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# GALVANIC PROCESS FOR COATING IRON ALLOYS WITH MAGNESIUM HYDROXIDE

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8 Claims. (Cl. 204—56)

This invention relates to a process for galvanically coating iron alloys with a magnesium hydroxide film that is suitable for conversion into an electrical insulating and high temperature separating coating.

Grain oriented magnetic silicon steels used as flux-carrying members in electrical induction apparatus, such as transformers, dynamos, and the like, must often be provided with an electrical insulating coating; the coating should also maintain separation between contacting layers of the steel when several layers are stacked and annealed at high temperatures. The grain oriented silicon steels referred to may be made by several well known commercial processes which usually include the following steps: A ferrous alloy containing up to about 6% silicon and relatively minor amounts of impurities is cast into ingots; hot worked, usually by rolling as a continuous strand; and then subjected to varying schedules of usually unidirectional cold rolling. The steel is then heat treated by several combinations of treating cycles which cause primary recrystallization of the grains, decarburization, secondary recrystallization of the grains, and purification by removal of sulfur and other impurities. The grain orientation of the magnetic steels produced by the above type of process is usually referred to as the (110) [001] type in the standard notation by Millers' Indices. This designation is intended to indicate that the [001] direction of the crystals is parallel to the rolling direction and the (110) plane is parallel to the rolling plane. Considering the crystals as cubes, the designation indicates a cube on edge position of the crystal in the plane of a sheet of the material. It is to be understood, of course, that the specific process by which such steels are made forms no part of the present invention.

One material that is suitable for use as an electrical insulating and high temperature separating coating on magnetic silicon steels of the type described above is magnesium silcate ($Mg_2SiO_4$). This coating is normally obtained by applying magnesium hydroxide

$$[Mg(OH)_2]$$

to semi-processed silicon steels and then heating at high temperatures during the final grain growth and purification anneal of the steel. During the high temperature anneal a chemical reaction takes place in which the water of hydration of the magnesium hydroxide is driven off and the resulting magnesium oxide (MgO) is available to combine with silicon in the steel to form an adherent, refractory, high strength electrical insulating and high temperature separating coating of magnesium silicate. It is to be understood that the specific process by which a magnesium hydroxide coating on such steels is converted into magnesium silicate forms no part of the present invention.

This invention is directed to an improved process for depositing magnesium hydroxide on iron alloys, such as the magnetic steels described above. Examples of prior art processes for applying magnesium hydroxide to magnetic steels are (1) passing the steel through a water slurry of magnesium oxide, and (2) depositing the magnesium hydroxide on the steel in electrolytic processes in which external current is required. The water slurry processes possess disadvantages in that the deposited coating often lacks uniformity in thickness with resulting variations in properties and often poor space factor. The electrolytic processes offer better control of coating thickness and hence resulting properties. However, electrolytic processes require an external source of current, and the peripheral edges of very thin sheet stock will not be coated unless the current density is held within certain critical limits. Furthermore, in the electrolytic processes the electrolyte salt is consumed; this requires a constant check on the content of the electrolytic solution to maintain proper concentration.

Accordingly, it is an object of this invention to provide an improved process for coating iron alloys.

Another object of the invention is to provide a process for galvanically coating iron alloys with magnesium hydroxide.

Another object of the invention is to provide an improved process for coating silicon steels with a uniform magnesium hydroxide coating without the application of an external current, the magnesium hydroxide coatings being suitable for conversion into magnesium silicate coatings.

A further object of the invention is to provide an improved process for obtaining electrical insulating and high temperature separating coatings on grain oriented silicon steels.

Another object of the invention is to provide a galvanic process for coating iron alloys with magnesium hydroxide in which the electrolytic salt is not consumed.

Another object of the invention is to provide an improved process for coating thin sheets of grain oriented silicon steel in which the edges of the sheet are coated, the process being characterized by the absence of an external current.

Other objects and advantages of the invention will become apparent from the following detailed description, and the scope of the invention will be pointed out in the claims.

