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PRODUCTION OF SILICON STEEL SHEET STOCK HAVING INSULATIVE SURFACES

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In the production of efficient power transformers, the need for insulating the various laminations of a stacked core or the various layers of a wound core from each other in order to reduce interlamination loss has been recognized, to the extent of attempts to provide such insulation by coating the laminae with an insulating substance e. g. silicate of soda. Coating processes are not fully satisfactory however, because they are expensive and time consuming, and further because inequalities in the thickness of the coating reduce the space factor of the laminations in the core.

It is an object of our invention to provide a mode of producing silicon steel sheet stock for magnetic uses, which mode results in the production of sheet stock already characterized by insulative surfaces.

It is an object of our invention to provide a way of forming insulative surfaces on silicon steel sheet stock in the process of manufacture of the sheet stock, and without adding significantly to the cost of manufacture.

It is an object of our invention to provide a way of producing a superior insulative coating upon silicon steel sheet stock, which coating is thinner and more uniform, providing a better space factor, and not likely to become broken, damaged, or dislodged in any of the operations performed upon the silicon steel in handling, shipment, core formation, or reannealing.

It is an object of our invention to provide as an insulative surfacing for silicon sheet stock, a thin, tightly adherent coating of glass.

It is an object of our invention to provide a way of controlling the thickness of such a layer of glass accurately, whereby to provide an extremely thin insulative surfacing, and at the same time a surfacing so uniform as to be of dependable insulative value.

It is an object of our invention to provide a process for the formation of insulative coatings of glass, in which the silicious constituent of the glass is derived principally from the silicon in the silicon steel. This not only gives us an insulative coating which is keyed into the surface of the silicon steel sheet stock, but also gives a coating of great thinness and uniformity.

It is an object of our invention to provide a method of producing a glassy coating on silicon steel sheet stock in which method the heat treatments necessary for the production of the glass may be those heat treatments desirably employed in the finishing of the silicon steel, so that the cost added to the manufacture of the steel in the production of our glassy coatings is negligible.

It is an object of our invention to provide a coat-

ing on silicon steel sheet stock which will prevent the sticking together of the individual sheets or coil turns during high temperature annealing even in hydrogen-bearing atmospheres.

It is an object of our invention to provide a surface coating which will withstand subsequent annealing and be stable in transformer oils and their decomposition products.

Our process is capable of producing a high and uniform insulative effect upon the surfaces of silicon steel. It will be understood that the insulative effect is primarily required in connection with the core laminations of high efficiency transformers, such core laminations being usually of silicon steel of around 3½% silicon content and processed to have a high and highly directional permeability at high inductions. Such silicon steel may be manufactured in accordance with the teachings of U. S. Letters Patent No. 2,158,065. The utility of the invention is not however confined to such silicon steel. The invention is applicable to any silicon steel in any use in which eddy currents or other losses due to excessive conductivity between laminations would be objectionable. Our coatings are very highly insulative; but it will be understood hereinafter that by the term insulative coating, we are referring to a coating having the property of producing a resistance between laminae of at least one ohm per square centimeter per lamination at a pressure of 50 pounds per square inch. Also by a satisfactory space factor we mean a space factor of at least 95%.

Briefly, our invention consists of a sequence of steps including the formation of particles of silica in the surface of the material principally from the silicon of the sheet, and the coating of the sheet with a substance like hydrated magnesia, which when heated in a reducing atmosphere to a high temperature will prevent the sheets or coil turns from sticking together, and which will form with the silica an insulating glass firmly attached to the sheet.

The objects of our invention set forth above and others which will be apparent to the skilled worker in the art upon reading these specifications, we accomplish by that series of process steps of which we shall now describe an exemplary embodiment.

In our manufacture of high permeability silicon steel sheet stock, the final heat treatments after reduction to gauge may include an open anneal followed by a box anneal with the material either in sheets or in coils. We make use of this sequence in producing our insulative coatings, so

that the production of our material in this instance requires no heat treatments which are not already a part of the routing. But it will be understood that in forming the insulative coating on other grades of silicon steel, such heat treatments may be employed as our process contemplates, whether or not they form normal parts of the regular routing for the material.

