METHOD FOR FORMING AN INSULATING FILM ON AN ORIENTED SILICON STEEL SHEET

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References Cited

UNITED STATES PATENTS
2,564,864 8/1951 Thompson

3,150,015 9/1964 Boyer et al.
3,207,636 9/1965 Wada et al.
3,522,113 7/1970 Kohler
3,528,863 9/1970 Foster et al.
3,533,861 12/1970 Foster et al.
3,670,278 6/1972 Foster et al.

Primary Examiner—Ralph Husack
Attorney, Agent, or Firm—Wenderoth, Lind & Ponack

ABSTRACT

A method for producing an oriented silicon steel sheet which provides a surface film, which improves iron loss and magnetostrictive characteristics of the steel sheet, comprising the steps of applying to the surface of the oriented steel sheet a coating solution composed of 4 to 16 wt. percent of colloidal silica, 3 to 24 wt. percent of aluminum phosphate and 0.2 to 4.5 wt. percent of at least one compound selected from the group consisting of chromic anhydride and chromate with or without the addition of 1 to 5 grams of boric acid and baking the thus applied coating solution at a temperature above 350°C.

5 Claims, 1 Drawing Figure
COATING ACCORDING TO THE PRESENT INVENTION

COATING OF MAGNESIUM PHOSPHATE

IRON LOSS BEFORE THE COATING (W/kg)

IRON LOSS AFTER THE COATING (W/kg)
This invention relates to the production of an oriented silicon steel sheet having a surface film which improves the iron loss and magnetostriction characteristics of the direction silicon steel sheet.

It has been recognized since long ago that the magnetostriction of an oriented silicon steel sheet is one of the main causes of the noise of a transformer made of this steel sheet. Reducing the magnetostriction oscillation induced by the magnetostriction is important to subdue the noise of the transformer, and the surface film formed on the steel sheet is known as an industrially effective means to this purpose. The action of this surface film is caused by the tension exerted by the surface film on the steel sheet, because in the magnetization of the oriented silicon steel sheet under this tension the magnetization process, which does not take part in the magnetostriction, that is, that which is caused by the movement of the magnetic wall by 180°, becomes dominant. This is explained from the view point of the magnetic section theory. The tension exerted by the surface film on the steel sheet is produced during the steel sheet being cooled in the heat treatment due to the difference in the thermal expansion coefficient between the steel sheet and the surface film.

Further, the tension of the surface film on the steel sheet is effective also to the improvement of the iron loss of the oriented silicon steel sheet. It has been discovered by one of the present inventors that particularly the more complete the orientation, the higher the effect [see Jr. Appl. Phys., 41, 2981 (1970)].

The term "oriented steel sheet" used here means a single oriented steel sheet of Fe-Si alloy containing up to 6 percent by weight of Si or most commonly about 3 percent by weight of Si, having a so-called "cube-on-edge" or a (110) [001] crystal structure as repeated by Miller index obtained by a combination of proper known rolling and heat-treatment of the steel sheet of this composition, in which the rolling direction is magnetically most easy to magnetize. There are marketed, for instance, under the trade marks of "Orient core" (Trade Mark of Nippon Steel Corporation) or "Orient core-H11" (Trade Mark of Nippon Steel Corporation), which has more complete orientation than before (see U.S. Pat. Nos. 3,159,511 and 3,287,183).

It is usual that the surface film made on an oriented silicon steel sheet consists of a glassy film formed during the high temperature finishing annealing or a phosphat film applied onto the glassy film or directly onto the naked steel sheet having no glassy film.

The glassy film is formed by the reaction of magnesia, which is an annealing separating agent, or an oxide added, as required, to the magnesia and a surface oxidized layer of the steel sheet, and consists mostly of magnesium silicate. The phosphate film is made by applying an aqueous solution of such metallic phosphate as magnesium phosphate or aluminium phosphate to a steel sheet and baking the same.

