noted that the method of the present invention is utilized with, and applied to material which possesses the desired final gauge thickness in which the product is to be used; that is to say, the starting material for the process of the present invention comprises sheet or strip material which will not be further reduced in gauge. This starting material has a silicon content of from about 2.5% to less than about 4.0%, and optimumly exhibits a preferred orientation to a predominating amount of the grains contained therein. Outstanding results have been obtained where silicon steel having about 3.25% silicon and a cube-on-edge orientation has been employed as the starting material.

The starting material is thereafter reacted while at a predetermined temperature of 1900° F. to 2300° F. with a silicon-containing compound in order to deposit silicon on the surface of the starting material and diffuse the same inwardly. In this respect, both batch and continuous type operations are contemplated. It has been found that regardless of whether a batch type operation or a continuous operation is employed, the starting material, when subjected to the silicon-containing compound must be reacted at a temperature of at least 1900° F. and preferably not to exceed about 2300° F. The heating of the starting material must be effected substantially instantaneously if, during the heating, the material is exposed to the thermally decomposable silicon compound utilized as the source of the additional silicon. On the other hand, the material may be heated to the reaction temperature in a protective atmosphere, and the thermally decomposable silicon compound introduced at temperature; said heating rate need not then be substantially instantaneous. On the other hand, where a continuous operation is contemplated, the steel may be heated to the required temperature in one chamber from which it enters a reaction chamber and is maintained within the reaction chamber at the required temperature for the required period of time and thereafter removed from said reaction chamber and allowed to cool normally. Thus, it becomes apparent that whether batch or continuous type operations are used, the reaction of the wrought silicon steel with the thermally decomposable silicon compound must take place within the described temperature range and for the required period of time, and siliconizing of the material either during heating to the critical temperature range or cooling from the critical temperature range must be substantially avoided in order to prevent deterioration to the magnetic characteristics of the siliconized material usually accompanied by porosity.

The reaction of the starting material with the thermally decomposable silicon compound must take place at a minimum temperature of 1900° F. where a mean delivery rate of about 0.0075×10^{-3} gm./cm.^{2}/min. of silicon to the silicon-iron sample is employed in order to obtain a material which will ultimately exhibit outstanding magnetic characteristics. Attempts to employ lower temperatures at the same mean delivery rate have resulted in poor magnetic properties and often porosity within the steel. On the other hand, where the mean delivery rate of the silicon from the thermally decomposable silicon compound to the silicon-iron material to be reacted therewith was increased to about 0.075×10^{-3} gm./cm.^{2}/min., the minimum critical temperature increased to about 2000° F., in order to obtain good magnetic characteristics and avoid porosity. Further increases in the mean delivery rate of silicon to the surface of the silicon-iron material resulted in requiring the use of a corresponding increase in temperature until a maximum delivery rate of about 7.5×10^{-3} gm./cm.^{2}/min. is achieved at which time it appears that a minimum temperature of 2300° F. is indicated. However, since the temperature of 2300° F. approaches the solidus temperature, it is preferred to limit the mean delivery rate to less than about 7.5×10^{-3} gm./cm.^{2}/min.

It will be noted that reference has been made to the "mean delivery rate." Such "mean delivery rate" contemplates the rate at which silicon is delivered to the steel being reacted and is independent of the method of delivery. While a flowing atmosphere may be inferentially contemplated, it will be appreciated, however, that a static atmosphere can also be employed and the silicon steel reacted with the silicon contained within the static atmosphere. In this event, the instantaneous or incremental delivery rate can exceed the maximum limit of 7.5×10^{-3} gm./cm.^{2}/min. initially and can be for less than the minimum limit of 0.0075×10^{-3} gm./cm.^{2}/min. at the termination of the process, and good results will be obtained. Nonetheless, the mean delivery rate for the entire process will fall within stated limits and the critical temperatures for the mean delivery rate employed must be observed in order to ultimately develop the desired magnetic characteristics.