By the time of the final box anneal in our process, the sheet stock should have a very low carbon content. This is not because the quantity of carbon has anything to do with the formation of the insulative coatings, but rather because in the final anneal the conditions are such as to produce some decarburization of relatively high carbon silicon steel, which decarburization is likely to be of spotty or uneven character. Where the final anneal is practiced upon stacks of sheets of relatively high carbon silicon steel, substantial decarburization is likely to occur inwardly of the edges of the sheets but not in the centers of the sheets, thereby resulting in non-uniform and inferior magnetic properties.

As indicated, we shall describe our process in connection with the manufacture of a high permeability, highly directional silicon steel sheet stock of low core loss and low carbon content. The silicon steel is hot rolled to an intermediate gauge. It is then box annealed, usually in coils. We prefer to anneal it before pickling, and while the hot mill scale is still on the surfaces of the intermediate gauge material, in accordance with the teachings of Patent No. 2,236,519. This results in a substantial decarburization, usually reducing the carbon to an average of .01%. Then after pickling, the material is cold reduced to gauge, usually in a plurality of cold rolling reductions of the order of 40% to 85% with intervening heat treatments and a final heat treatment. The result of these steps is to produce in the material a crystal orientation which is highly directional and of the twin-derivative type. The final heat treatment, as we have indicated, may have two parts: an open, (i. e. continuous strand) anneal followed by a box anneal.

By an open anneal, we mean the passage of the material in sheet or strip form through a continuous furnace, the heat treatment of the material occupying a relatively short time cycle, dependent upon its speed of travel and the length of the furnace. The word "open" does not imply in this instance that the material is exposed to the air or to an uncontrolled atmosphere during the heat treatment, since it is the current practice in making silicon steels of this type to maintain controlled atmospheres in the open annealing furnace, and in particular to anneal in so called "wet hydrogen" for decarburization in accordance with the teachings of the copending application of Victor W. Carpenter et al., Serial No. 312,258 filed January 3, 1940. Where the cold rolling has been carried on with the material in sheet form, it may be found convenient to join the sheets into a continuous supply of indefinite length by welding in accordance with the teachings of Patents Nos. 2,172,080, 2,172,081, 2,219,493, 2,175,615, 2,175,616 and 2,196,941. For flatness, tension may be employed during the continuous anneal in accordance with the teachings of the copending application of C. E. Gifford et al., Serial No. 385,756 filed March 29, 1941. The material may be sheared apart into sheets for the final box anneal, or it may be box annealed in coils, giving a strip material suitable for the manufacture of transformers.

Briefly, in the formation of the insulative coatings, we continuously anneal the silicon steel sheet stock under conditions to prevent the oxidation of iron but to permit controlled oxidation of silicon. This results in the formation of silica (SiO_2). Some of the silica lies at the surface of the sheet stock, and the rest forms tiny inclusions near the surface. A continuous layer is not formed in this manner, however, and no effective insulative layer is produced. We have found, however, that by causing the silica to segregate at the surface of the sheet stock, and then by employing the silica as the silicious base for a glass, we can form an insulative layer having the characteristics referred to in the stated objects of the invention. The thickness of the glass layer can thus be controlled by the amount of silica produced in the first heat treatment; and the resultant glass coating is not only exceedingly thin, uniform, and free of imperfections, but is tightly keyed to the surfaces of the sheet stock. The procedure outlined implies the provision of a second heat treatment, namely the box anneal, having sufficient time duration first for the segregation of the silica at the surfaces of the sheet stock and second for the joining of the silica with another ingredient to form glass; and it also involves the addition of an ingredient capable of forming a glass with silica and capable of acting as a separator to prevent sticking of the sheets or of the convolutions of the coil during the box anneal.

