United States Patent Office

3,484,344

Patented Dec. 16, 1969

3,484,344

PRODUCTION OF ELECTRICALLY RESISTIVE COATINGS BY ANODIC DEPOSITION FROM AQUEOUS MONOALUMINUM PHOSPHATE

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No Drawing. Filed May 10, 1965, Ser. No. 454,710
Int. Cl. C23b *11/00, 5/52*
U.S. Cl. 204—37 11 Claims

ABSTRACT OF THE DISCLOSURE

Electrically resistive insulating coatings are applied to silicon steel members by immersing said members as anode in an aqueous bath containing dissolved monoaluminum phosphate and then passing a unidirectional electrical current through a sacrificial aluminum cathode and then through said bath to deposit a gelatinous coating on the silicon steel member which is then removed from the bath and dried at elevated temperature.

The present invention relates to the deposition of an inorganic electrically insulating layer on ferrous members, especially ferrous magnetic stock in order to adapt the same for use in electro-magnetic apparatus. More specifically, the present invention relates to the anodic deposition of an insulating layer onto silicon steel sheet stock to provide the high surface resistivity needed in order to use these sheets in the production of laminated cores for electro-magnetic apparatus.

The magnetic cores utilized in generators, transformers, electric motors, and the like, are preferably constructed by laminating a plurality of silicon steel sheets which are provided with electrically insulating coatings thereon to form an insulated laminate which, when the core is used in an electro-magnetic application, minimizes the flow of magnetic eddy currents therethrough.

It is known to employ coatings of organic nature, e.g., varnishes, in order to electrically insulate the silicon steel sheet. However, the varnishes tend to break down upon prolonged exposure to the elevated temperatures which are encountered in use. As the varnishes break down, odorous fumes are generated and the desired dielectric properties of the coatings fall off. It is also known to apply inorganic coatings which are fired prior to use. These have been found to possess superior temperature resistance. On the other hand, the inorganic coatings have been expensive and have lacked desired uniformity and resistivity.

The present invention provides an inexpensive electrolytic system for uniformly depositing a thin aluminum oxide insulating layer on the ferrous members to be insulated.

In accordance with the present invention a unidirectional electrical current is passed through a sacrificial aluminum cathode immersed in an aqueous acidic electrolytic bath containing monoaluminum phosphate and then through the ferrous member to be insulated which forms the anode of the system. It is believed that in this way aluminum oxide is deposited in thin, continuous and uniform films on the surface of the ferrous member. These films are believed to include some water and some aluminum hydrate and, after baking at elevated temperatures, form adherent films of high resistivity.

In preferred practice, the unidirectional electrical current is connected before the ferrous anode is immersed in the electrolytic bath to prevent reaction of the ferrous body with the solution which causes several problems. More particularly, it avoids contamination of the electrolytic bath by preventing formation of iron phosphates

therein which cause the bath to become cloudy and hazy. Also, the loss of iron from the steel anode allows carbon to be freed which forms a black coating on the surface of the steel. Thus, and in practice, the current is turned on before the anode is dipped into the bath to provide more uniform coatings and avoid deterioration of the bath as well as the parts or sheets which are coated.

It is also preferred to remove the coated anode slowly while the current remains on since the coating is fragile and gelatinous prior to baking and may be damaged by rapid anode removal and/or osmotic forces if the current is turned off prior to removal.

Other and further features of the invention will become apparent from the description which follows.

In accordance with the present invention, ferrous metal plates to be insulated are prepared for use in the process of the invention. These plates are ferrous in nature and may include iron, wrought iron, cold rolled steel, nickel steel, chrome steel and any alloys of iron and steel which are predominately ferrous in nature, though silicon steel, commonly called electrical steel, is preferred.

The surface of the ferrous metal plates are normally contaminated with grease or other organic agents and these interfering agents are removed prior to the electrolytic treatment. To illustrate effective removal of grease and the like, the plates are washed with heated trichloroethylene under pressure. While the use of trichloroethylene is preferred, one may use any suitable cleaner or degreaser which can effectively remove the organic contaminates from the ferrous members prior to electrolytic treatment.