In the embodiments illustrated hereinafter, the starting silicon-iron material is reacted within the specified temperature range for a time period of up to about 5 hours, depending upon the mean delivery rate of the silicon thereto and the desired final silicon content. The requirement of removing any concentration gradients in the material is necessary in order to obtain the desired degree of squareness to the hysteresis loop, thereby compressing the area of the hysteresis loop. Stated in other terms, where a substantially square hysteresis loop is obtained, lower core losses are obtained in the finished material. Consequently, sufficient time must be provided after the reaction is complete for the diffusion to take place and complete the homogenization treatment to produce a uniform silicon distribution of the desired silicon concentration.

Silicon tetrachloride has been found to be effective for the source of silicon when the same is introduced with a protective carrier gas such as argon or nitrogen. Preferably, the furnace atmosphere comprises argon which contains between about .01% and about 23% or argon which has been saturated with silicon tetrachloride maintained at a temperature of about 78° F. Other silicon compounds can be used such as silane, trichlorosilane and other thermally decomposable silicon-containing substances. It will be appreciated, however, that while some substances will have various drawbacks (for example, the reaction product of trichlorosilane may involve hydrochloric acid, and silane possesses a very disagreeable pungent odor and is highly inflammable) nonetheless, these compounds can be used, although it is preferred to use silicon tetrachloride since it is safe, economical by comparison, and the reaction product involves iron chloride which can be readily condensed as a powder.

The reaction time varies inversely with the concentration of the decomposable silicon compound in the carrier gas, and preferably in order to provide a nominal silicon content of about 5.2% in the reacted product, it is desirable to react the wrought silicon steel at the required temperature for up to 3 minutes when the protective atmosphere of argon contains about 23% of argon saturated with silicon tetrachloride having a mean delivery rate of 0.8375×10^{-3} gm./cm.^{2}/min. and up to about 5 hours where the concentration of argon saturated with silicon tetrachloride is about .01% and a mean delivery rate of 0.0075×10^{-3} gm./cm.^{2}/min. These times at the respective concentrations refer to the time required to deposit a given amount of silicon, usually a minimum, for ultimately obtaining a homogeneous silicon content of at least 5%. The times stated do not include the required time at temperature to remove concentration gradients. While it may be possible to employ a more dilute concentration than set forth herein or react the wrought silicon steel at lower temperatures for longer periods of time, present economic considerations dictate practical times, temperatures and concentrations commensurate with magnetic characteristics. Consequently the time, temperature and concentration limits set forth herein are preferred.

As previously stated, an alternative to substantially instantaneously heating the starting material to the reaction temperature in the presence of the thermally decomposable silicon compound is to heat the steel to the reaction temperature in a protective gas atmosphere to react with the heated steel. Regardless of the way in which the siliconizing is accomplished, it has been found that a minimum temperature of 2000° F. has been necessary where the atmosphere, as admitted to the reaction chamber, contains 1% of argon saturated with silicon tetrachloride at 78° F. with a mean delivery rate of about 0.075×10^{-3} gm./cm.^{2}/min. and the time at temperature while under the influence of the silicon-containing atmosphere is about 33 minutes for obtaining at least 5% silicon in the steel. This reaction, when carried out at this temperature for a time period of 33 minutes followed by removal of the silicon-containing atmosphere followed by holding at temperature for 12 minutes and additional homogenizing for 10 minutes at 2100° F. produces a marked improvement in the exhibited magnetic properties as will be set forth more fully hereinafter. On the other hand, where about 23% of argon saturated with silicon tetrachloride at 78° F. is employed in the argon atmosphere at a mean delivery rate of about 0.8375×10^{-3} gm./cm.^{2}/min. and reacted with the starting material, a minimum temperature of about 2150° F. was found to be necessary, the steel being held at such temperature for a time period of up to about 3 minutes. After removal of the silicon-containing atmosphere, the steel was held for a further 12 minutes at this temperature followed by an additional homogenizing for 10 minutes at 2100° F., in order to obtain optimum magnetic characteristics.

It is to be noted that in the process of the present invention, the reaction time, in order to obtain a given amount of silicon, will vary as a function of temperature; that is to say, where various gas concentrations are used and the critical minimum temperatures are observed, holding times at these temperatures may result in not only the reaction taking place for the deposition of the silicon on the surface layers of the starting material, but also the diffusion of the silicon inwardly to substantially increase the silicon content of the starting material to the same relative level throughout the cross section. In other words, while it may be possible to obtain the maximum amount of silicon, or the desired amount of silicon, on the surface layers of the starting material after a relatively short period of time, additional time is necessary in order to diffuse the silicon completely throughout the cross section of the material. Thus, it is possible to approximate this facet of the process into two steps, namely,

the deposition of the silicon into the surface layers of the strip material which may be accomplished in a relatively short time, depending upon the concentration of the silicon in the reaction atmosphere and, the homogenizing of the strip material thus treated to remove the concentration gradients therein.