The conditions during an open anneal in "wet hydrogen" are not difficult to control to oxidize silicon to a desired extent, and are capable both of considerable variation with the attainment of good results and of fairly exact control to vary the quantity of silicon oxidized. It is possible to obtain the desired result over the entire range of conditions which will produce rapid decarburization by open annealing in wet reducing atmospheres in accordance with the previously mentioned Victor W. Carpenter et al. application, which teaches an effective temperature range of 1350° to 1650° F. and moisture content varying from 2 to 35% by volume. Where the open anneal is primarily for the purpose of oxidizing silicon, temperatures higher than 1650° F. can be used even up to the limits of commercial open annealing equipment. By way of example, we are currently making our material by giving it an open anneal at temperatures between 1500 and 1600° F. in a hydrogen bearing reducing atmosphere having a dewpoint of 130° F. (approximately 15% water vapor by volume). In our furnaces the time cycle is such as to give a heat treatment of about 2 minutes' duration for 29 gauge material. It will be seen that under constant conditions of temperature and atmosphere, the variation of the time of treatment forms a convenient way of controlling the extent of the formation of silica; but atmosphere or temperature may alternatively or additionally be varied for purposes of control.

The water vapor effects rapid oxidation of the carbon in the silicon steel sheet stock, while the reducing character of the atmosphere prevents oxidation of the iron. The conditions, as determined principally by the presence of the water vapor are, however, sufficiently oxidizing to form silica. If the material is sectioned and viewed under the high-powered microscope after the open anneal, some silica will be seen at the surface usually in interspaced islands, and some will be seen as inclusions near the surface. As we

have already indicated, this procedure alone does not give a satisfactory insulative coating.

While we have indicated the open anneal as a decarburizing anneal, it may be an anneal practiced on low carbon material. So far as the production of our insulative coatings is concerned, the object of the anneal is to produce controlled amounts of silica at or near the sheet surfaces, hence to oxidize silicon without oxidizing iron. We are thus not limited to an anneal in wet hydrogen. We may in general use any atmosphere which, under the heats employed or employable, is neutral or reducing toward iron but oxidizing toward silicon. The use of water vapor in an atmosphere otherwise reducing is a convenient way of accomplishing our result. In general, a reducing atmosphere is necessary where water vapor is employed, in order to bring about the required selectively oxidizing conditions. Water vapor, in the presence of an inert or slightly oxidizing atmosphere cannot usually be controlled to attack the silicon without attacking the iron. A heat treatment in which there is some oxidation of the iron does not prevent the formation of our coatings, since the conditions in the final anneal are preferably strongly reducing as will be pointed out hereinafter, and may be controlled to reduce the iron oxide before the temperature of glass formation is reached. But the formation of iron oxide in the first anneal represents an economic waste and is to be avoided. If oxidation of the iron is uncontrolled, trouble may be had through loss of silica in subsequent handling operations in which the iron oxide is dislodged, or in the formation of coatings which do not adhere well to the surfaces of the sheet stock.

It is not necessary, however, that the open anneal (in which the silicon is controllably oxidized) immediately precede the box anneal hereinafter described. Silicon steel sheet stock in which sufficient silica has been developed at the surfaces may even be further reduced by cold rolling prior to the final box anneal as would be the case when the controlled oxidation of the silicon is carried out at the intermediate annealing gauge. It also may be given another open anneal. But in the routing of material of the class which constitutes our exemplary embodiment, an open anneal followed by a box anneal is usual routing with us; and the steps for the formation of our insulative coatings may be confined to practices in connection with these two final heat treatments.

The silicon steel sheet stock in which silicon has been developed at or near the surfaces as just described is prepared for box annealing by being given a coating of a substance capable of serving both as a separator to prevent sticking and as a glass forming ingredient. The best substance which we have found is a magnesium bearing substance. In general our procedure is to coat the sheet stock with milk of magnesia, i. e. hydrated magnesium oxide. But prolonged research has been necessary in the development of a satisfactory coating substance. The coating has to be applied for greatest convenience in the form of a liquid suspension or slurry. It is relatively easy in this manner to apply a uniform coating of controlled thickness, and to dry the coating on the surfaces of the sheet stock. No great capital invention is required, it being necessary only to get the material onto the sheet surfaces and then control its thickness by some such means as doctors or rubber rolls, and finally to effect drying by either passing the stock through

