

UNITED STATES PATENT OFFICE

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PROCESSES OF PRODUCING GLASS
COATED SILICON STEELVictor W. Carpenter, Franklin, and Samuel A.
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Steel Corporation, a corporation of OhioNo Drawing. Application July 23, 1945,
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4 Claims. (Cl. 148—6.35)

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In the copending application of ourselves and Joseph E. Heck, Serial No. 389,962, filed April 23, 1941, and entitled The production of silicon steel sheet stock having insulative surfaces, which has now matured into Patent No. 2,385,332 dated September 25, 1945, there is described a process of producing thinly and uniformly a glassy, insulative coating upon silicon steel stock. The process as practiced and as disclosed in that application involves a plurality of steps: The silicon steel is subjected to a heat treatment in a continuous furnace in an atmosphere of "wet hydrogen." This results not only in decarburization, which improves the electrical qualities of the steel, but also oxidizes silicon at or near the surfaces of the steel to silica while leaving iron unoxidized, a phenomenon which we have referred to as "preferential oxidation."

After this treatment the silicon steel is coated with a material capable at once of acting as a separator during annealing and of combining with silica to form a glass-like substance. Of such materials magnesia has been found the best and most available. It is mixed with water, whereupon it hydrates in large part to magnesium hydroxide, forming a slurry with which the silicon steel is easily coated. The coating is then dried.

Next the coated silicon steel is subjected to a high temperature box anneal, in which several actions occur. The magnesium hydroxide gives up its combined water, reverting to magnesium oxide or magnesia. The silica formed near the surfaces of the silicon steel tends to migrate to the surfaces. Upon further rise in temperature, some of the magnesia combines with the silica to form a glassy coating next and firmly bound to the surfaces of the silicon steel, the remainder of the magnesia acting as an annealing separator.

The thickness of the glassy coating is rigidly controlled because it depends upon the silica produced in or on the sheet surfaces; and it is both thin and uniform. After annealing, the silicon steel sheets or strips are easily separated or decolled; and the excess magnesia may readily be brushed or cleaned from their surfaces leaving the durable insulative film.

The objects of the present invention are the provision of improvements in the procedure for producing glass-coated silicon steel, accompanied by savings in cost and the attainment of improved products.

These and other objects of the invention which will be set forth hereinafter or will be apparent to one skilled in the art upon reading this specification, we accomplish by the procedure which

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we shall now outline in an exemplary embodiment.

While excellent commercial results have been obtained in the process of the copending application, experience has indicated that there are a number of disadvantages in the conversion, in the box annealing step, of the magnesium hydroxide to magnesia. The evolution of large quantities of water in the annealing box renders atmospheric control difficult, and also necessitates the use of special heating cycles, since the combined water in the hydroxide begins to come off at approximately 660° F. When the dehydration of magnesium hydroxide occurs during box annealing there is usually a difference in appearance of the glassy film between the center and edges of the sheets, which we believe due to water from the center of the charge passing between the hotter sheet edges. On occasion a phenomenon of peeling of the coating at the center of the sheets is encountered, which is not explained, but seems related to the matter of water elimination, since it does not occur in the procedure of this application.

These considerations indicate that it would be desirable to eliminate the water prior to the box anneal. It should be explained at this point that we are referring to the chemically combined water in the magnesium hydroxide. The free water in the initial slurry is quite easily and rapidly driven from the coating on the steel by heating to 212° F. or slightly higher, as may be done with gas flames playing upon the surface of the steel. Such temperatures are well below oxidation temperatures and do not affect the qualities of the steel.

But as explained above, the magnesium hydroxide requires heating to temperatures of 660° and higher before its combined water begins to come off. Thus, attempts at dehydration, as we use the term, require heat treatments of some considerable magnitude and cost; and the addition of a separate step and furnace is economically unsound. Moreover the temperatures are well above the oxidation temperatures for iron and, as we have found, the heat treatment would have to be conducted in a protective atmosphere, adding to the expense. Depending upon how the treatment is conducted, it might deleteriously affect the electrical properties of the steel.

Again a lengthy heat treatment was thought to be indicated, at relatively moderate temperatures, say not more than one or two hundred degrees above 660° F. Attempts have hitherto been made to dehydrate magnesium hydroxide to serve as a separator on ferrous sheets prior to box an-

nealing. The understanding was that slow drying resulted in tight adherence, and drying times of four to five hours have been recommended. It was further understood that rapid evolution of water vapor would disrupt the coating and blow or blast it from the surfaces of stacked or coiled materials.