The concentration of silicon introduced into the sample will depend on the concentration of the silicon in the reaction atmosphere, the time reacted, and the temperature, the latter governing the rate of reaction. However, merely depositing silicon on the surface is not enough. The optimum magnetic characteristics are developed only when the concentration gradients are removed. Consequently, further heat treatment is necessary. However, the temperature of said heat treatment must also be controlled because temperatures which are low appear to require times which may be exorbitant, whereas temperatures which are high may exceed the solidus temperature and thereby result in surface melting. For example, the silicon content on the surface at the end of the reaction may exceed 12% so that heating to a temperature of more than about 2300° F. may exceed the solidus line of the iron-silicon phase diagram resulting in intergranular melting which adversely affects magnetic properties. In actual practice, temperatures in excess of 2300° F. during the reaction have resulted in a melting and rounding of the corners of silicon-iron strip material on which the silicon has been deposited. Accordingly, it is preferred to homogenize at the same temperature range within which the reaction takes place both the time and temperature being related to the concentration of the thermally decomposable silicon compound. Consequently while two steps may be employed, a single reaction-homogenization step is quite practical.

Where the critical limitations set forth hereinbefore are not maintained, the magnetic properties are poor and porosity in the strip often develops. Thus, it has been found that the method of the present invention requires a minimum temperature within the range of 1900° F. to 2150° F. where the amount of the non-reactive gas saturated with silicon-containing reactant at 78° F. introduced into the protective atmosphere varies from .01% up to 23%. The maximum temperature which will produce sound material appears to be about 2300° F. with the above gas mixtures. By the same token, it has also been found that where higher concentrations and higher temperatures are employed, shorter periods of reaction and diffusion time may be employed in order to obtain highly improved magnetic characteristics in the product produced by the method of the present invention. In this respect, it may be stated in general terms that the critical minimum temperature varies proportionally with the mean delivery rate of the thermally decomposable silicon reactant compound and inversely proportional to the time, it being noted that these relationships are not necessarily linear. By observing these trends with the critically controlled variables of time, temperature, concentration and mean delivery rate, excellent magnetic characteristics are attainable.

As stated hereinbefore, the variables of time, temperature and concentration must be critically controlled in order to obtain a sound siliconized product which exhibits outstanding magnetic characteristics with a substantially uniform silicon content throughout its cross section. It is to be noted, however, that it is desirable to clean the surface of the starting material so as to remove all contaminants to the surface prior to treating the steel as described in order to obtain the desired degree of siliconizing. It has been found that even the presence of a sub-scale is detrimental to the deposition and diffusion of silicon by the method of the present invention. Consequently, the surface of the wrought, grain oriented silicon steel is preferably cleaned in the method of the present invention, usually by degreasing and descaling in

order to provide a clean surface for the deposition and diffusion of silicon therein.

In order to more clearly demonstate the method of the present invention, reference is directed to the following schedule which details one mode of practicing the present invention.

(1) Grain oriented silicon steel of nominal 0.014 inch gauge and having a silicon content of between 2.5 and 4%, preferably about 3.25% is employed as the starting material.

(2) Prepare surface by degreasing and descaling.

(3) Place in reaction chamber and fill reaction chamber with argon containing 23% argon saturated with silicon tetrachloride at 78° F.

(4) Substantially instantaneously heat silicon steel starting material to 2150° F. in reaction chamber.

(5) Hold 15 minutes at temperature.

(6) Cool to room temperature substantially instantaneously.

(7) Homogenize.

Reference is directed to Table I which shows the test results of the 15,000 B core loss on the silicon steel having a silicon content as noted after being treated by the method of the present invention as set forth in the schedule hereinbefore.

TABLE I.—15,000 B CORE LOSS (W.P.P.)