a sufficient path of travel through the open air or by applying to the sheet stock a gentle heat sufficient to evaporate the uncombined water. But the coating must be made to adhere even in dried condition sufficiently so that it will not be dislodged by the handling operations through which the sheet stock must necessarily go prior to the final box anneal. A drying temperature high enough to drive off the chemically combined water from the magnesium hydroxide should be avoided, since this has been found to result in a coating which flakes off readily. While it is not necessary to have a great quantity of the magnesia present to form the glass, yet since the coating must also serve as a separator in the final anneal, it should be present in sufficient quantity to serve that purpose. The problem is especially apparent when annealing stacked sheets (which have the greatest tendency to stick together during annealing); and the nature of the coating must be such as to withstand handling of the individual sheets, and must persist in sufficient thickness in the parts of the sheets rubbed by the bare or gloved hands of the workmen.

Yet another difficulty with the coating is the fact that the hydrated magnesia gives up its water of crystallization at relatively high temperatures. Difficulty with the evolution of large volumes of water at high temperatures may be minimized by furnace control as set forth hereinafter; but this difficulty, in part, and the difficulty mentioned above are rendered much less troublesome by controlling the nature of the coating substance.

Calcined magnesia is available in a number of different forms, differing largely in characteristics due to the temperatures at which the material was roasted. Magnesium carbonate (basic), calcined at around the lowest temperatures suitable for driving off the water and carbon dioxide, forms a very light and fluffy powder. It hydrates very readily and when mixed with water at about 0.5 lb./gal. forms a very thick, pasty and adherent suspension. Such a suspension sticks very well to the surfaces of the sheet stock, and is most resistant to dislodgment in handling when dried.

Beyond the lightest and fluffiest grade of magnesia (which is known as extra light powder) there are other grades calcined at higher temperatures. These progressively provide powders which are heavier, bulk for bulk, which progressively hydrate less and less readily, and which display less and less of the property of forming thick, glutinous and adhesive suspensions in water. The commercially available grade of magnesia calcined at the highest temperature is known as "nonhydrating magnesia." When mixed with water it scarcely hydrates at all; and suspensions could be made of such a material or of other grades calcined at somewhat lower temperatures, which would give up very little water at high temperatures. Suspensions made of such grades however, are extremely thin and watery and settle out rapidly. It is difficult to apply such suspensions, and when the coatings are dried, they do not adhere to the surfaces of the sheet stock and are very easily dislodged. Such coatings therefore are not suitable for our purpose, though the magnesia is suitable for combination with silica to form a glass, and the dried coating would contain the minimum of combined water.

But we have found that by making a thick, creamy and adhesive suspension of extra light

powder or other light and fluffy grades of magnesia in water, we can provide a vehicle which may be loaded up with considerable quantities of the substantially "non-hydrating" forms of magnesia. In commercial practice, by way of example, we agitate in 135 gallons of water 30 pounds of extra light powder, and 75 pounds of non-hydrating magnesia, giving us a coating substance suitable for our purpose. It will be understood that these quantities can be varied widely, and that with care any single grade of magnesia may be employed which will give a coating capable of withstanding the handling to which it must necessarily be subjected. While the purity of the magnesia used is of little importance in forming the insulative film, we prefer to use U. S. P. grade in order to prevent contamination of the steel and thereby obtain the best possible magnetic results.

The procedure which we have outlined is the one preferred by use as giving a satisfactory result with the greatest economy and convenience. While other procedures can be used without departing from the spirit of the invention, the other procedures which we have investigated are not as advantageous. Difficulty is encountered with vehicles other than water for example. Organic substances are likely to deposit carbon on the sheets and increase their carbon content. The same thing is true of organic agglutinants added to water; while inorganic adhesives such as sodium silicate have a tendency to produce fusion throughout the thickness of the magnesia coating thereby causing the sheets to stick together.