We have, however, found that these problems can be met and solved by the procedure herein outlined.

Having otherwise finished and cleaned our silicon steel sheet or strip (in the claims we use the word "stock" to include sheets or strip material) we first coat it with a slurry of hydroxide coating substance. Preferably, as indicated, we use magnesium hydroxide, but other substances will serve, e. g. calcium hydroxide. Then the free water is driven from the coating by gentle heat, as by passing the stock through or against open gas flames.

The coating may be done in any suitable way as by dipping or spraying, and it is usual with us to pass the coated stock through rubber wiping rolls to control the thickness of the coating. Driving off the free water is desirable because roller conveyors or pinch roll combinations subsequently used to move the stock tend to pick up and accumulate wet coating, and will give trouble. When the free water is gone, we have found that the stock is easily handled through subsequent operations by pinch roll or conveyor means without disruption of the coating, with no greater precautions than the avoidance of scraping contact, and the driving of the rolls at peripheral speeds as nearly as possible the same as the linear speeds of the stock.

The sheets or strips are then delivered to a continuous annealing furnace. By this we mean an elongated furnace in which all surfaces of the sheets or strips are open or exposed to the atmosphere of the furnace, to which end the sheets or strips are sent through individually. In this furnace the stock is subjected to a rapid rise in temperature in a controlled atmosphere.

We have found that at temperatures around 1550° F. in a continuous furnace we can drive off the combined water in our coatings within the space of about two minutes, which is a time of treatment well within the range of operation of continuous furnaces at good operating speeds.

The coating is not disrupted by our treatment, nor blown off.

But we have further found that with a properly controlled atmosphere in the furnace the decarburization and preferential oxidation referred to above can proceed concurrently and can be concluded within the same space of time. We therefore introduce into our furnace a non-oxidizing, hydrogen bearing atmosphere which may be hydrogen itself or any neutral atmosphere rich in hydrogen, e. g. cracked ammonia.

In order to perform the decarburization and preferential oxidation the furnace atmosphere must be hydrogen bearing and "wet." The ranges of temperature and moisture content set forth in the said copending application for this procedure are 1350 to 1650° F. for the temperature and 2 to 35% of water vapor by volume for the moisture content of the furnace atmosphere. In the process of the present invention temperatures below about 1500° F. have been found to produce so slow a dehydration of the magnesium hydroxide that it becomes difficult to accomplish it within the scope and normal speed of conventional open annealing furnaces. On the other

hand, if the temperature is carried much above 1650° F., while dehydration becomes more rapid, decarburization becomes slower; and since for most high quality silicon steel decarburization is important, we set forth as our preferred temperatures those lying between substantially 1500° and substantially 1650° F. Within these limits treatments of the order of about two minutes have been found satisfactory for dehydration, decarburization and preferential oxidation, from one to four minutes being a general operating range.

We have also found that at such temperatures in the ordinary continuous furnace the amount of water given up by the coating on the sheet or strip stock is generally sufficient to maintain a desired working humidity of the furnace atmosphere. This constitutes an important advantage and economy since the maintenance of furnace humidity has always involved something of an operating problem. Needless to say, however, no departure from the principles of our invention is made by practicing additional controls upon the furnace atmosphere or by adding moisture to it in other ways.

It is of the utmost significance, however, that we have found that the decarburization and preferential oxidation proceed in our furnace concurrently with dehydration of the magnesium hydroxide coating and are not inhibited or prevented by it.

By way of a single example, we have found that silicon steel stock of .013 gauge containing initially .025% of carbon when coated with magnesium hydroxide, dried as described for the elimination of free water, and then continuously annealed for two minutes at 1550° F., had its carbon content lowered to .0065% and the water content of its coating lowered from an initial 30.5% to 2.6%. Also sufficient silicon in the silicon steel was oxidized to silica to produce a satisfactory glassy coating in the subsequent steps.

At the conclusion of the steps just described the silicon steel stock is stacked if in sheet form, or coiled if in strip form, and is then box annealed. The box annealing is usually and preferably done in an atmosphere of dry hydrogen at a temperature of or around 2100° F.

