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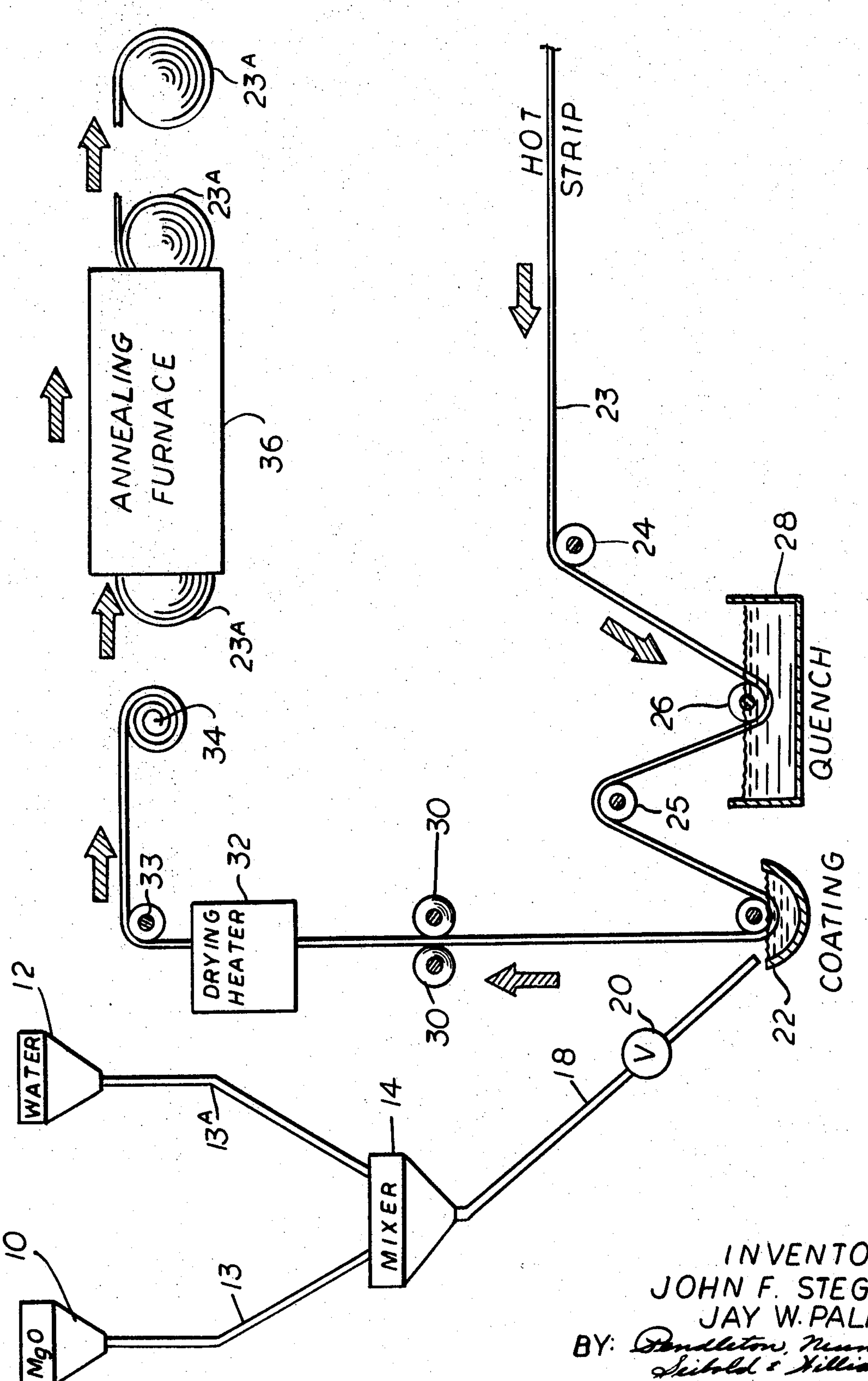