Sample No.	Initial Silicon (percent)	Before Siliconizing (w.p.p.)	Final silicon (percent)	As siliconized (w.p.p.)	Siliconized and homogenized 16 hrs. at 2,100° F. (w.p.p.)	Siliconized homogenized and magnetically annealed (w.p.p.)
72	3.25	0.555	3.25			0.563
67	3.25	0.555	5.6	0.713	0.434	0.408
183	3.25	0.555	5.4	0.746	0.459	0.382
236	3.25	0.614	5.1	0.674	0.422	0.386

It is to be noted from Table I that the steel before siliconizing had a watt loss between .555 and .614 watt per pound. From the test data set forth in Table I, it is noted for Sample No. 72 which was not siliconized that magnetic annealing results in a small deterioration of the observed magnetic properties. This fact has been substantiated with both laboratory and commercial materials. However, where the steels were treated according to the method of the present invention, the opposite and more pronounced trend is noted. For the balance of the samples in Table I, after substantially instantaneously heating the materials to 2150° F. and holding for about 15 minutes, the steel exhibited higher core loss than before siliconizing. However, after homogenizing under the conditions set forth in Table I, these steels exhibited an outstanding improvement in core loss properties. Moreover, when the steels were subjected to a magnetic anneal in the with-grain direction which consisted of heating the steel in a field of 1000 H for one hour at a temperature of 1300° F. followed by cooling at a rate of 100° F. per hour to 400° F., these steels exhibited a marked further decrease in the core loss. Thus it is clear that through the method of the present invention, the magnetic characteristics of the steels are greatly improved.

Reference is now directed to the drawings, and to FIGS. 1 through 4, inclusive. Samples of wrought, grain oriented silicon steel strip having a thickness of 0.014 inch and containing nominally 3.25% silicon and having a watt loss of 0.614 watt per pound were substantially instantaneously heated in silicon-containing atmosphere in order to deposit the required amount of silicon, following which the samples were held at temperature for an additional 12 minutes. Thereafter, these treated samples were heated for various additional periods of time at a temperature of 2100° F. All such treated samples had an average silicon content of about 5.1%.

The hysteresis loops set forth in FIGS. 1 through 4, inclusive are AC hysteresis loops. Consequently, they are directly convertible to core loss which is measured in watts per pound. Thus the area enclosed by the AC hysteresis loop is indicative of the core loss exhibited by the material. FIG. 1 clearly shows the bent-over and strung-out character of the hysteresis loop of the material as it has been siliconized and held at temperature for an additional 12 minutes. Corroborating the test data set forth in Table I, it is seen that this treatment adversely affects the magnetic characteristics exhibited by the steel. Where, however, the concentration gradients within the steel are eliminated, improvements are noted in the observed magnetic characteristics. Thus, after homogenizing for an additional 3 minutes at 2100° F. a marked improvement in the character and area of the AC hysteresis loop is noted as illustrated in FIG. 2. Comparing FIG. 2 with FIG. 1, it becomes clear that the area bounded by the hysteresis loop is considerably smaller with the result that the hysteresis loop is becoming more erect and starting to square. At this point the core loss exhibited by the material after siliconizing, holding for 12 minutes, and homogenizing for 3 additional minutes at 2100° F. is less than that of the original starting material in the unsiliconized condition.

FIGS. 3 and 4 show the effect of further time at the homogenizing temperature, the time periods being 10 minutes and 35 minutes respectively. The areas bounded by these AC hysteresis loops are progressively smaller with the result that once the time period of about 30 minutes homogenizing at 2100° F. has been surpassed, further holding at this temperature does not appear to materially affect the shape nor the area of said hysteresis loop. Consequently, it has been determined that optimum magnetic characteristics are exhibited by the siliconized steel where the steel has been subjected to a homogenizing heat treatment at about 2100° F. for a time period of about 30 minutes after the original deposition of silicon on the surface of the material.