As a material for combining with silica to form a glass, we have found magnesia preferable, as indicated above. The glass formed is satisfactory as an insulative coating, it lies at the surface of the sheet stock, and is uniform and without contamination by conductive particles. Attempts to substitute calcium compounds for magnesia have encountered the difficulty that, while a glass substance is formed, the insulative coating has a tendency not to be uniform and effective in all instances. Materials upon the surfaces of which a lime-silica glass is formed have been found which, under the high powered microscope, show islands of conductive metallic particles interrupting the surface of the glass; and such materials do not possess coatings of dependable insulative quality in such instances. But along with magnesia, we may employ other materials in minor quantities even when employing magnesia as the primary substance for combination with silica. We have found instances where the addition of commercial lime to magnesia may be practiced without detriment and even with some advantage. There are a variety of glass forming substances which may be so used. For reasons which will be apparent from the description above, we do not have to add silica to our magnesia coating, preferring to have the silica developed in the sheet surfaces during the open anneal, whereby to control the thickness and adhesion of our insulative coating. The magnesia itself may contain some silica as a natural impurity, but this does no harm.

Two fundamental actions occur in the final anneal. The first is the segregation of the developed silica on the surfaces of the silicon steel sheet stock. If a piece of sheet stock is given a box anneal (or equivalent laboratory treatment) without the magnesia coating, and is sectioned and examined under the high power microscope, it will be found to differ from its appearance after

the open anneal in that the silica which before existed in part as inclusions near the surface has now migrated to the surface. The surface will be found covered with a fairly uniform but exceedingly thin coating of silica powder, which rubs off readily and does not provide adequate interlamination resistivity.

In our practice, therefore, we coat the material with magnesia; and the second function of the final anneal is that of causing a part of the magnesia to combine with the silica to form an adherent glass. The first function is dependent upon time at sufficient temperature, while the second is dependent upon the attainment of a temperature high enough for glass formation. These functions are of course in addition to the normal functions of the box anneal in developing the magnetic characteristics of the silicon steel, and do not interfere with such action.

It should be noted that the quantity of magnesia applied is far in excess of that required to combine with the silica. This is necessary to prevent sticking together of the sheets or coil convolutions. Temperatures are reached in the final anneal in which the metal would stick together; and at temperatures of glass formation the glassy coatings of the sheet stock would fuse together in the absence of a separator. A condition of excess magnesia is almost unavoidable however, since so little of it is required to combine with the silica. For this reason, we have given no specific instructions as to the quantity or weight of the coating. In practice our coatings are about 1.2 gms. per square foot of sheet surface.

We place our coated coils or stack our coated sheets on a platform and cover them with a box, sealing around the edges of the box in such a way as to enable us to maintain a desired atmosphere in the box. Our annealing cycle in practice is substantially as follows:

Heat very slowly up to 1100° F. (24-30 hours for a 20 ton charge) to drive off chemically combined water from the magnesium hydroxide. A hydrogen-bearing atmosphere is used above 850° F.

Heat to around 2100° F. in approximately 50 hours.

Soak 24 hours at around 2100° F.

Slow cool to below 1000° F.

The atmosphere which we employ is preferably hydrogen bearing, and may be hydrogen or hydrogen diluted with nitrogen; but the hydrogen may be considerably diluted. It will be noted that our heating cycle is relatively slow. This is to bring about the substantially complete evolution of water vapor at the temperatures at which magnesium hydroxide gives up its combined water. We have found this to be of great importance because if the water is caused to be evolved at higher temperatures, metallic globules form on top of the insulative film, resulting in very poor interlamination resistivity. With coatings of the kind and weight which we have set forth above as exemplary, there may be an evolution of as much as ten pounds of water per ton of metal treated. The water vapor is disadvantageous, in that it has an oxidizing effect. It will not ordinarily decarburize, because our materials are already preferably decarburized. But it tends to oxidize both silicon and iron; and the difficulty is primarily that its effect is uneven and strongest at the edges of the sheets. We therefore control our atmosphere in such a way as to sweep the evolved water vapor out of the box as rapidly

as possible, and furthermore maintain the hydrogen concentration such that the water-hydrogen-iron-iron oxide equilibrium is as nearly non-oxidizing as possible during the time that the magnesium hydroxide is losing its water. If recirculation of the atmosphere is attempted, it should be dried during recirculation, as by using silica gel or other suitable drying substance. The employment of a reducing atmosphere tends of course to prevent the actions referred to above, and to reduce any oxide of iron which may be formed. By heating slowly, and sweeping the water vapor out of the box, we are able to prevent excessive oxidation of iron.