It has been found that among the above-mentioned surface films the glassy film has an action effective to the improvement of the iron loss and magnetostriction characteristics. However, the formation of this film is so easily influenced by the characteristics of magnesia, the state of the surface oxidized layer of the steel sheet, the annealing atmosphere and temperature conditions that it is difficult in fact to obtain a uniform thickness and characteristics. Therefore, with only the glassy film, it is insufficient to utilize the effect of the surface film. On the other hand, the phosphate film is low in the effect of the surface film and may even occasionally deteriorate the characteristics to be lower than in case the surface film is made of the glassy film only.

There have been suggested various methods for developing the effect of the surface film more than ever. For example, in Japanese Patent Publication No. 32815/1970 (U.S. Pat. No. 3,522,113), there was formed a potassic silicate glass film on a silicon steel sheet covered with a glassy film and/or phosphate coating film. In Japanese Patent Publication No. 18605/1971 (U.S. Pat. No. 3,528,863), a glass suspension made by crushing a glass frit lower in the thermal expansion coefficient than the silicon steel is applied and baked on a complex compound having magnesium as a substrate. Further, a method, wherein a glass frit is ceramic-coated in the same manner as in the latter, is suggested in British Pat. No. 1,077,377.

An object of the present invention is to provide an oriented electromagnetic steel sheet, on which is formed a surface film serving to improve the iron loss and magnetostriction characteristics.

Another object of the present invention is to provide an oriented electromagnetic steel sheet, on which is formed a surface film having good adhesive properties.

A further object of the present invention is to obtain a uniform surface film on the above-mentioned steel sheet.

Other objects will become clear from the below described matters and accompanying drawing.

The accompanying drawing is a graph showing the difference in the effect on the iron loss between the coating of the present invention and a conventional magnesium phosphate coating applied to bare oriented steel samples after having removed the surface film formed on the silicon steel sheet products respectively.

It has been discovered by the present inventors that a surface film formed by applying and baking a coating solution having colloidal silica as a main component, aluminium phosphate and at least one compound selected from the group consisting of chromic anhydride and chromates as a binder in the fundamental composition has a great effect on the improvement of the iron loss and magnetostriction characteristics of an oriented silicon steel sheet. An aqueous dispersion of supermicron-granular (for example, of a granule diameter of 10 to 20 μm) colloidal silica performs a film formation. When the aqueous solution is applied onto a steel sheet and is baked, a film can be formed. However, this film has a disadvantage that it is low in the adhesion to the steel sheet. If a mixed aqueous solution of aluminium phosphate and one or more of chromic anhydride and chromates is added to this aqueous dispersion of colloidal silica, the adhesion of the film can be improved. This is thought to be attributable to the fact that the above-mentioned mixture acts as a binder. Even with aluminium phosphate alone as a binder, the adhesion may be improved but, when the film is long exposed to a wet atmosphere, there occurs a phenomenon that the silica lamina is isolated. In order to prevent this phenomenon, it is effective to add one or more of chromic anhydride and chromates to the solution.

The reason, why the effects of improving iron loss and magnetostriction characteristics of an oriented silicon steel sheet, obtained by a surface film composed of
colloidal silica as a main component of the coating solution of the present invention become very high, as shown in the later described examples, resides in the following facts, that is, due to the low thermal expansion coefficient of silica in general the surface film composed of colloidal silica as a main component is also so low in the thermal expansion coefficient that the tension exerted by the surface film on the steel sheet is high, and further due to a characteristic action of supermicron granular colloidal silica of filling minor defects of the surface any unevenness of the glass film can be corrected.

Further, this surface film has not only the above-mentioned features but also the following features for the oriented silicon steel sheet. Even when thickly applied to, it presents an beautiful appearance and the adhesion is not impaired thereby. Therefore, a high interlayer resistance and voltage resistance can be easily obtained. The film is also so flat and smooth that, even if it is thickly applied, a practically sufficient space factor can be obtained. Further, the film is so compact that it is high in the heat-proofness, atmosphere-proofness and anticorrosion. These additional features make the effects of improving the iron loss and magnetostriiction characteristics of the surface film of the present invention more positive.