Briefly stated, according to one aspect of the invention, a coating of magnesium hydroxide may be deposited on iron alloys by a galvanic process in which an iron alloy article is immersed in a water solution of a magnesium salt; a magnesium metal article is also immersed in the solution; and the iron alloy article and magnesium metal article are electrically connected to each other.

My experiments have shown that an adherent magnesium hydroxide coating can be deposited on iron alloys with about 50% and above iron content by a galvanic process. The iron alloy is used as the cathode and magnesium metal is used as the anode. Anodes of commercially pure metallic calcium, zinc, and aluminum were tried without success. The electrolyte should be a water solution of a magnesium salt, and magnesium acetate $[Mg(C_2H_3O_2)_2]$, magnesium chloride ($MgCl_2$), magnesium nitrate $[Mg(NO_3)_2]$, and magnesium sulfate $[Mg(SO_4)_2]$ have all been successfully employed as the salt. The concentration of the salt should be between about 10 grams per liter and 100 grams per liter. No gain in results was obtained from concentrations above about 100 grams per liter, and when the concentration is decreased below 25 grams per liter, the immersion coating time should be increased. The temperature of the electrolyte should be above about 25° C. in that the weight of the deposited coating is a function of temperature; for temperatures below 25° C. the coating immersion time had to be increased beyond commercially practical limits. No gain in results was found when the electrolyte temperature was raised above about 80° C. The above-described processes can be successfully employed for depositing magnesium hydroxide on 50% iron–50% nickel alloys. However, satisfactory results could not be obtained when copper or aluminum are used as the cathode.

By way of illustration, listed below in Table I are results obtained for magnesium hydroxide coatings deposited on grain oriented silicon steel. The steel was a commercially available, 3¼% silicon alloy, having a (110) [001] type of grain orientation, and a thickness of .012". The steel was semi-processed in that it had not been given its final grain growth and purification anneal. The anode was magnesium metal, and consisted of an assembly of two banks of 1/16" diameter commercially pure magnesium rods which were 6 inches in length, and embedded at one end in a rectangular copper holder. Each bank was formed by placing six rods next to each other in the longer sides of the copper holder with the rods being spaced about ½" apart. The silicon steel strip being coated was placed midway between the two banks of magnesium rods and connected to the rods by means of a copper wire grounded to the copper holder. The silicon steel strips measured 6" x 1" and were approximately one inch away from either bank of magnesium rods. The assembly was then lowered into a water solution of a magnesium salt with the magnesium and steel members, but not the copper holder or wire, being immersed. The formation of bubbles was immediately noted at the surface of the steel, and it was also apparent that a cotaing was being produced on the steel. In all of the examples listed in Table I, the iron and magnesium were immersed in the electrolyte for about 3 minutes. The values given for coating weight are based on the weight of the magnesium hydroxide coating deposited on the surface area of the steel strips.

The Franklin insulation values were for magnesium silicate coatings produced by taking the silicon steel specimens coated with magnesium hydroxide and giving them a standard high temperature grain growth and purification anneal in dry hydrogen for 8 hours at 1175° C. In the standard Franklin test employed, readings of 1 ampere represent no surface insulation and readings of 0 ampere represent perfect insulation. Generally speaking, Franklin insulation values below about 0.4 ampere are preferred for high voltage electrical applications. Higher Franklin values (i.e., less insulation strength) are acceptable in some applications where high voltages are not encountered.

*Table I*

| Sample Designation | Electrolyte Salt | Concentration (grams/liter) | Electrolyte Temp. (° C.) | Coating Weight[1] (oz./ft.$^2$) | Franklin Value (amperes)[1] |
|---|---|---|---|---|---|
| 1 | Magnesium Acetate. | 100 | 80 | .018 | .32 |
| 2 | do | 50 | 80 | .020 | .30 |
| 3 | do | 25 | 80 | .018 | .34 |
| 4 | do | 100 | 55 | .017 | .36 |
| 5 | do | 50 | 55 | .016 | .32 |
| 6 | do | 25 | 55 | .012 | .47 |
| 7 | Magnesium Chloride. | 100 | 80 | .028 | .27 |
| 8 | do | 50 | 80 | .027 | .23 |
| 9 | do | 25 | 80 | .019 | .39 |
| 10 | do | 100 | 55 | .028 | .20 |
| 11 | do | 50 | 55 | .029 | .16 |
| 12 | do | 25 | 55 | .022 | .29 |

[1] Average for two specimens.