It may be noted that the combined water begins to leave hydrated magnesia at a temperature of about 620° F. This is too low a temperature to be favorable to the oxidation of silicon, but is a temperature not too low for the oxidation of iron in the presence of a fairly large concentration of water vapor. Thus the evolution of water vapor in the heating cycle of the final box anneal cannot be relied upon to produce the silica at the sheet surfaces, particularly on wide sheets. It would be possible on pieces not over several inches wide to calcine the magnesia first in the box annealing procedure and then, having raised the temperature sufficiently, to oxidize the surface silicon to silica by the introduction of water vapor in the gases at that stage, thereafter allowing segregation to proceed by prolongation of the soaking cycle. But for reasons which will now be apparent, the most feasible and convenient practice especially for material of greater width is to develop the silica in an initial open anneal.

By the conclusion of the heating cycle of the final box anneal the temperatures will have reached a point suitable for the formation of glass by the combination of silica and a portion of the magnesia. Since the quantity of silica is limited, the amount of glass formed is likewise limited. This leaves the greater bulk of the magnesia free to serve as a separator. At the conclusion of the final box anneal and after the cooling of the material, the box is opened, the sheets separated or the coils unwound, and the loose magnesia removed from their surfaces. This may be accomplished by brushing or by washing or by a combination of these steps. The sheet stock after being so cleaned is found to be covered with a thin, uniform, glassy layer of substantially continuous character serving as an efficient insulator between the laminae of a core or other magnetic structure. The sheets have a uniform and attractive grayish appearance due to the presence of the glass and the particles of magnesia which are adhering to its surface. It will be understood that some particles of the magnesia are caught in the surface of the glass at temperatures at which the glass is tacky. The insulating coating is very firmly bonded to the sheets and is capable of withstanding bending without rupture. The glass forming the coating is further of such high melting point that wound cores, stampings or punchings can be reannealed for the relief of the working strains without danger of sticking even though no separators be employed.

In the claims and elsewhere throughout this specification we are employing the term "sheet stock" to mean silicon steel of sheet thickness, irrespective of whether the material is in the form of individual sheets or in the form of coiled strip material.

Modifications may be made in our invention without departing from the spirit of it.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A process of producing a tightly adherent insulative coating on the surfaces of silicon steel sheet stock, which comprises preferentially oxidizing silicon in the sheet stock at and adjacent the surfaces thereof to form silica, coating the surfaces of said stock with a magnesia bearing substance, and in a heat treatment causing the silica so formed to migrate to the surfaces of the silicon steel sheet stock, and causing the said silica at the surfaces of the sheet stock to combine with said magnesia to form a tightly adherent layer of glassy substance on said surfaces, said layer being tightly bonded to said surfaces, and the thickness of said layer being controlled by the quantity of silica therein primarily derived from the silicon steel.

2. A process for the production of silicon steel sheet stock having on its surfaces a tightly adherent insulative coating, which comprises preferentially oxidizing silicon to produce silica at and adjacent the surfaces of decarburized silicon steel sheet stock, coating the surfaces of said stock with a magnesia bearing substance, and in a heat treatment causing said silica to migrate to the surfaces of said sheet stock and to fuse with a portion of said magnesia to form a glassy layer, the thickness of which is controlled by the quantity of silica so produced.

