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PROCESS FOR PROVIDING MAGNETIC SHEET STEEL WITH AN INSULATIVE FILM

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The present invention relates to a process of providing magnetic sheet steel with an insulating oxide film. More particularly, the invention is concerned with the process of providing decarburized, low carbon, e. g., silicon steel sheet material with a thin, tightly adherent insulating oxide film, which process suitably may comprise part of the usual anneal given such material.

Various processes have been proposed and used for developing oxide films on ferrous alloys for decorative, protective, or insulating purposes. One of the oldest processes is that known as the "steam blue" process involving the use of steam for providing various alloys with a decorative blue surface. Other processes have involved the use of air, carbon dioxide or steam at various temperatures for the purpose of obtaining a controlled and uniform oxidation of the steel surface.

Insofar as the electrical sheet steel art is concerned, none of these processes has been fully satisfactory. Some of the oxide films have been deficient from the insulating standpoint, while others have been comparatively thick and not sufficiently adherent to withstand the usual handling operations. As regards the various atmospheres, it is well known that air will not penetrate uniformly into a stack of wide laminations to effect the desired oxidation of the centers of the sheets, while oxidizing gases such as carbon dioxide and steam leave a gaseous reaction product. This gaseous product which like the nitrogen in air dilutes the oxidizing gas to render it less effective, may in some cases reverse an equilibrium reaction, and in other cases may act as a physically active or reducing gas which can penetrate further into a stack of laminations to protect the center from oxidation.

One object of the present invention is to provide a process for developing a surface oxide insulation on silicon steel which insulation is thin and tightly adherent.

A further object of the invention is to produce an insulating oxide film on the surface of silicon steel sheet stock by a process which suitably forms part of the regular box annealing treatment ordinarily given such material.

Another object of the invention is to provide a process for forming a thin, uniform, insulating oxide film on the surface of silicon steel of commercial widths while the steel is in the form of a tightly wound coil or a large stack of sheets.

The above and additional objects which will become apparent from the following description of the invention are obtained by heat treating the wound coils or stacked sheets of magnetic sheet steel at a temperature of at least about 500° and not more than about 600° C. in an oxy-

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gen atmosphere. The term "oxygen atmosphere" or "atmosphere of oxygen" as used herein and in the appended claims refers to an atmosphere obtained by introducing into the heat treating furnace or box an atmosphere consisting essentially of oxygen containing not over 1 per cent impurities other than water vapor, the water vapor content not exceeding that necessary to saturate oxygen at room temperature.

As compared with carbon dioxide, air, or steam, oxygen is a most favorable atmosphere as the only reaction product with the silicon steel is a solid oxide so that there is no diluent or gaseous reaction product to interfere with the desired reaction. In tightly spaced laminations or when the sheet material is in roll form, the reaction of the gaseous oxygen to form only the solid reaction product, such as an iron oxide, has a further advantage of creating a vacuum between the laminations to cause more oxygen to enter between the laminations for further reaction with the surface of the material being treated.

In its preferred form, the present invention includes, or is part of, the usual anneal applied to silicon steel for the purpose of improving its magnetic properties. For example, much of the steel now employed for magnetic applications, particularly for transformer applications, is obtained by subjecting silicon steel sheet material to a decarburizing treatment which may consist of the heat treatment of the rolled material in a moist hydrogen atmosphere at an elevated temperature such that the carbon content is reduced to a fraction of a per cent, ordinarily less than about 0.02 per cent and to form on the surface thereof a thin, tightly-adherent metallic scale containing some silica. It has been known for some time that the magnetic properties of this decarburized steel can be further improved by a box anneal at a temperature of at least 850° C. and preferably from 900 to 1050° C. in a hydrogen atmosphere.

The insulating oxide films of the present invention are preferably formed during the cooling cycle, forming part of this anneal. By cooling the steel from the annealing temperature to a temperature of from 500° to 650° C., preferably from 500° to 600° C., and then replacing the hydrogen atmosphere by an oxygen atmosphere, there is obtained an oxidation of the sheets to form an insulating film which is reasonably uniform over the entire area of the sheet and is particularly good toward the center sheet material. The temperatures referred to in connection with the oxidation process are those of the rolled or stacked material and not those of the furnace in which the heat treatment is being carried out. The resultant oxide films are primarily distin-

guished by a bluish-red color which might also be described as a thin, tight, uniform red scale having a blue tint or cast. Providing the temperature of the rolled or stacked material is held within the ranges indicated, there is no tendency for the insulating film to peel or loosen even when the insulated sheet is bent sharply upon itself.