In the following a surface film of the present invention and a method of applying it to the production of oriented silicon steels shall be explained in detail.

The properties and mixing rates of component solutions of the coating solution to be used in the present invention are as follows. Supermicron granular colloidal silica which is dispersed in water and is a main component of the coating solution is required to obtain a stable mutual solubility with an aqueous solution of a phosphate, chromic acid or a chromate as a binder. For instance, commercial Snowtex O (Trade Mark of Nissan Chemical Industries, Ltd.) (of an SiO₂ content of 20 percent, hydrogen ion concentration (pH) of 3.0 to 4.0 and specific gravity of 1.15 at 20°C.) renders a suitable example for the present invention. Aluminum phosphate to be used as a binder may be nearly of a composition of aluminum biphosphate, in which a mixing ratio of Al₂O₃ and H₃PO₄ is about 0.16 by mols and the proper pH is about 0.9 (about 1.9 as corrected by the concentration) in an aqueous solution of 30 percent. It is needless to say that the present invention is not limited to the above-mentioned values. However, according to experiences, when the pH is low, the solution bubbles and its applicability is reduced. In order to obtain the above-mentioned pH value, the said mol ratio is suitable for the preparation and there is further an advantage that a commercial product can be utilized.

The proper mixing ratios of components of the coating solution of the present invention are as follows: 20 to 80 parts by volume of a 50 percent aqueous solution of aluminum phosphate are added to 100 parts by volume of a 20 percent aqueous dispersion of colloidal silica. This mixture corresponds to a coating solution composed of 10 to 16 percent by weight of colloidal silica and 9 to 24 percent by weight of aluminum phosphate (as calculated as aluminum biphosphate here and hereinafter). If the aqueous solution of aluminum phosphate is less than 20 parts by volume, there is shown a phenomenon that, after the baking, the adhesion of the above described silica lamina becomes insufficient and, if it is more than 80 parts by volume, after the baking, the film becomes turbid to be white and shows a bad appearance. Chromic acid is of chromic anhydride powder. The addition of 1 gram of chromic anhydride powder to 100 cc. of an aqueous solution of colloidal silica can present the above described isolation of the silica lamina which is to be caused in the case of adding no chromic anhydride powder. The proper range of the addition of chromic anhydride powder is 3 to 9 grams. In the case of adding chromate, for instance, more than 5 parts by volume of a 25 percent aqueous solution of magnesium chromate are to be added to 100 parts by volume of colloidal silica. Then, the above-mentioned isolation of the silica lamina may be prevented. The preferable range of the addition of chromate is 10 to 30 parts by volume.

The coating solution of the above-mentioned composition corresponds to an aqueous solution of about 8 to 16 percent by weight of colloidal silica, 7 to 24 percent by weight of aluminum phosphate and 0.4 to 4.5 percent by weight of chromic anhydride or magnesium chromate. Further, as required, in case a thus coated steel sheet is likely to stick during the heat-treatment, for instance, in case the heat-treatment is carried out at a temperature above 800°C., it will be effective to add boric acid or supermicron granular silica. It is proper to add 1 to 3 grams of boric acid or 0.25 to 2 grams of such supermicron granular silica as, for example, commercial Nipsil VN 3 (Trade Mark of Nippon Silica Industrial Co., Ltd.) (of 93 to 94% SiO₂, a granule diameter less than 10 μ and a pH (at 4 percent) of 5.8 to 6.8) to 100 cc. of an aqueous dispersion of colloidal silica.