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MAGNESIUM OXIDE COATING COMPOSITION AND PROCESS FOR PRODUCING ANNEALED STEEL PUNCHING STOCK

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ABSTRACT OF THE DISCLOSURE

Magnesium oxide coating compositions comprising a major proportion of magnesium oxide of a surface area of from 5 to 50 square meters per gram and a minor proportion of an alkaline earth metal fluoride. The compositions are used for coatings in a process for producing annealed magnetic steel sheet wherein the coatings are applied to silicon-magnetic steel sheet, dried, and the coated steel annealed. The coatings substantially prevent the formation of hard surface and sub-surface silicates and also prevent the fusing together of the steel sheet during the annealing process.

BACKGROUND OF THE INVENTION

Field of the invention

Electrical transformers and other types of electrical induction apparatus are made from steel sheet having soft magnetic properties. Such sheet is prepared by cold rolling silicon-containing steel into sheet form, coiling the steel sheet into rolls and thereafter annealing the coiled steel by a controlled heating process to produce a grain oriented structure having desirable magnetic properties. This product is known as a punching stock steel.

Magnesium oxide is used extensively as a highly heat resistant separator medium and protective coating for metal surfaces. It is also used as an electrical insulator for metals, as a "gatherer" for removing impurities, such as sulfur and carbon, from thin metal sheets and particularly as a protective coating for silicon steel on which it forms a film containing Mg_2SiO_4 which is thereafter converted to an effective electrical insulator by further treatment with hydrogen.

Description of the prior art

According to the present industrial practice, silicon-containing steel is cold rolled into sheets, decarburized and thereafter coiled into convenient rolls. Cold rolling develops in the steel the potential to form a grain oriented structure when the steel is later "annealed." The term "annealed" refers to a process whereby the steel is heated to about 1200° C. in an essentially pure hydrogen atmosphere (or vacuum) under programmed conditions with respect to time and temperature. This results in a growth in size of the steel grains and also in a specific grain orientation which provides the desired soft magnetic properties sought. During the annealing process, virtually all of the remaining carbon and sulfur content of the steel is lost. This type of annealing is known in the art as "box annealing."

During the box annealing process where the steel is in large coils, in the absence of a suitable separating medium, the coiled roll would fuse to itself and could not be unrolled. Conventionally, this is avoided by placing a thin coating of magnesium oxide on the steel prior to coiling. The magnesium oxide coating also serves to reduce impurities such as carbon and sulfur in steel by chemical reaction. In addition, magnesium oxide provides an insulating silicate layer by oxidation of and re-

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action with the silicon in the steel. There is evidence that some iron silicate is formed.

As hereinbefore stated, magnesium oxide coated on silicon steel tends to form magnesium silicates by reaction with the silicon normally present in the steel. These silicates formed in the prior art processes are relatively hard substances and are therefore undesirable when the steel must be cut or punched by means of dies to provide the various shapes required in producing transformers and other electrical apparatus. Obviously, the service life of the dies used to cut or punch the steel is shortened significantly when encountering hard silicates. Accordingly, in the prior art processes after annealing, the surface of the steel must be scrubbed and treated in a strong pickling acid bath (aqueous sulfuric and hydrofluoric acid) to remove the formed hard magnesium silicate coatings so that subsequent punching operations may be carried out on the steel sheet without unduly abrading the surfaces of punching dies and thereby impairing their utility and shortening their service life.

Accordingly, it would be desirable to provide magnesium oxide compositions for coating silicon steel which would form adherent coatings and prevent fusion or welding together during annealing of coiled sheets formed from such coated steel and which coatings formed from the compositions would substantially prevent the formation of undesirable hard silicates on the surface and in the sub-surface of the steel.

It is therefore an object of the present invention to provide magnesium oxide compositions for coating silicon steel which coatings prevent the fusion of steel to itself when formed into coils subjected to annealing.

