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3,697,322

MAGNESIUM OXIDE COATINGS

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5 Claims

ABSTRACT OF THE DISCLOSURE

Lithium additives in magnesium oxide/magnesium hydroxide coatings for silicon steel and the material coated by such process.

This application is a continuation-in-part of U.S. application Ser. No. 40,479, filed May 22, 1970, and now abandoned.

This invention relates to coatings for ferrous material and, more particularly, an improved magnesium oxide/magnesium hydroxide coating for grain oriented silicon steel, and the material coated by such process.

In many fields of use and, in particular, in the electrical industry, it is necessary to provide a coating on ferrous material. This coating desirably performs the function of separating and purifying the ferrous material and reacting with surface silica in the steel to form an electrical insulating layer. For example, in the transformer art, the cores of the transformers are usually formed of a ferrous material, such as, for example, silicon steel, which may be provided with a preferred grain growth orientation to provide optimum electrical and magnetic properties. It has been found necessary to provide a coating on the ferrous material prior to the final high temperature grain growth anneal. This coating will perform three separate functions. The first function of the coating is to provide separation of the various turns or layers of the coiled material to prevent their sticking or welding together during high temperature anneals. A second function is that of aiding in the chemical purification of the ferrous material to develop the desired optimum magnetic characteristics of such material. The third function of the coating is to form on the surface of the ferrous material a refractory type coating which will provide electrical insulation of one layer of ferrous material from the next, for example, during its use as a core in a transformer.

In the present state of the electrical apparatus art, the most widely used coating for the ferrous material which is used as the magnetic core of the electrical apparatus is a coating of magnesium oxide and/or magnesium hydroxide. These coatings are, in general, applied to the ferrous material in the form of a suspension of magnesium oxide and/or magnesium hydroxide in water. The suspension comprises a quantity of magnesium oxide in water and is mixed sufficiently for the desired application, the magnesium oxide being hydrated to an extent dependent on the character of the oxide used, the duration of mixing and the temperature of the suspension. Therefore, the term magnesium oxide coating is with reference to a coating of magnesium hydroxide which may include magnesium oxide which has not been hydrated.

As set forth in U.S. Pat. No. 2,385,332, in the names of Victor W. Carpenter et al., portions of an annealing separator of magnesium oxide can, during a heat treatment at suitable temperatures, be caused to react with silica particles on or near the surfaces of previously oxidized silicon-iron sheet stock to form a glass-like coat-

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ing, which coating is useful as an interlaminary insulator in the use of silicon-iron in electrical apparatus, e.g. in the cores of transformers.

In the production of silicon steel for the magnetic cores of transformers, the steel is generally annealed to provide optimum grain growth and grain orientation which develops the magnetic properties of the silicon steel. This anneal is usually carried out in a hydrogen atmosphere at temperatures ranging from approximately 950 to 1500° C. from about 2 to about 50 hours. This anneal also aids in purifying the steel, aided by the coating placed on the steel. During this anneal a portion of the magnesium oxide coating reacts with the silica on the surface of the silicon steel to form a glass-like coating of magnesium silicate. This glass-like coating provides electrical insulation during the use of the silicon steel in electrical apparatus, e.g., in the cores of transformers.

A number of additives have been proposed in the past to be added to the magnesium hydroxide and/or magnesium oxide in order to improve the MgO—SiO₂ reaction. For example, U.S. Pat. 2,809,137 (Robinson) involves the use of silica to be combined with the MgO and/or Mg(OH)₂ for the purpose of improving the insulating properties of the glass-like film obtained after high temperature annealing. U.S. Pat. 2,394,047 (Elsey et al.) relates to the use of additives to produce oxidized surface metal and to enhance glass film formation.

This invention relates to an improved MgO/Mg(OH)₂ coating which forms a superior insulating glass film when applied to silicon steel surfaces which have been previously oxidized. For example, one such method of oxidation which may be employed is taught in U.S. Pat. 2,385,332, discussed above. More particularly the invention concerns coatings containing magnesium oxide/magnesium hydroxide and organic or inorganic lithium bearing compounds which when applied to silicon sheet steel imparts unexpected and improved insulation qualities to the silicon steel after the final high temperature anneal.