The addition of boric acid or supermicron granular silica is carried out as follows:

A. Case of adding boric acid

For example, in the mixing rates of 100 cc. of an aqueous dispersion of colloidal silica, 60 cc. of an aqueous solution of aluminum phosphate, 6 grams of chromic anhydride and 2 grams of boric acid:

i. 2 kg. of boric acid are put into 15 liters of warm water above 60°C. and are well stirred to be dissolved. (This shall be a solution A.)

ii. 6 kg. of chromic anhydride are added to 60 liters of an aqueous solution of 50 percent aluminum phosphate and are well stirred to be dissolved and then 100 liters of an aqueous dispersion of colloidal silica are added to the solution. (This shall be a solution B.)

iii. The solutions A and B are mixed and stirred. The thus prepared solution is of a concentration of about 23 to 28 Bé.

B. Case of adding supermicron granular silica

For example, in the case of the mixing rates of 100 cc. of an aqueous dispersion of colloidal silica, 60 cc. of an aqueous solution of aluminum phosphate, 6 grams of chromic anhydride and 0.5 gram of supermicron granular silica:

6 kg. of chromic anhydride are added to 60 liters of a 50% aqueous solution of aluminum phosphate and are well stirred to be dissolved and then 100 liters of an aqueous dispersion of colloidal silica and 0.5 kg. of supermicron granular silica are added and stirred.

The thus prepared solution is of a concentration of about 26 to 31 Bé.

In applying the coating solution of the above-mentioned composition to an oriented silicon steel
sheet, it is used after adjusted to be of a concentration proper for the objective film deposition amount. That is to say, it is used in the state of the original solution so as to contain 4 to 16 percent by weight of colloidal silica, 3 to 24 percent by weight of aluminum phosphate and 0.2 to 4.5 percent by weight of one or more of chronic anhydride and chromates or as diluted with water.

The coating solution of the present invention is uniformly applied onto the surface of the above-mentioned oriented silicon steel sheet by dipping or spraying and thereafter is pressed with pressing rolls, or coated by any known method.

The coating solution of the present invention can be applied to an oriented silicon steel sheet, irrespective of the surface of the oriented silicon steel sheet being covered with a glassy film or with a phosphate film or both films or being bare without covered by them. However, when applying the coating solution of the present invention no phosphate is required. Phosphate film is not only uneconomic, but rather deteriorates the properties inherent to the coating of the present invention, excepting a special case of thinly applying the coating solution of the present invention for the purpose of supplying a deficiency of the phosphate film. Such an oriented silicon steel sheet having a bare surface is often produced in order to improve the punchability. It is known, however, that in such a case particularly magnetostriction characteristics of the steel sheet are remarkably deteriorated on account of the surface having no coating. When the coating of the present invention is applied to such steel sheet, the magnetostriction characteristics can be improved substantially to those of the case of being covered with a glassy film alone, as will be seen from the later described examples.

The coating solution of the present invention is baked after it has been applied to the surface of a steel sheet as above-mentioned. A favorable surface film can be obtained, when it is heated to a temperature above 350°C, preferably a temperature between 400°C to 900°C. It is a great advantage of the coating solution of the present invention that the baking temperature range is so wide as above-mentioned. On account of this the baking treatment can be carried out by various methods according to the object to be obtained. The lower limit of the baking temperature is set at 350°C, because, if the coating temperature is below this limit, the reaction of the coating solution is insufficient and the hygroscopicity remains in the formed surface film. As to the upper limit it is to note that the baking temperature may be raised up to a relatively high one, but practically the temperature above 900°C is not economical, and it is even feared that at such a high temperature above 900°C the characteristics of the surface film will be deteriorated depending upon the atmosphere and treating time. Thus, the baking temperature above 900°C is not desirable.

The atmosphere at the time of baking may be of air, nitrogen or a mixture of nitrogen and hydrogen. It has been found that, when the baking is carried out on the high temperature side of the above-mentioned temperature range or even in case it is carried out at a low temperature, if a strain-removing annealing is further carried out continuously or by batch at about 800°C as carried out by an ordinary consumer, the effects of improving the iron loss and magnetostriction characteristics of the surface film of the present invention can be increased. From the fact that the tension of the surface film on the steel sheet is caused by the difference in the thermal expansion coefficient, it is naturally presumed to be effective to bake it at a high temperature. Further, in the case of the baking being carried out at low temperature, it is thought that a surface film effective to the tension may be re-formed in the later high temperature treatment.