It is another object of the present invention to provide magnesium oxide compositions for coating silicon steel which coatings substantially prevent the formation of undesirable hard silicates on the surface and in the subsurface of the steel when the steel is annealed.

It is another object of the present invention to provide a novel simplified process for providing an annealed silicon steel punching stock which may be used in punching operations without further treatment or if desired, with only a mild pickling prior to punching to remove residual surface silicates and which annealed sheet is characterized as essentially free of hard subsurface silicates and hard surface silicates.

The fulfillment of these and other related objects of this invention may be more readily appreciated by reference to the following specification, examples and appended claims.

SUMMARY OF THE INVENTION

Broadly, the above objects are accomplished by the provision of magnesium oxide coating compositions consisting essentially of a major proportion of magnesium oxide and a minor proportion of an alkaline earth metal fluoride and more particularly, a fluoride selected from the group consisting of magnesium fluoride, calcium fluoride, strontium fluoride and barium fluoride.

The invention also is directed to a process for providing a coated and annealed silicon steel punching stock in sheet form wherein said coating acts as an adherent efficient separator medium during the annealing process which is characterized by relative freedom from the formation of hard sub-surface silicate layers on the steel, and which is further characterized by a minimum of surface silicate formation which is readily removable by mild pickling. Mild pickling involves the use of dilute acids such as HF and H_2SO_4. This process comprises applying to the surface of a silicon steel in strip form, an aqueous slurry of the said magnesium oxide coating composition, heating to remove water therefrom and form an adherent coating thereon, and thereafter, forming the coated steel into coils and annealing the coated steel at a temperature in excess of about 1000° C. preferably in excess of 1200° C.

The magnesium oxide employed in the coating has a surface area from about 5 to about 50 square meters per gram or an iodine number (iodine adsorption value) up to about 60 milligrams of iodine per gram of dry magnesium oxide. The surface area of magnesium oxide as referred to herein is determined by the standard Brunaeur-Emmet-Teller method. The iodine number is approximately 1 to 1.25 times the surface area in square meters per gram. The iodine number as referred to herein is determined by the following procedure:

Method of iodine number determination

(1) Weigh a 2 gram sample of magnesiuc oxide to the nearest milligram.

(2) Transfer to a clear, dry, 200 ml. glass-stoppered bottle.

(3) Add 100±0.2 ml. of 0.100 N iodine in carbon tetrachloride, free from traces of sulfur or carbon disulfide.

(4) Stopper the bottle and shake vigorously at ambient temperature in a suitable shaking device for 30 minutes (the test is relatively insensitive to temperatures so that no temperature controls are employed).

(5) Allow to settle for 5 minutes or longer and then pipette a 20 ml. aliquot of the clear solution into a 250 ml. Erlenmeyer flask containing 50 ml. of 0.03 N potassium iodide in 75 percent ethanol.

(6) Titrate the 20 ml. aliquot with standard 0.05 N sodium thiosulfate. The sodium thiosulfate should be standardized at least once every two weeks against a standard potassium iodate solution. A sharp end point is obtained without the use of starch indicator.

(7) Calculate iodine number in terms of milligrams of iodine per gram of sample according to the following equation:

$$318\ (V_2-V_1)N_1=MgI_2/g.=\text{iodine number}$$

where V_2 is the volume of thiosulfate equivalent to 20 ml. of the original iodine solution — before adsorption of iodine by the oxide; where V_1 is the volume of thiosulfate required by the 20 ml. aliquot after adsorption; and N_1 is the normality of the thiosulfate solution.

The MgO employed in these coating compositions broadly has a surface area of from about 5 to about 50 square meters per gram. If the surface area is less than about 5 square meters per gram then aqueous slurries formed therefrom tend to produce sludge and to have low viscosities unsuitable for a steel coating process. On the other hand, if the MgO surface area is much in excess of about 50 square meters per gram, the activity of the MgO is increased to the point where the unwanted reaction between MgO and the silicon present in steel is enhanced to form undesirable hard surface and sub-surface silicates.