Hitherto the box annealing of undehydrated magnesium hydroxide coated stock involved a very slow heating up to 1100° F., occupying about 24 to 30 hours for a 20 ton charge. During this initial heating cycle the chemically combined water was driven off from the magnesium hydroxide. Only thereafter could the material be raised to a temperature of 2100° F. which was the preferred annealing temperature. It took approximately 50 hours, following the above cycle to get the material up to the maximum temperature. It then was soaked for 24 hours at around 2100° F. and slowly cooled to a temperature below 1000° before the box was opened.

By treating our materials as set forth above, the initial part of the heating cycle which has just been outlined may be dispensed with, and the material may be raised to the highest temperature as rapidly as is consistent with good furnace operation in the particular equipment at hand. Thus a considerable saving may be made in fuel or power by reason of the shortened time cycle. Control of the atmosphere in the annealing box is also facilitated since it is not necessary to sweep from it large quantities of moisture driven off from the coating. During the anneal the ultimate electrical properties of

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the silicon steel are developed and the actions noted in the above entitled copending application occur, namely the migration of silica to the surfaces of the silicon steel stock and its combination there with some of the magnesia to form the desired thin controlled uniform glassy coating tightly adherent to the stock surfaces. The remainder of the magnesia acts as a separator during the anneal and is easily removed from the glass coated stock thereafter.

It will be understood that the amount of water required to be driven off to accomplish dehydration may be diminished by the use of oxides which are more difficultly hydrated, so long as a satisfactory coating slurry is obtained. For example, magnesia calcined at a high temperature hydrates less readily when placed in water than products fired at lower temperatures while still producing acceptable coating slurries. It is within the purview of our invention to take advantage of this known fact. Also where we speak of dehydration of the hydroxide coating, we do not limit ourselves to treatments in which all detectable quantities of combined water are driven out. From the example given above it will be apparent that our process is preferably directed to such a degree of dehydration that any remaining water will not sensibly affect the box annealing temperature.

Modifications may be made in our invention without departing from the spirit of it. Having thus described our invention in an exemplary embodiment, what we claim as new and desire to secure by Letters Patent is:

1. A process of producing silicon steel sheet or strip stock with insulative coating of glasslike character, which comprises imposing upon the surfaces of silicon steel stock a metallic hydroxide chosen from the class consisting of magnesium hydroxide and calcium hydroxide, capable of dehydrating to an oxide which acts as an annealing separator, and which also will combine with silica to form a glasslike substance, passing the coated stock through a continuous furnace and heat treating it at temperatures between substantially 1500 and substantially 1650° F. in a moisture containing hydrogen bearing atmosphere non-oxidizing to iron, whereby to dehydrate the hydroxide, to decarburize the silicon steel stock and to oxidize silicon at and below the surfaces thereof to silica, afterward box annealing the stock so treated at temperatures of around 2100° F. in a dry reducing atmosphere to cause migration of silica to the surfaces of the stock and to fusion of silica thereat with part of

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said oxide to form a glassy coating next said surfaces, with a remainder of uncombined oxide sufficient to act as an annealing separator.

2. The process claimed in claim 1 including the step of maintaining the atmosphere in the said continuous furnace with a moisture content of from 2 to 35% by volume, the time duration of the treatment in the said continuous furnace being from substantially 1 minute to substantially 4 minutes.

3. The process claimed in claim 1 in which the moisture content of the hydrogen bearing atmosphere in the continuous furnace is substantially 2 to substantially 35% by volume and in which the atmosphere during box annealing is a substantially dry hydrogen bearing atmosphere.

4. A process of producing silicon steel sheet or strip stock bearing upon its surfaces a glassy insulative coating which comprises imposing upon the surfaces of silicon steel stock magnesium hydroxide in a slurry in water to form a coating, drying free water from the coating by subjecting the stock to gentle heat at around 212° F., passing the coated stock through a continuous annealing furnace and subjecting it therein to temperatures from substantially 1500 to substantially 1650° F. in a water containing hydrogen bearing atmosphere non-oxidizing to iron, whereby to drive combined water from the hydroxide coating and to convert hydroxide into oxide, maintaining the water content of the furnace atmosphere in part at least by water so driven off from the coating whereby also to decarburize the stock and preferentially oxidize silicon at and near the surfaces thereof to silica, thereafter box annealing the treated stock in a dry, hydrogen-bearing atmosphere at a temperature of substantially 2100° F. to cause migration of the said silica to the surfaces and its fusion there with part of the said oxide, and whereby to develop the electrical properties of said stock.

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