In the production of an oriented silicon steel sheet, it is economical to continuously carry out the step of forming a surface film from the coating solution of the present invention in combination with other steps. Generally, the glassy film on an oriented silicon steel sheet is used to be formed by a high temperature finishing annealing. Then, the excess annealing separating agent is removed by water-washing or light pickling to leave the glassy film on the surface of the steel sheet. Or, for the purpose of improving the punchability, the glassy film may be also removed by pickling. Then, a so-called heat-flattening is made to remove a coil bent of the steel sheet and to flatten the steel sheet. This heat-treatment is carried out at 800°C to 900°C for not more than about 3 minutes. This condition corresponds to the high temperature side of the above-mentioned baking condition. Therefore, if the coating solution is applied before the heat-flattening, the heat-flattening and baking are able to be simultaneously carried out. Further, as in such case, the interlayer resistance and voltage resistance are often impaired by flaws caused by builds-up on hearth rolls, the coating solution may be again applied and baked at a low temperature in order to remedy the above-mentioned defect. Or, it is also possible to apply the coating solution and baking the same at a low temperature of 400°C to 500°C after the heat-flattening. In such case, a sufficient interlayer resistance and voltage resistance can be easily obtained, but, in order to more sufficiently develop the effects of improving the iron loss and magnetostriction characteristics by the surface film, it is necessary to anneal the film at about 800°C continuously or by batch by a consumer or manufacturer.

The above-mentioned respective steps can be carried out continuously on one continuous line but, needless to say, may be carried out on separate lines as divided into any number of steps.

Examples of the present invention are shown in the following:

**EXAMPLE 1**

Samples taken adjacent to another from the same commercial coil of an oriented silicon steel sheet of a thickness of 0.30 mm. were treated with a mixed acid of sulfuric acid and hydrofluoric acid to remove the surface films and were then continuously annealed at 800°C in hydrogen for 3 minutes to remove stains. Thus, the samples for the test have been prepared. To these samples there were applied a phosphate coating solution of magnesium phosphate and a coating solution of a composition of 100 cc of a 20 percent aqueous dispersion of colloidal silica, 60 cc. of an 50 percent aqueous solution of aluminum phosphate, 6 grams of chromic anhydride and 2 grams of boric acid of the present invention respectively, and were then baked at 800°C. For 15 seconds in a nitrogen atmosphere in a continuous oven so that the coating deposition might be 4 gr./m² on one surface. The magnetic properties
and magnetostriction characteristics were measured with a single plate measuring device before applying the coating and after having applied and baking it. The sample was of a length (in the rolling direction) of 50 cm. and a width of 10 cm.

The Figure shows the results of the measurements of iron losses \(^{\#} 15/50\) and \(^{\#} 17/50\) before and after forming films of respective coatings. The reduction in iron loss obtained by the coating solution of the present invention is very large.

Table 1 indicates the results of the measurements of the magnetostriction characteristics. The sample by the coating solution of the present invention is low in the magnetostriction and is also low in the deterioration to be caused by the compressive force.