The concentration of alkaline earth metal fluoride in the coating composition is broadly from about 3.5 to 20 percent by weight with the balance being magnesium oxide having a surface area of from 5 to 50 square meters per gram. Preferably the concentration of alkaline earth metal fluoride ranges from about 3.6 to about 10 percent. This concentration of fluoride has been found satisfactory in coating steel sheet having a standard steel industry width of 32 inches. When steel is coated with the present composition, formed into coils and annealed according to the procedure hereinbefore described, some fluorides are lost from the coating due to volatilization. However, enough fluoride remains to prevent the formation of undesirable silicates. The amount of fluorides lost due to volatilization during coil annealing appears generally to be inversely proportional to the width of the steel strip coated. Since the loss of fluoride due to volatilization is commensurately greater in the case of coated steel coils having a width less than 32 inches, amounts of fluoride in the upper end of the range are preferable in narrower strips.

For coating purposes, an aqueous suspension of the above described magnesium oxide composition is prepared by adding a convenient quantity of the composition to water. The quantity employed depends on the viscosity of the resultant suspension desired and its leveling and flow-out characteristics. Generally from about 5 to about 20 weight percent of the magnesium oxide composition, based on water, is satisfactory to provide an aqueous slurry having the requisite viscosity and flow properties suitable for coating onto steel sheet.

The coating slurry may be applied to the magnetic steel sheet by any suitable means such as by immersion, brushing, or spraying. It has been found convenient to use an immersion technique whereby the steel sheet is passed through a tank containing the coating slurry. The slurry coated sheet is thereafter heated to dry the coating and the sheet is coiled and placed in a furnace for box annealing as previously described. During the annealing process, the coating of this invention forms an adherent, electrically insulating, corrosion-resistant layer which also functions as a separator medium to prevent the coiled metal sheet from sticking or fusing to itself during annealing and primarily the formation of undesirable hard silicate coatings is substantially eliminated by the presence of one of the aforementioned fluorides. Thus in punching operations, the service life of costly punching dies is significantly increased.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic diagram of a conventional process for coating the compositions of the present invention on steel strip. As therein illustrated, a magnesium oxide composition prepared in accordance with the present invention and held in hopper **10** and water in tank **12** are fed via lines **13** and **13***a* respectively to mixing tank **14** to form an aqueous coating suspension or slurry. The aqueous coating slurry is conducted through line **18** equipped with valve **20** to coating trough **22**. Newly formed, hot steel sheet **23** is passed in the direction indicated by arrows over roller **24** and under roller **26** through quench tank **28** and thence over roller **25** and through coating trough **22** where it acquires a layer of the coating slurry. The steel sheet coated with an aqueous slurry of the coating composition is then passed between adjustable pinch rollers **30** which regulate the coating thickness and then to drying heater **32**. In the heater, water is volatilized from the slurry layer on the surfaces of the steel strip to provide an adherent dried coating. The dried coated steel sheet is then passed over roller **33** and coiled into suitable lengths at take-up roll **34**. The coated coiled steel roll **23A** is thereafter passed through annealing furnace **36**, as indicated by the arrows, and thence to storage.

EXAMPLE 1

Magnesium oxide having a surface area of about 30 square meters per gram was thoroughly admixed with magnesium fluoride in the proportion of 96.3 weight percent of MgO and 3.7 weight percent of MgF_2. The admixture was thereafter comminuted to a particle size of about 200 mesh (U.S. Standard Sieve Series) to form a coating composition (Coating Composition A).

An aqueous slurry or suspension suitable for coating onto steel sheet was prepared by admixing 25 parts by weight of Coating Composition A with 150 parts by weight of water. The resultant suspension was coated onto steel sheet having a width of 32 inches according to the method depicted in the drawing wherein the coating was leveled and the coated steel was then dried in air at a temperature of about 1000° F. The dried coated steel sheet was then coiled into rolls of convenient size and annealed by heating in a hydrogen atmosphere at a temperature of about 1200° C. for about 60 hours. The coil was cooled and inspected. No sub-surface silicate formation and essentially no surface silicate formation were observed when viewed by microscopic examination of the coated steel surface at a magnification of 2000 diameters. The coil was easily unrolled with no evidence of sticking or fusing.