The cleaned plates are then connected as anodes to a unidirectional electrical current source. The current source should, in general, be able to provide voltages up to 400 volts and current densities of from 2–60 amps per square foot.

The voltage and amperage may be varied together with the time of electrolytic treatment to obtain specific thickness of coating which is desired for the purpose at hand. For example, silicon steel is adequately coated at 8 amps per square foot and 4.2 volts whereas cold rolled steel is desirably coated at 16 amps per square foot and 8 volts.

The ferrous anode is immersed in an aqueous electrolytic bath containing dissolved monoaluminum phosphate, an aluminum salt which is highly soluble in water and inexpensive. While the salt may be formed in situ in an aqueous acidic solution e.g., using aluminum hydrate, phosphoric acid and water, it is preferable to use the salt itself because this salt is available commercially and is easily soluble in water to provide up to 50% solids content solutions (all parts and percentages are by weight). Preferably, the aqueous solution utilized as the electrolyte should have a pH in the range of 1–5 (normally provided by the acidity of the monoaluminum phosphate), the most preferred range being from 1.0 to 2. Referring to a preferred aqueous solution of monoaluminum phosphate, best results are presently obtained using a solution having a weight ratio of 1 part monoaluminum phosphate to 5 parts water (about 16% by weight) and a pH of about 1.5.

If superior electrical properties are desired in the finished plate, the electrolytic bath may be modified by the addition of sodium salts thereto. In preferred practice, 100 milliliters of a 3% solution of sodium fluoride is added to 7400 milliliters of the monoaluminum phosphate:water bath solution and this addition tends to provide an approximate twofold improvement in the electrical properties of the coated plates.

The electrolytic solution includes a sacrificial aluminum cathode immersed therein. This cathode provides free aluminum ions for the solution while the cell is operating to assist in maintaining the ionic equilibrium of alumi-

num to phosphate. While there is no intention of being limited to any particular theory of operation, it is believed that electrolytic decomposition of water and the ionization of aluminum at the cathode results in the production of a negatively charged aluminum hydroxide ion which then moves toward the anode and is plated out there as aluminum oxide to thereby provide a gelatinous aluminum oxide coating. The sacrificial cathode is consumed in the process of the invention.

The temperature of the electrolytic solution is not material but it should be maintained at about room temperature (60–80° F.) and preferably about 70° F. for best results. Variations in temperature may require adjustment of current densities for more economical operation.

The relative distance between the cathode and anode also contributes to the economies of the system. If the cathode is too far from the anode, uneconomical uses of current may be necessary for proper coating.

The thickness of the insulative coating depends on the immersion time and current densities. Generally, a coating of adequate thickness (0.1 mil) may be obtained by immersion time of 3–5 minutes using the average current densities set forth hereinbefore.

Following the coating operation; the plates are slowly removed from the bath while the current is still on. These steps are important for best results since the coating while in the bath is of a fragile and gelatinous nature and does not firmly adhere to the plate. Rapid removal may cause the coating to physically break or tear or to otherwise become physically damaged. Accordingly, the plates should be removed from the bath slowly and carefully. The electrical current should also remain on to avoid disruption in the coating caused by back lash osmotic force which may cause the plating solution to become trapped within the gelatinous coating. When the electrical current is on, electroendosmosis causes the coating which is deposited to collapse onto the plate, forcing the bath solution away from the gelatinous deposit. When the current is off, the bath solution tends to permeate the coating via osmosis and this is desirably avoided as indicated. Thus, in preferred practice, the current remains on while the coated plates are slowly removed from the electrolytic bath.

Following removal from the bath, the coated plates are baked to drive off any trapped moisture and convert the gelatinous coating into a hard and highly resistive insulating film firmly adhered to the base. The baking should be at a temperature sufficient to drive off water of hydration from the aluminum oxide. Baking at 800° F. for 40–50 seconds accomplishes this result.