Further illustration of the siliconizing and homogenizing process may be had by reference to the drawings, and FIGS. *5a* through *5j*, inclusive. The plots identified as *5a* through *5j*, inclusive, of FIG. 5, are of the intensity of the X-ray microprobe trace across the section of the material, the amplitude of each plot being proportional to the local concentration of the silicon content present across the strip thickness. Plot **5***a* is representative of the starting material which contains approximately 3.25% silicon and which is substantially uniformly distributed throughout the cross section of the steel. Plots **5***b* through **5***j* are representative of the silicon distribution through the strip thickness as a function of the reaction time at 2150° F. in an atmosphere which is capable of producing the silicon steel product having a mean concentration of 5.5%. As clearly illustrated in plot **5***b*, a very high concentration of silicon is present on the surface with substantially no change in the central portion of the trace, it being noted that the central portion of said trace of plot **5***b* has an amplitude of substantially the same magnitude as that of the starting material. Thus adjacent to the surface of the strip material, a very high concentration of silicon is present with an exceedingly steep gradient extending a short distance inwardly from the surface. In progressing through plots **5***c* through **5***g*, each of which represents results obtained for time increments as stated in the description of FIG. 5, the concentration gradient of the silicon is greatly diminished with increasing time so that after 15 minutes only a small concentration gradient remains as graphically

illustrated in plot 5*g*. Holding for a time period of 30 minutes substantially completely eliminates concentration gradient as illustrated in plot 5*h*, and is corroborative of the data set forth hereinbefore especially as manifested by the hysteresis loops of FIGS. 1 through 4), inclusive. Holding for a time period up to one-hour, as represented by plot 5*j*, shows no change from that originally presented in plot 5*h*, indicating that substantially complete homogenization is accomplished after about 30 minutes at 2100° F.

Reference is directed to FIG. 6 which graphically illustrates the effect of time at the homogenizing temperature on the magnetic characteristics exhibited by the steel which has been siliconized to a silicon content of about 5.2%. The initial starting wrought material of .014 inch gauge had a 15,000 B core loss of .614 watt per pound. This material was thereafter siliconized, in a 15-minute treatment at 2150° F. and, after subsequent holding for various periods of time at 2100° F. the core loss was redetermined, thereby producing a curve of the time at 2100° F. homogenization temperature versus the core loss measured in watts per pound. As clearly demonstrated by the single curve of FIG. 6, the time required to sufficiently homogenize the material to remove the concentration gradients is about 30 minutes. Thus, as corroborative of the hysteresis loops of FIGS. 1 through 4, inclusive, as well as the X-ray microprobe traces of plots 5*a* through 5*j* inclusive, of FIG. 5, the observed magnetic characteristics as plotted in FIG. 6 clearly substantiate the aspect that all concentration gradients must be removed in order for the siliconized silicon steel strip material to exhibit optimum magnetic characteristics, and that homogenizing for a time period of about 30 minutes at a temperature of about 2100° F. is sufficient to produce outstanding results. Holding for longer periods of time at this temperature does not appear to have any beneficial effect on the observed magnetic characteristics.

Reference is directed to Table II which illustrates the effect of the variables of temperature, concentration and time at the indicated mean delivery rate on the physical characteristics of the samples, as well as the core loss of the materials, as siliconized which included a stress relief anneal at 1475° F. for two minutes, and as homogenized for 10 minutes at 2100° F. following the treatments given during the siliconizing processing including thereafter, magnetically annealing under the same set of conditions as set forth hereinbefore with respect to Table I.

As clearly set forth from the test results recorded in Table II, a minimum temperature of about 2150° F. appears to be necessary in order to obtain a sound as-siliconized product where the siliconizing atmosphere comprised a mixture of argon and 23% of argon saturated with silicon tetrachloride at 78° F. and the mean delivery rate approached about 0.8375×10^{-3} gm./cm.^{2}/min. The process was effective where the temperature was maintained within the range between about 2150° F. and about 2300° F. for a total reaction time of 15 minutes. It should be pointed out at the juncture, that while the total reaction time consisted of a lapse of 15 minutes, most of the actual siliconizing took place in the first 3 minutes of the treatment. Thus, although the mean delivery rate was about 0.8375×10^{-3} gm./cm.^{2}/min. at the beginning of the treatment the instantaneous delivery rate was quite high, and after about three minutes the delivery rate was far less than about 0.8375×10^{-3} gm./cm.^{2}/min. The temperature of 2150° F. appears to be the indicated minimum in order to obtain a product which has the visual appearance of being sound, and is characterized by a surface which is bright and smooth. This material, after stress relief annealing at 1475° F. for 2 minutes, was tested for its magnetic characteristics and it was found that in the as-siliconized condition as above described, the steel exhibited a watt loss which was not significantly different from the watt loss of the unsiliconized starting material However, upon homogenizing at a temperature of 2100° F. for 10 minutes followed by furnace cooling and thereafter magnetically annealing the material, an outstanding improvement is noted in the demonstrated magnetic characteristics. It is to be noted that regardless of the condition or temperature of the later homogenizing heat treatment, the temperature of about 2150° F. appears to be the indicated minimum under these conditions of siliconizing atmosphere concentration, mean delivery rate, and reaction at the indicated temperatures for the indicated time periods.