3. A process for the production of silicon steel sheet stock having a highly insulative, highly adherent, glassy coating, which comprises subjecting silicon steel stock to a continuous, brief heat treatment in an atmosphere reducing to iron and containing moisture, the conditions of said heat treatment being such as to reduce the carbon content of said silicon steel to a low value and such as to oxidize silicon to silica at and adjacent the surfaces thereof, thereafter coating said silicon steel with a layer of material containing magnesia, and annealing said silicon steel in a closed space for such a length of time as to cause said silica to migrate to the surfaces thereof and at such temperature as to cause said magnesia to fuse with said silica to form a glassy coating, the thickness of which is controlled by the thickness of said silica so produced.

4. The process set forth in claim 3 wherein said glass forming ingredient comprises a hydrated magnesia, and in which said last mentioned heat treatment is a heat treatment carried on in a reducing atmosphere to prevent oxidation of iron in said silicon steel.

5. The process set forth in claim 3 wherein said glass forming ingredient comprises a hydrated magnesia, and in which said last mentioned heat treatment is a heat treatment carried on in a reducing atmosphere to prevent oxidation of iron in said silicon steel, and in which the silicon steel is heated slowly through temperatures at which said hydrated magnesia gives up its water, the said water, in the form of vapor, being continuously removed from the space surrounding the said silicon steel.

6. A process as set forth in claim 3 wherein said glass forming ingredient comprises hydrated magnesia and is formed by stirring into water a quantity of light and fluffy magnesia capable of forming a thick and adhesive slurry, and further adding to the suspension so formed a quantity of

magnesia having the property of being resistant to hydration.

7. A process of producing silicon steel sheet stock having an insulative, glassy coating on its surfaces, which process comprises subjecting silicon steel sheet stock to a continuous anneal in a free hydrogen bearing atmosphere containing water vapor, the temperature and quantity of vapor employed in said anneal being such as to reduce the carbon content of said silicon steel to a low value at least as low as around 0.01% and concurrently preferentially to oxidize silicon to silica at and adjacent the surfaces thereof, thereafter coating the silicon steel so treated with a suspension of a glass forming ingredient consisting principally of hydrated magnesia, drying the coated stock and box annealing the coated stock in a reducing atmosphere at temperatures and for a length of time sufficient first to cause said silica to migrate to the surfaces of said sheet stock and thereafter to cause said silica to fuse with said magnesia to form a glass coating on said sheet stock, the thickness of said coating being controlled by the quantity of silica so developed in said sheet stock.

8. The process of claim 7 wherein the first heat treatment is a heat treatment of short duration at a temperature of approximately 1350 to 1650° F. and in which the second heat treatment includes carrying the material to a temperature as high as approximately 2100° F.

9. The process of claim 7 in which the magnesia is applied to the surfaces of the sheet stock in excess, whereby the excess magnesia serves as a separator in said second heat treatment.

10. The process of claim 7 in which the magnesia is applied to the surfaces of the sheet stock in excess, whereby the excess magnesia serves as a separator in said second heat treatment, and in which said magnesia is applied to the surfaces of the silicon steel sheet stock in the form of a slurry in water.

11. A process of producing silicon steel sheet stock having an insulative glassy surface coating, which comprises continuously annealing silicon steel sheet stock in a hydrogen bearing atmosphere containing water vapor to decarburize said stock and to oxidize silicon to silica at and adjacent the surfaces thereof, coating the silicon steel sheet stock as so treated with a slurry of magnesia in water, drying the coated sheet stock and box annealing the coated sheet stock so as to drive combined water from said magnesia coating, so as to cause said silica to migrate to the surfaces of said silicon steel sheet stock and so as finally to cause said silica to fuse with a portion of said magnesia.

12. A process of producing silicon steel sheet stock having an insulative glassy surface coating, which comprises continuously annealing silicon steel sheet stock in a hydrogen bearing atmosphere containing water vapor to decarburize said stock and to oxidize silicon to silica at and adjacent the surfaces thereof, coating the silicon steel sheet stock as so treated with a slurry of magnesia in water, drying the coated sheet stock and box annealing the coated sheet stock so as to drive combined water from said magnesia coating, so as to cause said silica to migrate to the surfaces of said silicon steel sheet stock and so as finally to cause said silica to fuse with a portion of said magnesia while maintaining in both of said heat treatments conditions minimizing the oxidation of iron.