Representative members of the class of organic and inorganic lithium bearing compounds includes the following:

- lithium acetate
- lithium borate, such as lithium metaborate, lithium metaborate hydrate, lithium pentaborate, lithium tetraborate and lithium borohydrate
- lithium chromate
- lithium fluoride
- lithium hydroxide
- lithium lactate
- lithium nitrate
- lithium phosphate
- lithium silicate
- lithium sulfate
- lithium zirconate
- lithium zirconium silicate
- lithium hydroxide monohydrate
- lithium carbonate
- lithium acetylsalicylate
- lithium metaaluminat
- lithium aluminum hydride
- lithium amide
- lithium antimonide
- lithium orthoarsenate
- lithium azide
- lithium benzoate
- lithium bromide
- lithium bromide, dihydrate
- lithium carbide
- lithium bicarbonate
- lithium chlorate

lithium chlorate hydrate
 lithium perchlorate
 lithium perchlorate trihydrate
 lithium chloride
 lithium chloride monohydrate
 lithium chloroplatinate
 lithium bichromate dihydrate
 lithium dichromate
 lithium citrate
 lithium fluosilicate
 lithium fluosulfonate
 lithium formate monohydrate
 lithium gallium hydride
 lithium gallium nitride
 lithium metagermanate
 lithium hydride
 lithium iodate
 lithium iodine
 lithium iodide, trihydrate
 lithium laurate
 lithium permanganate
 lithium molybdate
 lithium myristate
 lithium nitrate trihydrate
 lithium nitride
 lithium nitrite
 lithium oxalate
 lithium acid oxalate
 lithium oxide
 lithium palmitate
 lithium metaphosphate
 lithium orthophosphate
 lithium orthophosphate hydrate
 lithium dihydrogen phosphate
 lithium salicylate
 lithium selenide
 lithium metasilicate
 lithium orthosilicate
 lithium silicide
 lithium stearate
 lithium sulfate
 lithium hydrogen sulfate
 lithium sulfate monohydrate
 lithium sulfide
 lithium hydrosulfide
 lithium sulfite monohydrate
 lithium tartrate
 lithium thallium di-tartrate
 lithium dithionate
 lithium thiocyanate
 lithium tungstate
 lithium titanate
 lithium manganite
 lithium vanadate
 lithium cobaltite

and the like.

It will be appreciated that lithium compounds which have a relatively high weight percent of lithium are preferred for use in the instant invention since the anion portion of the lithium compound (assuming it to be a salt) would ordinarily serve no purpose. It should be emphasized, however, that any lithium compound (or mixtures of such compounds) may be utilized to obtain the advantageous function here involved since the key to this function is the presence of the lithium atom or ion. Analysis of the composition of the glass film formed according to the practice of this invention reveals a novel film containing predominately well crystallized MgO, magnesium silicate and lithium.

The concentration of the lithium bearing compound calculated as Li_2O with respect to the amount of the MgO employed in the coating is not critical and may vary from about 0.1 to about 30 weight percent of the magnesium oxide. A satisfactory concentration for most

practical purposes (calculated as Li_2O) has been found to be from about 0.2 to 12.5 weight percent of MgO. It should be noted that the particular grade of MgO to be utilized is not critical and any commercially available

- 5 MgO may be employed in the practice of the invention. The lithium-MgO/ $\text{Mg}(\text{OH})_2$ coatings of the invention may be applied to the grain-oriented silicon steel using techniques conventionally employed in the coating of these materials. Among the well known procedures that are presently employed in applying the MgO/ $\text{Mg}(\text{OH})_2$ coatings, a continuous strip of the ferrous material is passed through a bath containing the MgO/ $\text{Mg}(\text{OH})_2$ suspension and then through a drying furnace. In addition to employing conventional coating techniques, the amount of MgO/ $\text{Mg}(\text{OH})_2$ (exclusive of lithium additive) that is applied to the silicon steel in the practice of this invention is similar to those amounts that heretofore had been employed in MgO/ $\text{Mg}(\text{OH})_2$ coatings and in general will vary from about 0.020 to 0.060 ounce of MgO per square foot of steel surface.

The manner and time at which the lithium compounds are combined with the magnesium oxide is not critical. As described by the various examples set forth below, these procedures include adding the lithium compound to a magnesium material, such as magnesium basic carbonate or $\text{Mg}(\text{OH})_2$, prior to their conversion to the magnesium oxide; blending the lithium material with the MgO or $\text{Mg}(\text{OH})_2$, adding the lithium compound separately during coating slurry make-up; or mixing the lithium material in the water used for coating slurry make-up prior to the addition of the MgO powder.