The invention will be illustrated by the examples which follow:

EXAMPLE I

A 6 inch x 5 inch x 0.145 inch silicon steel plate is washed with trichloroethylene in the form of hot vapor until clean. The plate is then connected to a unidirectional electrical current source of 7 volts and 4 amps. The plate is immersed into an electrolytic solution of 1 part monoaluminum phosphate to 2 parts of water, the solution having a specific gravity of 1.159, a pH of about 1.5, a percent solids of 16.6%, and a temperature of about 70° F. The panel is centrally placed between two sacrificial aluminum cathodes also immersed in the electrolytic solution. The panel is maintained in the electrolytic solution for 3 minutes and removed slowly while the current remains on. The plate is then placed in a baking oven at 250° F. for one minute then the temperature is raised to 800° F. for 45 seconds. The plate has a 0.15 mil insulating film thereon per side characterized by good initial resistivity with thinner films, improved uniformity of coating, and reduced deterioration of resistivity with pressure and time.

Film thickness may be determined by the following procedure. Ten uncoated plates are inserted and clamped between the lips of an hydraulic C-clamp which can maintain a pressure of 200 p.s.i. over a 100 cm.^{2} area in the center of the plates. The distance, d_1, between the lips is measured with a micrometer.

A portion, X, of the ten plates is then coated with the coatings. The ten plates (including both the coated and uncoated plates) are again clamped in the C-clamp and the distance, d_2, between the lips is measured with the micrometer. By subtracting the second measurement from the first the total thickness of the coating, Z, which the X plates received is obtained.

$$D_2-D_1=Z$$

To obtain the thickness of each coating, V, it is necessary to divide the total thickness Z by the number of sides coated and measured, which is double the number of plates coated or 2X.

$$V=Z/2X$$

For example, 10 plates measure 1.4453 inches before coating and 1.4459 inches after 2 plates were coated giving a total coating thickness of 0.6 mil.

$$1.4459-1.4453=0.0006 \text{ inch}=0.6 \text{ mil}$$

Dividing 0.6 mil by the number of coated sides (4) provides the thickness per side of 0.15 mil/side.

$$V=0.6 \text{ mil}/4 \text{ sides}=0.15 \text{ mil/side}$$

Interlaminary resistivity of the insulating coatings and their interface may be determined by any accepted procedure. One such procedure measures the resistivity of two coated metal plates plus one interface by clamping them in the hydraulic C-clamp as described above under 200 p.s.i. An electrode is used to penetrate the two outer coatings so that the resistivity of the two center coatings can be measured.

The resistivity is determined by measuring the resistance of the coatings with an ohmmeter. This result was then multiplied by the area (A) of coating involved and divided by the distance (D_3) between laminated plates (total thickness of 2 coatings) to obtain the interlaminary resistivity in ohm-centimeters of the coatings at 200 p.s.i. In mathematical terms:

$$P=R\times A\times\frac{1}{D_3}=\frac{RA}{D_3}$$

Since the resistivity of the coatings decreases with time after the application of pressure, care must be taken to record the times at which the data is taken after the application of pressure if comparisons are to be made. A stable resistivity is eventually attained which is, of course, more important than the initial values.

At two minutes after the 200 p.s.i. pressure was applied, the resistance of the 100 centimeter area in the center of the two coated plates measured 170,000 ohms. The distance D_3 between the plates on the total of the thickness of two coatings as determined above is 0.3 mil or 7.6×10^{-4} cm. Therefore:

$$P=R\times\frac{A}{D_3}=170{,}000\times\frac{100}{7.6\times10^{-4}}$$

$$=22{,}400\times10^6 \text{ ohm-centimeters}$$

EXAMPLE II

One hundred clean 3 inch x 5 inch x 0.145 inch cold rolled steel panels were progressively in series immersed in an electrolytic solution of 1 part of monoaluminum phosphate to 2 parts of water, the solution having a specific gravity of 1.159, a pH of about 1.5, a percent solids of 16.6% and a temperature of about 70° F. The panels were connected as anodes to a unidirectional current source of 8 volts and 4 amps and immersed for 5 minutes between two aluminum plates connected as cathodes. After 84 panels had been coated the specific gravity of the solution was 1.1736. The completion of the 100 series showed a specific gravity of 1.1742, percent solids of 21.3%

and a pH of 1.6. The two aluminum cathodes immersed in the solution showed a decrease in weight by 0.108% and 0.093% respectively. The plates so produced were baked at 800° F. for 45 seconds and showed a film thickness of 0.1 mil per side and a resistivity similar to that obtained with Example I.