13. A process of producing silicon steel sheet

stock having an insulative glassy surface coating, which comprises continuously annealing silicon steel sheet stock in a hydrogen bearing atmosphere containing water vapor to decarburize said stock and to oxidize silicon to silica at and adjacent the surfaces thereof, coating the silicon steel sheet stock as so treated with a slurry of magnesia in water, drying the coated sheet stock and box annealing the coated sheet stock so as to drive combined water from said magnesia coating, so as to cause said silica to migrate to the surfaces of said silicon steel sheet stock and so as finally to cause said silica to fuse with a portion of said magnesia while maintaining in said box anneal conditions minimizing the oxidation of iron and finally conditions which are reducing toward iron.

14. A process of producing silicon steel sheet stock having an insulative glassy surface coating, which comprises continuously annealing silicon steel sheet stock in a hydrogen bearing atmosphere containing water vapor to decarburize said stock and to oxidize silicon to silica at and adjacent the surfaces thereof, coating the silicon steel sheet stock as so treated with a slurry of magnesia in water, drying the coated sheet stock and box annealing the coated sheet stock, said box annealing comprising a sufficiently slow initial heating cycle to drive all combined water from said magnesia coating at temperatures not exceeding substantially 1100° F., and a further heating to a temperature of at least substantially 2100° F.

15. A process of producing silicon steel sheet or strip, containing from 0.05% to 4.00% silicon, and having an insulative glassy surface coating, which comprises continuously annealing said sheet or strip at a temperature substantially within the range of 1350 to 1650 degrees F., in a hydrogen bearing atmosphere containing water vapor substantially within the range of 2 to 35%, to decarburize said stock and to oxidize silicon to silica at and adjacent the surfaces thereof, coating the silicon steel sheet stock as so treated with a slurry of magnesia in water, drying the coated sheet stock and box annealing the coated sheet stock in a reducing atmosphere predominantly of hydrogen, said box annealing comprising a sufficiently slow initial heating cycle to drive substantially all of the combined water from said magnesia coating at temperatures not exceeding substantially 1100 degrees F., and a further heating to a temperature of at least substantially 2100 degrees F.

16. A silicon steel stock of sheet width and gauge, the surfaces of which are covered with a tightly adherent, fused, insulative, glass layer which is uniform and substantially impervious, comprising the fusion product of silica and magnesia, and in which the silica is derived primarily by preferentially oxidizing silicon in the sheet stock at and adjacent the surfaces thereof to form silica, and causing the silica so formed to migrate to the surfaces of the silicon steel sheet stock, in which the glass is formed in a heat treatment by causing the silica so formed to combine with magnesia from a coating of a magnesia bearing substance imposed upon the surfaces of the silicon steel sheet stock, and in which the thickness of said layer is controlled by the quantity of silica therein primarily derived from the silicon steel.

17. A decarburized silicon steel stock of sheet width and gauge having its surfaces covered with a tightly adherent, fused, uniform and substan-

tially impervious, insulative layer comprising fused silica-magnesia glass, in which the siliceous component is primarily derived from silicon at and adjacent the surfaces of said silicon steel sheet stock by oxidation of the silicon steel sheet stock in accordance with the process claimed in claim 7.

18. A decarburized silicon steel sheet of commercial width and gauge for magnetic applications having its surface covered with a tightly adherent electrically insulative, thin, uniform and substantially impervious, fused, glass-like coating consisting principally of the reaction product of silica derived from the steel by sub-

jecting the steel sheet to a heat treatment in hydrogen including water vapor, and magnesia derived from a coating subsequently imposed thereon, the surfaces of said fused coating possessing imbedded and adhering magnesia particles whereby adjacent sheets in a stack thereof and bearing the formed coating are free from the tendency to stick together during subsequent annealing, the said sheet stock being produced by the process of claim 15.

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