The above-mentioned results demonstrate that the effects of improving the iron loss and magnetostriction characteristics of the surface film by the coating solution of the present invention are large.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Magnetic permeability at 10 Oe</th>
<th>Magnetostriction (^{\times} 10^{-6}) at 17 kg.</th>
<th>Magnetostriction under compression of 30 kg/cm(^2).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before applying the coating:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1933</td>
<td>+1.17</td>
<td>+3.64</td>
</tr>
<tr>
<td>2</td>
<td>1907</td>
<td>+1.17</td>
<td>+4.81</td>
</tr>
<tr>
<td>3</td>
<td>1920</td>
<td>+1.56</td>
<td>+4.29</td>
</tr>
<tr>
<td>After applying and baking the coating of the present invention:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1935</td>
<td>-0.13</td>
<td>+1.82</td>
</tr>
<tr>
<td>2</td>
<td>1912</td>
<td>-0.29</td>
<td>+1.69</td>
</tr>
<tr>
<td>3</td>
<td>1924</td>
<td>-0.39</td>
<td>+1.82</td>
</tr>
<tr>
<td>Before applying the coating:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1921</td>
<td>+2.47</td>
<td>+5.55</td>
</tr>
<tr>
<td>5</td>
<td>1903</td>
<td>+0.91</td>
<td>+3.64</td>
</tr>
<tr>
<td>6</td>
<td>1933</td>
<td>+1.30</td>
<td>+3.00</td>
</tr>
<tr>
<td>After applying and baking magnesium phosphate coating:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1922</td>
<td>+0.65</td>
<td>+2.99</td>
</tr>
<tr>
<td>5</td>
<td>1902</td>
<td>+0.26</td>
<td>+2.21</td>
</tr>
<tr>
<td>6</td>
<td>1923</td>
<td>+0.26</td>
<td>+2.73</td>
</tr>
</tbody>
</table>

**Example 2**

Samples taken adjacent to one another from the same coil of an oriented silicon steel sheet of a thickness of 0.30 mm., as finished annealed at a high temperature, were subjected to water-washing and light pickling to remove an annealing separating agent remained on the surfaces of the samples and to leave the glassy films and were then annealed to remove coil bends and strains. Thus, the samples for the test were prepared. To these samples covered with the glassy films there were applied a phosphate coating solution of magnesium phosphate and a coating solution of 100 cc. of a 20 percent aqueous dispersion of colloidal silica, 60 cc. of a 50 percent aqueous solution of aluminum phosphate, 6 grams of chromic anhydride and 0.75 gram of supermicronangular silica of the present invention respectively in the same manner as in Example 1 and were thereafter baked at 850°C. for 10 seconds in air in a continuous oven.

Table 2 shows the results measured in the same manner as in Example 1 before applying the coating and after applying and baking it. The effect of the surface film by the coating solution of the present invention is large.

In Table 3 there are shown characteristics of the surface film samples by the coating solution of the present invention after subjected to a strain-removing annealing at 800°C. for 4 hours in a dry atmosphere of 10% H\(_2\) and 90% N\(_2\). The effect of the surface film is not lost even by the heat-treatment of a long time.

Table 4 shows the results of measuring the coating deposition, interlayer resistance and space factor of these surface films. The surface film of the present invention is high in the interlayer resistance and is very small particularly in the reduction in resistance to be caused by the annealing in a reducing atmosphere. Though it is high in the coating deposition, it keeps a high space factor.

These results show that the surface film of the present invention is very smooth and compact.
EXAMPLE 3

Samples were prepared in the same manner as in Example 2. A coating solution of a composition of 100 cc. of a 20 percent aqueous solution of colloidal silica, 60 cc. of a 50 percent aqueous solution of aluminum phosphate, 15 cc. of a 25 percent aqueous solution of magnesium chromate and 0.75 gram of supermicron granular silica of the present invention was applied to these samples having glassy films and was baked at about 450°C for 10 seconds in an open oven. These samples were further continuously annealed to remove strains at 810°C for 2 minutes in a nitrogen atmosphere.

Table 5 shows the results measured in the same manner as in Example 1 before and after the strain removing annealing. The improvements of the iron loss and magnetostriction characteristics after the annealing are large, showing the better characteristics than in the case of the glassy film only. This shows that, even when the coating solution of the present invention is baked at a low temperature, a sufficient effect of the surface film can be obtained by a subsequent annealing at a high temperature.