It is essential that the temperature of the steel be within the stated range in order to obtain a tightly adherent film having the desired insulating properties. This will become apparent from a consideration of the following runs differing only as to the temperature employed during the oxidation step. In each run the load was a 6-inch stack of decarburized silicon steel laminations 6.5 inches wide and 20 inches long with no spacing material between the sheets. The annealing cycle was constant in every case with the load (within an annealing box) being placed in the annealing furnace at 750° C. roof temperature, the temperature raised to 980° C. and held at this roof temperature for 8 hours. The load was then furnace cooled overnight to the desired oxidizing temperature at which temperature the hydrogen was flushed from the box with nitrogen and the nitrogen then replaced with oxygen.

RUN 1

When the load center temperature in this run was about 650° C. to 700° C., the hydrogen was replaced by nitrogen which, in turn, was replaced by moist oxygen. The furnace continued to cool at the rate of 12° C. per hour and at the end of eight hours when the roof temperature had dropped to 500° C., the load was removed from the furnace with the oxygen continuing to flow into the annealing box until the load was cold.

Following anneal the laminations separated easily with no sticking. In color they were all alike, red-brown around the edge and bluish-red in the center. On direct rubbing the scale did not loosen, but when the laminations were bent sharply the center scale peeled off easily.

Ten laminations selected at random throughout the load were subjected to Franklin insulation tests.

Average Franklin insulation amperes:

Ends of laminations	.53
Edges of laminations	.55
Centers of laminations	.27

In the Franklin test a reading of 1.0 ampere corresponds to zero insulation and a zero ampere reading represents perfect insulation. It is the usual practice to operate the contacts of the Franklin test at 500 to 600 lb. per sq. in. contact pressure. However, to assure conservative readings, all of the tests described herein were made at 900 lb. per sq. in. contact pressure. In practice, a Franklin test of 0.5 ampere or less is considered to be perfectly good for transformer insulation purposes.

While the insulating properties of the oxide film gained at the load temperatures of 650 to 700° C. was good, there was a tendency for the resultant film to scale off, showing that it would not be suitable for commercial applications.

RUN 2

The second pack anneal of large laminations was similar to Run 1 except that oxygen was introduced at a load temperature of 600° C. to 650° C. Following treatment, these laminations had a red-brown color around the edges with spotty red with some gray in the center and very little trace of blue oxide. Upon bending there was a tendency for scale peeling at the center of the laminations so that the product was in this respect comparable to that of Run 1.

The average Franklin insulation amperes were:

Ends of laminations	.51
Edges of laminations	.58
Centers of laminations	.58

RUN 3

In the third pack anneal the load was allowed to cool to a load center temperature near 600° C. Wet oxygen was introduced, the furnace and load temperature brought back to 600° C. and held for two hours. At the end of this period the boxed load was removed from the furnace with the oxygen left flowing until the load was cold.

These laminations showed a thin, tight, uniform red scale, tinted blue. A narrow strip of light gray appeared along the ends of all laminations. No peeling could be seen whatever on bending of the sample.

Average Franklin insulation amperes:

Ends of laminations	.56
Edges of laminations	.48
Centers of laminations	.14

In the commercial practice of the present process it may be desirable to cool the furnace to a temperature less than 500°, as for example 300° C. or even to room temperatures, in order to insure that the center of the load is not over 600° C. However, since the oxidation at temperatures less than 500° C. is unsatisfactory electrically, it is thereafter necessary to reheat the load to a temperature within the prescribed range. Thus the process as applied to a factory load may suitably comprise cooling the annealed load to a temperature of about 320° C. in hydrogen at which temperature the center of the load will be somewhat under 500° C. At this temperature, the hydrogen is replaced by commercial oxygen and the temperature thereafter gradually raised to 600° C. for a two-hour period and held at this poinnt for about two hours. Employing this sequence of operations, there has been obtained an oxide coating which was uniform blue-red except for a gray-red line along the edges of the laminations. The coating was thin, smooth, and tight under all of the tests and the average Franklin insulation amperes were:

Ends of laminations	.39
Edges of laminations	.41
Center of laminations	.28

To compare the oxidizing effects of steam, carbon dioxide, pure dry oxygen and pure wet oxygen (saturated at room temperature), packs of ten epstein strips were tightly wired together and annealed in a quartz tube furnace at 980° C. in dried H_2. Samples were furnace cooled to various temperatures, hydrogen replaced with the desired oxidizing gas, and the furnace cooling continued down to about 150° C. All gas flow was maintained at about 10 cu. ft./hr.

The cooling period from about 600° C. to 150° C. in the furnace used requires about 7 hours. In general, the oxidizing gas was maintained during this cooling period from initial introduction temperature to 150° C. However, some duplicate runs were made in which the oxidizing gas was introduced at the selected temperature which was then held for one hour. At the end of this period the oxidizing gas was replaced by nitrogen and the cooling allowed to proceed to

150° C. The two systems of oxidation always produced identical results, indicating that the surface reaction is very rapid and proceeds to its final state in a reasonably short time. The results also indicate that no alteration of the oxide film, as far as insulation resistance is concerned, occurs on the down temperature cycle as long as the atmosphere is kept oxidizing or neutral during this period.