Table II further indicates the effect of the time, temperature, concentration and mean delivery rate. Thus, where the siliconizing is accomplished in an atmosphere containing argon and 10% of argon saturated with silicon tetrachloride maintained at 78° F., and a mean delivery rate of $.3125\times10^{-3}$ gm./cm.^{2}/min., the minimum temperature for obtaining a sound, bright and smooth surface appears to be about 2100° F. As-siliconized the material again shows the necessity for completing the homogenizing process since no marked improvement in the magnetic properties is observed. Once again it is noted that the core loss values of these materials show a significant improvement after homogenization and magnetic annealing. Substantially similar results were obtained where the atmosphere comprised a mixture of argon and 1% of argon saturated with silicon tetrachloride, the total reaction time being 45 minutes. Thus, with this atmosphere and the reaction time as indicated, the lower limit of the siliconizing temperature range appears to be about 2000° F., where the mean delivery rate is about 0.075×10^{-3} gm./cm.^{2}/min. The trend in magnetic characteristics is substantially the same as for the balance of the table wherein the differenent atmospheric concentrations were employed. At this point it should be indicated that excellent results were obtained where the temperatures of up to 2300° F. were employed. Where, however, higher temperatures were utilized the corners of the samples melted, thereby resulting in vastly inferior magnetic characteristics. Further testing indicates that with a mean delivery rate of about 0.0075×10^{-3} gm./cm^2/min., a minimum temperature of 1900° F. appears necessary. Thus if lower temperatures are employed, it is necessary to reduce the mean delivery rate, thus increasing the time component to where it is inordinately long and uneconomical. The data as set forth in Table II clearly establishes the range for the mean delivery rate of between 0.0075×10^{-3} and 7.5×10^{-3} gm./cm.^{2}/min. and a reaction temperature range of 1900° F. to 2300° F.

Reference is directed to FIG. 9 wherein the interrelationship between the reaction temperature and the mean delivery rate is graphically illustrated. So long as the temperature and means delivery rate are regulated so as to be within the area ABCDEGA, satisfactory conditions are present for obtaining the desired degree of siliconization. While it is preferred to operate within the range CDEGFC, and the optimum results are obtained when the temperature and mean delivery rate are maintained within the area CDEFC, nonetheless operation within the broad area will produce satisfactory results as demonstrated hereinbefore. It will, of course, be apparent that the relationship, as graphically illustrated in FIG. 9, is based upon the test results tabulated in Table II hereinbefore.

As stated hereinbefore, the steel, when processed according to the method of the present invention, will show an increase in the resistivity of the steel with increasing silicon content. Reference is directed to Table III which indicates the effect of silicon on the resistivity. These data clearly show that up to 5.66% silicon increases the resistivity with increasing amounts of silicon.

TABLE III.—EFFECT OF SILICON ON RESISTIVITY

Sample No.	Si content, percent	Resistivity, ohm-cm.
Starting material	3.2	
8	3.32	48.6
9	3.66	50.6
10	4.06	54.9
11	4.86	65.3
12	5.66	77.3

Steel when processed according to the present invention processes improved magnetostriction resulting from higher silicon contents present. The magnetostriction exhibited by a material designed for usage in power transformers is of primary importance because it is considered to be the source of the noise emanating from such power transformers leading to energy loss and also is a great nuisance in the care of transformers located in highly populated areas as many of them are. It is a very costly and inconvenient process to damp out noise in a large transformer to acceptable limits. As a result silicon steels which are used for the cores of such power transformers carry very stringent magnetostriction specifications. The cross-grain magnetostriction is much larger than the with-grain magnetostriction. Reference is directed to Table IV which shows the test results of the cross-grain magnetostriction for .014" silicon-iron material treated by the method of the present invention and otherwise to obtain various levels of silicon in the annealed condition.