### Table 5

<table>
<thead>
<tr>
<th>Samples</th>
<th>Magnetic permeability at 10 Oe</th>
<th>Iron loss (%/kg.)</th>
<th>Magnetostriction (x 10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15/50</td>
</tr>
<tr>
<td>In the case of glassy film only:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 1946</td>
<td>0.809</td>
<td>1.099</td>
<td>-0.13</td>
</tr>
<tr>
<td>2 1991</td>
<td>0.842</td>
<td>1.158</td>
<td>-0.26</td>
</tr>
<tr>
<td>3 1926</td>
<td>0.800</td>
<td>1.099</td>
<td>-0.26</td>
</tr>
<tr>
<td>After applying the coating of the present invention and baking it at a low temperature:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 1945</td>
<td>0.812</td>
<td>1.102</td>
<td>+0.13</td>
</tr>
<tr>
<td>2 1991</td>
<td>0.845</td>
<td>1.160</td>
<td>+0.26</td>
</tr>
<tr>
<td>3 1925</td>
<td>0.803</td>
<td>1.101</td>
<td>+0.19</td>
</tr>
<tr>
<td>After continuous annealing in N₂ at 810°C for 2 minutes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 1947</td>
<td>0.780</td>
<td>1.046</td>
<td>-0.52</td>
</tr>
<tr>
<td>2 1993</td>
<td>0.815</td>
<td>1.108</td>
<td>-0.65</td>
</tr>
<tr>
<td>3 1929</td>
<td>0.778</td>
<td>1.036</td>
<td>-0.52</td>
</tr>
</tbody>
</table>

EXAMPLE 4

After the treatment in Example 2, a coating solution of 100 cc. of a 20 percent aqueous dispersion of colloidal silica, 60 cc. of a 50 percent aqueous solution of aluminum phosphate and 15 cc. of a 25 percent aqueous solution of magnesium chromate of the present invention (the original solution was of about 25 Be) as diluted with water to be of about 15 Be was applied to the steel sheet and was baked at 400°C for 10 seconds in an open oven. The obtained surface film was flat, smooth and uniform.

This shows that the coating solution of the present invention can be used also for improving the interlayer resistance and voltage resistance and further for recoating for the purpose of securing the insulation of the part, after a protrusion thereof has been removed by shearing or slitting.

What is claimed is:

1. A method for forming an insulating film on an oriented silicon steel sheet, comprising the steps of applying to the oriented silicon steel sheet a coating solution composed of 4 to 16 wt. percent of colloidal silica, 3 to 24 wt. percent of aluminum phosphate, calculated as aluminum biphosphate, and 0.2 to 4.5 wt. percent of at least one compound selected from the group consisting of chromic anhydride and chromate and baking the thus applied coating solution at a temperature above 350°C.

2. The method according to claim 1, in which boric acid is added to the coating solution in an amount of 1 to 5 grams per 100 cc. of a water dispersion of colloidal silica.

3. The method according to claim 1, in which supermicron granular silica is added to the coating solution in an amount of 0.25 to 2 grams per 100 cc. of a water dispersion of colloidal silica.

4. A method for producing an oriented silicon steel sheet with a surface film which improves iron loss and magnetostriction characteristic of the steel sheet, comprising the steps of forming a glassy film on the oriented silicon steel sheet by a reaction with an annealing separating agent during a high temperature finishing annealing of said steel sheet, thereupon applying to this glassy film a coating solution composed of 4 to 16 wt. percent of colloidal silica, 3 to 24 wt. percent of aluminum phosphate, calculated as aluminum biphosphate, and 0.2 to 4.5 wt. percent of at least one compound selected from the group consisting of chromic anhydride and chromate, baking the thus applied coating solution at a temperature above 350°C and then subjecting the
steel sheet to a heat-treatment in a temperature range of from 800° to 900°C after or during the said application of the coating solution and baking thereof.

5. The method for producing an oriented silicon steel sheet with a surface film which improves iron loss and magnetostriction characteristics of the steel sheet, according to claim 4, in which the glassy film formed on the surface of the steel sheet during the high temperature finishing annealing is removed by a pickling and then the coating solution is applied to the surface of the steel sheet.