The final coatings on all samples were refractory and showed good high temperature separation properties. The coatings were uniform in thickness and were tenaciously bonded to all surfaces of the steel strips including the thin edges. The coating weights were in the range of from about .010 to .030 ounce per square foot. Table I shows that coatings having excellent electrical insulation properties were obtained after various combinations of electrolyte concentration and temperature had been employed. Coatings with Franklin values below 0.4 ampere were also obtained with the magnesium chloride electrolyte in only ninety seconds under the same concentration and temperature conditions as samples 10 and 11. Franklin values of between 0.5 and 0.7 ampere were obtained with the magnesium acetate electrolyte in only ninety seconds under the same concentration and temperature conditions as samples 4 and 5. Thus, when the Franklin insulation strength need not be below 0.4 ampere, the immersion coating time can be reduced accordingly.

The over-all reaction for a galvanic coating process in accord with my teachings is as follows:

$$Mg+2H_2O \rightarrow Mg(OH)_2+H_2$$

The over-all reaction is brought about by the following re-actions: Water dissociates to produce hydrogen ions and hydroxyl ions:

$$H_2O \rightarrow H^+ + OH^- \qquad (1)$$

Magnesium goes into solution to produce magnesium ions:

$$Mg-2e^- \rightarrow Mg^{++} \qquad (2)$$

The hydrogen ions are discharged to form hydrogen gas at the surface of the iron leaving an excess of $OH^-$. (Equation 1.)

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

Magnesium ions from the electrolyte migrate to the iron alloy (cathode) where they combine with the excess hydroxyl ions and deposit magnesium hydroxide on the surface of the iron alloy:

$$Mg^{++}+2(OH)^- \rightarrow Mg(OH)_2 \qquad (4)$$

These magnesium ions are replenished by the dissolution of the Mg anode. (Equation 2.) The magnesium salt is not used up but merely acts as a conductor. Thus the materials consumed in this process are the magnesium and water. This makes it easy to control the process over extended periods of time in that the amount of magnesium present is readily ascertained merely by observation, and the magnesium can be replenished by inserting other magnesium articles in the electrolyte and connecting them to the iron alloy. It is easy to determine the amount of water being used merely by observing the level of the electrolyte solution. Also, since water is being consumed, the concentration of the solution becomes stronger; this means that the process will not produce poor results if the water level is inadvertently allowed to fall.

It has thus been shown that by the practice of my invention, uniform, adherent magnesium hydroxide coatings can be deposited on iron alloys by a galvanic process that does not require the application of an external current. The process has the advantage of permitting accurate control of the thickness and weight of the coating by proper combination of salt concentration, temperature, and immersion coating time, with a resulting uniformity of properties being assured. My process is thus adaptable for use as a step in large scale continuous strand production operations in which grain oriented electrical silicon steels are continuously processed by coating them with magnesium hydroxide before they are given their final grain growth and purification anneal, during which anneal an electrical insulating and high temperature separating magnesium silicate coating is produced on the exterior surface of the steel.

It will be understood, of course, that while the forms of the invention herein described constitute preferred embodiments of the invention, it is not intended herein to describe all of the equivalent forms or ramifications thereof. It will also be understood that the words used are words of description rather than of limitation; and that various changes may be made without departing from the spirit or scope of the invention herein disclosed, and it is aimed in the appended claims to cover all such changes as fall within the true spirit and scope of the invention.

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

1. The process comprising arranging an iron alloy member and a magnesium metal member directly electrically connected to each other in a water solution having a concentration of above about 10 grams per liter of a magnesium salt for sufficient time to deposit a magnesium hydroxide coating on the iron alloy member by galvanic action, and recovering the thus coated iron alloy member.

2. A galvanic coating process for depositing magnesium hydroxide on an iron alloy article comprising: immersing the iron alloy article in a water solution having a concentration of above about 10 grams per liter of a magnesium salt at a temperature about about 25° C., immersing a magnesium article in said solution, and directly connecting said iron alloy article to said magnesium article through an electrical conductor.