When cold, each side of every epstein strip was insulation tested. A summary of test result averages for the various atmospheres applied at various temperatures is given below.

TABLE

Surface oxidation of SX–10 strip Franklin test results in amperes

Temperature at Which Gas Was Introduced	Atmosphere			
	Steam	CO_2	O_2	Wet O_2
680° C.			.35	
650° C.	.19		.40	.18
600° C.	.80		.49	.47
550° C.	.40	.91		
500° C.		.92	.53	
450° C.			.86	
350° C.			.89	

For comparison, a similar anneal run at 980° C. and furnace cooled in hydrogen shows a Franklin test of 0.93 ampere.

Some notation of the surface condition of the various samples can be made.

Carbon dioxide in both cases formed a narrow band of blue-gray oxide around the edges of strips, leaving the center bright gray.

Oxygen caused scale-to-scale adhesion to an unsatisfactory degree at 685° C., with slight indication of the same effect at 650° C. Temperatures in this range, therefore, should be avoided in oxidizing of stack annealed material. At all temperatures the scales developed were thin and tightly adhering to the steel, varying in color from a steel blue when formed at 350° C., changing to a blue with rust cast as the higher temperatures of oxidation are reached.

Wet oxygen showed effects exactly the same as dry oxygen noted above, showing that the usual commercial oxygen is as effective as dry oxygen for the practice of the invention.

Steam tended to form a much bluer scale, with less rust colored cast, at all temperatures studied. This lack of red oxide formation may possibly explain the erratic insulation results when steam is used.

Standard D.-C. magnetostriction tests made on a number of samples obtained by the dry hydrogen anneal at 980° C. followed by oxidation in moist oxygen at 500 to 600° C. by the test described in U. S. Patent 2,312,888 showed that the effects on magnetostriction of the oxidized layer are either negligible or have a tendency to decrease the values toward 0 and in some cases, to cause a minor magnetostrictive contraction. The film apparently has no effect upon the rusting characteristics of the steel nor upon the space factor of the assembled structures. While it does not protect the steel from rusting in humid atmospheres, it at the same time does not accelerate rusting so that the oxide coated laminations may be stored for a reasonable period of time without damage.

Analysis for the determination of the chemical nature of the oxide film by electron diffraction studies have shown that the coating primarily consists of Fe_2O_3 plus some FeO. The Fe_2O_3 is present in the greatest amount and only the strongest FeO lines are present. This is believed to indicate that the surface layer is Fe_2O_3 and is slightly less than 500 angstrom units in thickness, while the FeO is present below the Fe_2O_3 layers. There has been no indication that Fe_3O_4 is present anywhere in the sample surface. The coating is particularly characterized by the complete absence of metallic iron within the oxide layer which accounts for its high insulation values and by its extreme thinness which allows particularly favorable space factors in the lamination assembly.

What I claim as new and desire to secure by Letters Patent of the United States, is:

1. The method of providing a decarburized silicon steel sheet material with an insulating oxide coating which comprises box annealing said material at a temperature above 800° C. in a reducing atmosphere with no spacing between adjacent laminations of the sheet material, cooling the material to a temperature of from about 500° to 600° C. and while holding the steel at this temperature replacing the reducing atmosphere with nitrogen and replacing the nitrogen with an oxygen atmosphere.

2. The method of annealing and insulating stacked decarburized silicon steel sheets which comprises box annealing the stacked sheets in a hydrogen atmosphere with no spacing material between adjacent sheets, cooling the stacked sheets to a temperature of from 500° to 600° C., removing the hydrogen atmosphere and thereafter surrounding the stacked sheets with an oxygen atmosphere to obtain on the surface of the sheets a thin oxide coating consisting substantially of FE_2O_3.

3. The method of annealing and insulating decarburized silicon steel sheet material having on the surface thereof a thin, tightly adherent metallic scale containing some silica, which method comprises box annealing the material with no spacing material between adjacent laminations at a temperature of about 980° C. in a hydrogen atmosphere, cooling the material to a temperature below about 600° C., replacing the hydrogen atmosphere with nitrogen and replacing the nitrogen with an oxygen atmosphere, heating the material in the oxygen atmosphere to a temperature of from 500° to 600° C. to form on the surface thereof a thin, smooth, adherent iron oxide coating red scale having a bluish cast.

4. The method of claim 3 wherein the oxygen atmosphere consists of moist oxygen.

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