TABLE IV.—CROSS-GRAIN MAGNETOSTRICTION

Sample No.	Percent Si	Magnetostriction in./in. at 12.75 kb. annealed
113	3.2	+8.85
112	4.1	+8.40
105	4.7	+5.50
111	5.2	+4.4
107	5.4	+4.25
106	6.3	+1.35
114	6.7	+0.52
108	6.9	−0.42

The data set forth in Table IV were measured at 12.75 kb. and clearly demonstrate that with increasing silicon content, the steel has greatly improved cross-grain magnetostriction. It appears that the cross-grain magnetostriction goes through zero at about 6.75% silicon and that such decrease in the magnetostriction is linear with increasing silicon contents. It should be pointed out, however, that these values as set forth in Table IV were measured on samples which did not contain any insulating coating. Consequently, the values are higher than those normally encountered in production materials which do carry an insulating coating thereon. Nonetheless this trend is valid, and it is only the level which is measured which varies, the trend being the same whether the materials are coated or uncoated.

In order to more clearly demonstrate the data set forth in Table IV, reference is directed to FIG. 7 which plots the data set forth in Table IV. In FIG. 7, the single curve illustrates the effect of silicon on the magnetostriction of steels with varying silicon contents which were thereafter annealed. As set forth in FIG. 7, while the steels substantially undergo zero magnetostriction at about 6.75% silicon, any silicon content in the range between 6% and slightly more than 7% will show outstanding magnetostriction properties.

The method of the present invention may be used in a batch, or a continuous, type operation. Reference is directed to FIG. 8 which schematically illustrates equipment for practicing the method of the present invention on a continuous basis. This equipment comprises a zoned furnace, shown generally at **10**, having at least three zones contained therein, that is, a preheating zone **12**, a reaction zone **14** and a cooling zone **16**. These zones are separated by internal walls **18**, and the end wall **20** cooperates with one of the walls **18** to define the longitudinal limits of the preheater zone **12**; the other wall **18** and end wall **22** define the longitudinal limits of the cooling zone **16**. The longitudinal limits of the reaction zone **14** are defined by the internal walls **18**. Each of the end walls **20** and **22**, as well as each of the internal walls **18**, is provided with an aligned aperture **24** to facilitate the movement of strip material **26** through the furnace. A pay-off reel **28** and a support roll **30** are provided adjacent the preheater zone **12** of the furnace **10** for supplying the strip material **26** to the furnace. In order to feed the strip through the furnace, a pair of pinch rolls **32** are provided in the cooling section adjacent the aperture **24** of the wall **18**. The cooling section **16** is also provided with a cutting means which is schematically illustrated as an anvil **34** and a cooperating shear knife **36** which is employed to cut the silicon steel into predetermined lengths. To facilitate the removal of the cut lengths of strip, an endless delivery belt is also provided, as shown at **38**, which is disposed to be rotatable about support rolls **40** and guide rolls **42**. Thus, at predetermined times the siliconized strip **26** is sheared into the desired lengths which may be delivered to the exterior of the furnace by means of the endless belt **38** and stacked as illustrated at **44**. A protective atmosphere inlet means **46** is provided for the preheater zone **12**, and a corresponding protective atmosphere inlet **48** is also provided in the cooling zone **16** of the furnace **10**. A source of protective atmosphere (not shown) for example, argon, is supplied to said inlets **46** and **48** at such a rate as to maintain a positive pressure at the apertures **24** so that the outside atmosphere is prevented from leaking into the furnace and the atmosphere in the reaction chamber is maintained at a relatively constant level. A similar inlet **50** and an outlet **52** are provided for the reaction zone **14** of the furnace **10**, thereby permitting the reaction atmosphere to encompass the strip and the reaction products to be removed from the furnace through the exit port **52**. The reaction zone **14** may also be provided with water-cooled induction heater **54** which function to heat the strip substantially instantaneously to the reaction temperature. Where, however, it is desired to preheat the strip material, the heater, shown at **54**, may be completely removed and the furnace **10** may be heated by means of a muffle surrounding the entire furnace. Regardless of the manner in which the heating takes place, it is preferred to maintain a positive pressure in both the preheating section and in the cooling section of the furnace in order to completely eliminate the outside atmosphere and to confine the reaction atmosphere to the reaction zone **14**. The pinch rolls **32** can be controlled so as to maintain the steel at the reaction temperature in the reaction zone for the required period of time in order to deposit and/or diffuse the silicon inwardly from the surface in order to obtain a substantially homogeneous distribution of silicon throughout the cross section of the material being treated.