3. A galvanic coating process for depositing magnesium hydroxide on an iron alloy article comprising: immersing the iron alloy article in a water solution having a magnesium salt concentration above about 10 grams per liter, immersing a magnesium article in said solution, and directly connecting said iron alloy article to said magnesium article through an electrical conductor.

4. In the process for coating a magnetic steel article having up to about 6% silicon content with a uniform, adherent, refractory magnesium silicate coating having electrical insulating and high temperature separating properties, said process requiring depositing a film of magnesium hydroxide on the surface of the steel article and then annealing at an elevated temperature, the improvement in a method for depositing the magnesium hydroxide on the steel article comprising: immersing the steel article in water solution having a magnesium salt concentration above about 10 grams per liter at a temperature above about 25° C., immersing a magnesium article in said solution, and directly connecting said steel article and said magnesium article through an electrical conductor, whereby magnesium hydroxide will be deposited on the steel by galvanic action.

5. In the process for coating a grain oriented magnetic steel article having up to about 6% silicon content with a uniform, adherent, refractory magnesium silicate coating having electrical insulating and high temperature separating properties, said process requiring depositing a film of magnesium hydroxide on the surface of the steel article and then annealing at an elevated temperature, the improvement in a method for depositing the magnesium hydroxide on the steel article comprising: immersing the steel article in a water solution having a magnesium salt concentration of from about 10 to 100 grams per liter at temperatures from about 25 to 80° C., immersing a magnesium article in said solution, and directly connecting said steel article to said magnesium article through an electrical conductor, whereby magnesium hydroxide will be deposited on the steel by galvanic action.

6. The process of applying a coating of magnesium hydroxide on an iron containing member which comprises immersing the iron containing member and a magnesium metal member directly electrically connected thereto in an electrolyte comprising a water solution having a concentration of above about 10 grams per liter of a salt selected from the group consisting of magnesium acetate, magnesium chloride, magnesium nitrate, and magnesium sulfate, for a sufficient time to deposit a magnesium hydroxide coating on the iron containing member by galvanic action, and recovering the thus coated iron containing member.

7. The process of applying a coating of magnesium hydroxide on an iron alloy member which comprises immersing the iron alloy member and a magnesium metal member directly electrically connected thereto in an electrolyte comprising a water solution of a salt selected from the group consisting of magnesium acetate, magnesium chloride, magnesium nitrate, and magnesium sulfate, for a sufficient time to deposit a magnesium hydroxide coating on the iron alloy member by galvanic action, said solution having a concentration of said salt of about 10 to 100 grams per liter and having a temperature of about 25 to 85° C., and recovering the thus coated iron alloy member.

8. The process of applying a coating of magnesium hydroxide on a silicon steel member containing up to about 6% silicon which comprises immersing the silicon steel member and a magnesium metal member directly electrically connected thereto in an electrolyte comprising a water solution having a concentration of above about 10 grams per liter of a salt selected from the group consisting of magnesium acetate, magnesium chloride, magnesium nitrate, and magnesium sulfate, for a sufficient time to deposit a magnesium hydroxide coating on the silicon steel member by galvanic action, and recovering the thus coated silicon steel member.

**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,200,469 | 5/40 | Cox | 204—56 XR |
| 2,534,234 | 12/50 | Cox | 204—56 |
| 2,597,456 | 5/52 | Coleman et al. | 136—100 |
| 2,729,551 | 1/56 | Cohn | 204—140.5 X |
| 2,779,699 | 1/57 | Langworthy | 148—122 |
| 2,957,817 | 10/60 | Wales | 204—248 |
| 3,036,141 | 5/62 | Goldenberg et al. | 136—100 |

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# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,208,922

September 28, 1965

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 27, for "cotaing" read -- coating --; column 5, line 16, for "about", first occurrence, read -- above --; lines 32 and 48, for "surface", each occurrence, read -- surfaces --.

Signed and sealed this 19th day of April 1966.

(SEAL)
Attest:

**ERNEST W. SWIDER**
Attesting Officer

**EDWARD J. BRENNER**
Commissioner of Patents