The annealing of the silicon steel that has previously been coated with the coating composition of the invention may be carried out in a reducing atmosphere at temperatures ranging from approximately 950 to 1500° C. for from about 2 to 50 hours using techniques well known to the art.

The unobvious and unexpected properties of the instant invention are clearly revealed by the following examples:

EXAMPLE 1

A slurry containing about 1 lb. MgO/gal. concentration was made up by mixing 60 g. of a commercial grade MgO with 6 g. of a reagent grade lithium carbonate, and then adding 500 ml. of deionized water in a Waring blender for one minute. The resulting slurry was coated on strips of silicon steel (size 3 mm. x 30.5 mm.) at a coating weight of 0.038 oz./ft.², dried at 250°-275° C., and annealed in hydrogen atmosphere at 1200° C. for about 30 hours. For comparative purposes, identical silicon strips were coated with an identical MgO slurry at the same concentration but without the lithium compound. After annealing and cooling, the excess magnesium oxide coating was scrubbed off all samples with a nylon brush and a cloth. These strips were tested for resistance on both surfaces with a Franklin tester (ASTM-A344-60T). The results are:

Additive (MgO basis):	Resistance
0% -----	3.7 ohms-cm. ²
10% Li_2CO_3 (4.0% as Li_2O) ---	Infinity (complete insulation).

EXAMPLE 2

A slurry containing about 0.5 lb. MgO/gallon concentration was made up by mixing 30 g. of a commercial grade MgO with 0.3 g. of a reagent grade lithium carbonate and then adding 500 ml. of deionized water in a Waring blender for one minute. The slurry was coated on silicon steel strips and tested in the same manner as described in Example 1. Franklin test results show:

Additive (MgO basis):	Resistance, ohms-cm. ²
0% -----	3.9
1% Li_2CO_3 (0.4% as Li_2O) -----	11.0

5 EXAMPLE 3

60 g. of a commercial grade magnesium oxide was added to a Waring blender containing 500 ml. of deionized water. 4.8 g. of a reagent grade lithium hydroxide was then added and mixed thoroughly for one minute. The slurry was coated on silicon steel strips and tested in the same manner as described in Example 1. Franklin test results showed:

Additive (MgO basis):	Resistance
0% -----	1.8 ohms-cm. ²
8% LiOH (5.0% as Li ₂ O) -----	Infinity (complete insulation).

EXAMPLE 4

60 g. of a commercial grade magnesium oxide and 12 g. of a reagent grade lithium hydroxide monohydrate were mixed thoroughly before adding to 500 ml. of deionized water in a Waring blender. The resulting slurry was coated onto silicon strips and tested in the same manner as described in Example 1. Franklin test results show:

Additive (MgO basis):	Resistance
0% -----	1.8 ohms-cm. ²
20% LiOH·H ₂ O (7.1% as Li ₂ O) -----	Infinity (complete insulation).

EXAMPLE 5

0.3 g. of lithium fluoride was mixed with 500 ml. of deionized water. 60 g. of a commercial grade magnesium oxide was poured into the blender containing the lithium fluoride mixture and mixed for one minute. The resulting slurry was coated onto strips of silicon steel, dried and annealed in the same manner as described in Example 1. A comparative sample was also made utilizing identical strips of silicon steel and tested in the same manner. Franklin test results show:

Additive (MgO basis):	Resistance, ohms-cm. ²
0% -----	3.4
0.5% LiF (0.3% as Li ₂ O) -----	6.7

EXAMPLE 6

60 g. of a commercial magnesium oxide, 3 g. of lithium metaborate and 500 ml. of deionized water were added simultaneously into a Waring blender and mixed to form a smooth coating slurry. This slurry was coated on silicon steel strips and tested in the same manner as described in Example 1. Franklin test results show:

Additive (MgO basis):	Resistance
0% -----	2.6 ohms-cm. ²
5% LiBO ₂ (1.5% as Li ₂ O) -----	Infinity (complete insulation).