EXAMPLE 2

Magnesium oxide having a surface area of about 30 square meters per gram was thoroughly admixed with magnesium fluoride in the proportions of 96.6 and 98.3 weight percent of magnesium oxide and 3.4 and 1.7 weight percent of MgF_2 respectively. The admixtures were thereafter separately comminuted to a particle size of about 200 mesh (U.S. Standard Sieve Series) to form coating compositions as indicated:

	Coating composition	
	B, weight percent	C, weight percent
MgO	96.6	98.3
MgF_2	3.4	1.7

An aqueous slurry of each coating composition was prepared and coated onto steel according to the procedure of Example 1. In addition, a control consisting of the same MgO as employed in preparing Coating Compositions A, B, and C, and also pulverized to 200 mesh was coated onto steel sheet according to the procedure of Example 1. The coated steel was viewed microscopically as before.

RESULTS

Composition	Observations
Coating composition B	Trace of hard surface silicate and trace of hard sub-surface silicate formation.
Coating composition C	Moderate hard surface silicate formation and moderate hard subsurface silicate formation.
Control (no MgF_2)	Much surface silicate formation and excessive sub-surface silicate formation.

The foregoing examples illustrate that a magnesium fluoride composition containing 3.7 percent fluoride produces a punching stock that is relatively free from hard surface and subsurface silicates while magnesium oxide compositions containing 3.4 and 1.7 percent of fluoride result in the formation of traces and moderate amounts of hard surface and sub-surface silicates respectively. It should be observed that in the event that some soft silicate surface coatings are formed, they may be readily removed by the use of mild pickling agents, brushing, or the like.

What is claimed is:

1. A coating composition consisting essentially of a magnesium oxide having a surface area of from about 5 to 50 square meters per gram and from about 3.5

to about 20 percent by weight of an alkaline earth metal fluoride.

2. A composition according to claim **1** wherein the alkaline earth metal fluoride is present in an amount of from 3.6 to 10 percent by weight.

3. A composition according to claim **1** wherein the alkaline earth metal fluoride is selected from the group consisting of magnesium fluoride, calcium fluoride, strontium fluoride and barium fluoride.

4. A process wherein the fluoride is magnesium fluoride.

5. A process for producing an annealed silicon steel punching stock characterized by being essentially free from hard surface and sub-surface silicates which comprises coating an elongated sheet of silicon steel in strip form with an aqueous slurry of a coating composition consisting essentially of magnesium oxide having a surface area of from about 5 to 50 square meters per gram and an alkaline earth metal fluoride in an amount of from 3.5 to 20 percent by weight on a solids basis, drying said slurry coating to form a dried adherent coating layer, forming said coated strip into coils, and annealing the coiled coated steel strip.

6. A process according to claim **5** wherein the annealing is carried out at temperatures above about 1000° C.

7. A process according to claim **5** wherein the slurry has a solids content of from 5 to 20 percent by weight.

8. A process according to claim **5** wherein the fluoride is selected from the group consisting of magnesium fluoride, calcium fluoride, strontium fluoride and barium fluoride.

9. A process according to claim **5** wherein the fluoride is magnesium fluoride.

References Cited

UNITED STATES PATENTS

1,703,630	2/1929	Meehan	148—27X
3,039,902	6/1962	Miller et al.	148—113
3,084,081	4/1963	Carpenter	148—14
3,105,781	10/1963	Walter	148—113X
3,132,056	5/1964	McQuade	148—113X
3,151,997	10/1964	Harvey	148—113X
3,265,600	8/1966	Carter et al.	148—27X
3,389,006	6/1968	Kohler	148—113X

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