Since the steel as processed by the method of the present invention has been subjected to heat treatment in a protective atmosphere, no further treatment is necessary prior to utilizing the steel in power distribution transformers. As a result, certain aspects of manufacturing grain oriented silicon steels are obviated since no separating material is necessary during the high temperature annealing. Moreover, different insulation coatings can be employed on the siliconized material with the result that the steel of the present invention possesses an obvious commercial demand.

We claim:

1. In the manufacture of wrought silicon steel containing in excess of 4% silicon, the steps comprising, reacting at an elevated temperature finish gauge silicon steel containing less than about 4.0% silicon with a siliconizing atmosphere containing a mixture of a non-reactive gas and between about 0.01% and 23% by volume of a non-reactive gas saturated with a thermally decomposable silicon compound, regulating the mean delivery rate of the siliconizing atmosphere and the elevated temperature at which reaction is effected so that both the mean delivery rate and the elevated temperature fall within the area

defined by the lines connecting points ABCDEGA in FIG. 9 of the drawings, and thereafter heat treating the reacted steel.

2. A process as defined in claim 1 wherein the non-reactive gas is argon.

3. A process as defined in claim 2 wherein the reacted steel is heat treated in a magnetic field.

4. A process as defined in claim 1 wherein the 0.01% to 23% by volume of non-reactive gas is saturated with silicon tetrachloride at about 78° F.

5. A process as defined in claim 1 wherein the thermally decomposable silicon compound is silicon tetrachloride.

6. A process as defined in claim 1 wherein the reaction between the silicon steel and the siliconizing atmosphere and the subsequent heat treatment thereof are effected by continuously passing the steel through a furnace having a reaction zone in which contact is effected between the steel and the siliconizing atmosphere and also having a heat treating zone in which homogenization can be effected.

7. A process as defined in claim 1 wherein the mean delivery rate and the elevated temperature fall within the area defined by the lines connecting points CDEGFC in FIG. 9 of the drawings.

8. A process as defined in claim 1 wherein the mean delivery rate and the elevated temperature fall within the area defined by the lines connecting points CDEFC in FIG. 9 of the drawings.

9. In the manufacture of wrought silicon steel containing in excess of 4% silicon, the steps comprising reacting at an elevated temperature finish gauge silicon steel containing less than about 4.0% silicon with a siliconizing atmosphere containing a mixture of argon and from about 1% to about 23% by volume of argon saturated with silicon tetrachloride, said reaction being effected under conditions wherein the siliconizing atmosphere is introduced into contact with the silicon steel at a mean flow rate and is reacted with the steel at a temperature falling within the area defined by the lines connecting points ABCDEGA in FIG. 9 of the drawings, and thereafter stress relief annealing the reacted steel.

10. A process as defined in claim 9 wherein said reacted steel is subjected to a homogenizing heat treatment.

11. A process as defined in claim 9 wherein said reacted steel is subjected to a homogenizing heat treatment and is thereafter annealed in a magnetic field.

12. A process as defined in claim 10 wherein the homogenizing heat treatment is effected at times ranging from about 15 to 45 minutes.

13. A process as defined in claim 10 wherein the homogenizing heat treatment is effected at a temperature within the range of from about 2000° F. to 2300° F.

14. A process as defined in claim 1 wherein the reacted steel is heat treated at a temperature of from about 190° F. to about 2300° F.

References Cited

UNITED STATES PATENTS

2,109,485	3/1938	Ihrig	117—106
2,438,892	4/1948	Becker	117—106
2,501,051	3/1950	Henderson et al.	117—106
2,897,093	7/1959	Eckman	117—106
3,224,909	12/1965	Sixtus et al.	148—110

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