EXAMPLE III

Example I was repeated with an addition of sodium fluoride being made to the electrolytic solution in the proportions of 100 milliliters of a 3% solution of sodium fluoride to 7400 milliliters of the bath (1 part manoaluminum phosphate to 2 parts water). The insulated panel so produced exhibits improved electrical resistivity over the resistivity of a panel from Example I by a factor of 1.5 to 2.0.

The invention is defined in the claims which follow.

I claim:

1. A method of coating a ferrous member with an electrically resistive coating comprising:

(a) Passing a unidirectional electrical current through a sacrificial aluminum cathode immersed in an aqueous bath containing dissolved monoaluminum phosphate and then through said ferrous member as anode to deposit a coating thereon;

(b) Removing said anode from said bath; and

(c) Drying said coating at elevated temperature.

2. The method as recited in claim **1** in which said ferrous member is a sheet of silicon steel.

3. The method as recited in claim **1** in which the pH of said bath is from 1 to 2.

4. The method as recited in claim **1** in which about one part of said monoaluminum phosphate is used for about 2 parts of water to form said bath.

5. The method as recited in claim **1** in which said bath contains sodium salts.

6. The method as recited in claim **5** in which said salt is sodium fluoride and is used in the proportions of about 100 milliliters of a 3% solution of sodium fluoride to about 7400 milliliters of said bath.

7. A method of coating a ferrous member with an electrically resistive coating comprising:

(a) Connecting said ferrous member as an anode and an aluminum member as a sacrificial cathode to a unidirectional electrical current source;

(b) Immersing said ferrous member and said sacrificial cathode while the said current is on in an aqueous bath containing a proportion of dissolved monoaluminum phosphate sufficient to provide a pH in the range of 1–5 to deposit a gelatinous coating on said ferrous member;

(c) Removing said ferrous member from said bath; and

(d) Drying said coating at elevated temperature.

8. A method of coating ferrous members with an electrically resistive coating comprising:

(a) Passing a unidirectional electrical current through a sacrificial aluminum cathode immersed in an aqueous bath containing dissolved monoaluminum phosphate and then through said ferrous member as anode to deposit a coating thereon;

(b) Slowly removing said ferrous member from said bath while said current is still flowing; and

(c) Drying said coating at elevated temperature.

9. A method of coating ferrous members with an electrically resistive coating comprising:

(a) Connecting said ferrous member as an anode and an aluminum member as a sacrificial cathode to a unidirectional current source;

(b) Immersing said ferrous member while the said current is on in an aqueous bath containing dissolved monoaluminum phosphate and said sacrificial cathode to deposit gelatinous coating on said ferrous member;

(c) Slowly removing said ferrous member from said bath while said current is still flowing; and

(d) Drying said coating at elevated temperature.

10. A method of coating a silicon steel member adapted for use in electro-magnetic core laminates with an electrically resistive coating comprising:

(a) Connecting said silicon steel member as an anode and an aluminum member as a cathode to a unidirectional current source;

(b) Immersing said silicon steel member while the said current is on in an aqueous bath containing about 1 part by weight of dissolved monoaluminum phosphate to each 2 parts by weight of water and said sacrificial cathode to deposit a gelatinous coating on said silicon steel member;

(c) slowly removing said silicon steel member from said bath while said current is still flowing; and

(d) Drying said coating at elevated temperatures sufficient to drive off the water of hydration.

11. A method recited in claim **10** in which said coating is dried at about 800° F. for about 40–50 seconds.

References Cited

UNITED STATES PATENTS

571,531	11/1896	Langhans	204—56 XR
2,641,556	6/1953	Robinson	117—127 XR
2,871,143	1/1959	Getting	117—127
2,906,645	9/1959	Carpenter et al.	117—127
2,938,813	5/1960	Matsuda	117—127
3,054,732	9/1962	McQuade	204—56 XR
3,227,635	1/1966	Koretzky et al.	204—28

OTHER REFERENCES

Gray, A. G., "Modern Electroplating," page 375, 1953.

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U.S. Cl. X.R.

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