EXAMPLE 7

60 g. of a commercial magnesium oxide and 6 g. of lithium acetate (LiC₂H₃O₂·2H₂O) were thoroughly mixed and added to 500 ml. of deionized water in a Waring blender. The resulting slurry was coated on strips of silicon steel and tested in the same manner as described in Example 1. Franklin tests on the surfaces show:

Additive (MgO basis):	Resistance, ohms-cm. ²
0% -----	2.6
10% LiC ₂ H ₃ O ₂ ·2H ₂ O (1.5% as Li ₂ O) -----	38.3

EXAMPLE 8

60 g. of a commercial magnesium oxide, 0.6 g. of lithium sulfate and 500 ml. of deionized water were mixed in a Waring blender. The slurry was coated onto strips of silicon steel in the same manner as described in Example 1. Franklin tests show:

Additive (MgO basis):	Resistance, ohms-cm. ²
0% -----	1.8
1% Li ₂ SO ₄ ·H ₂ O (0.2% as Li ₂ O) -----	8.8

6 EXAMPLE 9

0.6 g. of lithium nitrate, 500 ml. of deionized water and 60 g. of a commercial grade magnesium oxide were mixed in a Waring blender and the slurry coated onto strips of silicon steel. The strips were dried, annealed and scrubbed in the manner described in Example 1. Franklin test results show:

Additive (MgO basis):	Resistance, ohms-cm. ²
0% -----	1.8
1% LiNO ₃ (0.2% as Li ₂ O) -----	7.4

EXAMPLE 10

According to the procedure set forth in Example 1 and using identical silicon steel strips the following results were obtained:

Additive	Level (MgO basis), percent	As percent Li ₂ O	Resistivity, ohms-cm. ²
Control	-----	-----	1.8
Lithium lactate (LiC ₃ H ₅ O ₃)	1 5 10	0.15 0.73 1.46	6.9 15.0 38.3
Lithium tetraborate (Li ₂ B ₄ O ₇ ·5H ₂ O)	1 5 10	0.12 0.58 1.15	4.3 (1) (1)
Lithium phosphate (2Li ₃ PO ₄ ·1/2H ₂ O)	1 5	0.36 1.80	8.0 24.7
Lithium silicate (Li ₂ SiO ₃)	1 5	0.33 1.67	4.7 10.3
Lithium zirconate (Li ₂ ZrO ₃)	1 5	0.20 0.98	12.1 (1)
Lithium zirconium silicate (2Li ₂ O·ZrO ₂ ·SiO ₂)	1 5	0.14 0.70	12.9 11.8
Lithium dichromate (Li ₂ Cr ₂ O ₇ ·H ₂ O)	1 5 10	0.12 0.60 1.20	3.8 12.4 (1)

¹ Infinity (complete insulation).

Accordingly, these experiments demonstrate that magnesium oxides currently employed to coat grain-oriented silicon steel give relatively low resistance whereas the same MgO coating containing a lithium compound results in the production of a film having a considerably higher resistance including values of infinity (complete insulation) depending upon the silicon steel strip employed in the study and on the amount and type of lithium compound utilized. Comparable results to that indicated above are achieved employing other representative lithium compounds encompassed within the scope of the invention. One skilled in the art will appreciate that subsequent treatments of the coated steel such as described in U.S. Pat. 2,501,846 may be utilized in the production of ferrous material which finds use in the electrical apparatus industry.

Although specific embodiments of the invention have been described herein, it is not intended to limit the invention solely thereto but to include all of the obvious variations and modifications within the spirit and scope of the appended claims.

What is claimed is:

1. A method of producing an electrical insulating film on magnetic silicon steel which comprises applying a coating composition consisting essentially of a material selected from the group consisting of MgO, Mg(OH)₂ and mixtures thereof and at least one lithium compound to surface oxidized silicon steel and annealing said silicon steel at an elevated temperature, said lithium compound being present at from about 0.1 to about 30 weight percent of magnesium oxide calculated as Li₂O.

2. The method of claim 1 wherein the annealing occurs at about 950–1500° C. for from about 2 to 50 hours.

3. The method of claim 2 wherein the lithium compound is selected from the group consisting of lithium carbonate, lithium hydroxide, lithium fluoride, lithium borate, lithium acetate, lithium sulfate, lithium oxide, lithium lactate, lithium phosphate, lithium silicate, lithium zirconate, lithium zirconium silicate, lithium dichromate, and lithium nitrate.

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4. The method of claim 3 wherein the lithium compound is lithium borate.
 5. The method of claim 4 wherein the lithium borate is lithium metaborate.

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