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INSULATING COATING AND METHOD OF MAKING THE SAME

Robert G. Hirst and George J. Desnoyers, Pittsfield, Mass., assignors to General Electric Company

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ABSTRACT OF THE DISCLOSURE

Electrically insulating coating for strand annealed magnetic silicon steel is composed of an aqueous mixture of (1) the reaction product of chromium trioxide, formic acid and phosphoric acid, (2) phosphoric acid, and (3) colloidal silica.

The present invention relates to coated magnetic sheet material and a method of making the same. More particularly, the invention concerns refractory coating material which is applied to such sheet material, and especially to strand annealed silicon steel strip, and serves as a permanent insulating coating in the use of the metallic sheet material in laminated electrical structures.

The forms of magnetic sheet material with which the invention is concerned include strip material such as used in wound transformer cores, and cut or punched laminations forming stacked transformer cores or other electrical apparatus. Examples of compositions of magnetic sheet materials which may be effectively coated in accordance with the invention are silicon steel (typically containing about 1–5% silicon), nickel-iron alloys, common iron, and other ferromagnetic materials.

The invention is particularly applicable to silicon steel strip which has been subjected to a grain growth and purification anneal treatment wherein the steel is heated in the form of a single strand, as distinguished from coiled or stacked form, in a suitable furnace through which the strand may be continuously passed during the heat treatment.

In the past, it has been the practice to subject the steel sheet material in coiled or stacked form to the annealing treatment, and in order to prevent sticking of the sheet surfaces to each other during such elevated heat treatment, an insulating coating material such as magnesium hydroxide has conventionally been applied to the sheet material prior to such annealing stage. Such coating material has served both to avoid the problem of sticking during the anneal and to provide electrical insulation to reduce eddy current loss in the laminated core formed by the sheet material in its use in a transformer, motor or the like. However, the application of insulating coatings in general to the steel sheet prior to the annealing treatment has the disadvantage in a strand anneal procedure that the presence of the insulating coating tends to delay the purification of the steel during the strand anneal, e.g., by hindering removal of sulfur from the steel, and consequently the strand anneal process is not as rapid as it might be in the absence of such coatings. Moreover, the prior types of inorganic insulating coating such as magnesium hydroxide require relatively high curing temperatures, e.g., over 1000° C., to produce final coatings of the requisite hardness, electrical insulating and other properties. While such elevated temperatures are employed during the usual grain growth and purification anneal, it has in many cases been found desirable to apply one or more additional insulating layers after the usual anneal and for this purpose the sheet material has to be heated again to elevated temperature to cure the added insulating layer.

It is, therefore, an object of the invention to provide an improved insulating material for metallic sheet material which avoids the above-mentioned disadvantages.

A further object of the invention is to provide an improved insulating coating composition for the above purposes which may be cured at relatively low temperatures.

Still another object of the invention is to provide an insulating coating composition which is particularly adapted for use on electrical steel sheet material treated by a strand anneal process.

It is another object of the invention to provide an improved method of making insulated steel sheet material of the above type.

Other objects and advantages will become apparent from the following description and the appended claims.

With the above objects in view, the present invention in one of its aspects relates to an insulating coating composition comprising a mixture of trivalent chromium, phosphoric acid, a finely divided refractory material selected from the group consisting of collaidal silica and colloidal alumina, and water. In a preferred embodiment of the invention, the trivalent chromium is obtained by reacting chromium trioxide and a reducing agent such as formic acid in phosphoric acid solution.

In a typical application of the present invention, the foregoing insulating mixture is deposited on the surfaces of silicon steel strip which has been subjected to a strand anneal process for producing the desired magnetic texture and removing undesired impurities therein. Such a strand anneal process is disclosed in detail, for example, in Fitz et al. Patent 2,986,485, and the disclosure of that patent is incorporated herein by reference. As there disclosed, the strand anneal process, which may be carried out on a continuous basis, comprises the steps of heating silicon steel material for about 5 to 60 minutes (preferably about 15 minutes) at a temperature of about 950 to 1050° C., and thereafter heating the material at a temperature of 1175 to 1250° C. for about 1 to 30 minutes (preferably about 15 minutes). The annealing treatment is preferably carried out in a reducing atmosphere in the furnace, such as in hydrogen or other reducing gases. In accordance with the invention, the thus annealed steel strip, which previous to the anneal had not been provided with an insulating coating, is then coated with the above-described mixture, and the latter is then dried by heating or otherwise cured to form a hard, tightly adherent, highly insulating coating on the steel surfaces.

A particular mixture found eminently satisfactory for preparing the coating in accordance with the invention has the following composition, shown in a preferred and a range of proportions in percent by weight:

	Preferred, percent	Range, percent
Chromium trioxide-CrO_3	2.2	1–10
Formic acid-HCOOH	1.5	1–10
Phosphoric acid-H_3PO_4	18.8	10–40
Colloidal silica	31.6	15–50
Water	45.9	Balance

As a result of the reaction whereby the formic acid reduces the six-valent chromium of the chromium trioxide to trivalent chromium in phosphoric acid solution, the following compositions are ultimately obtained from the above compositions:

	Preferred, percent	Range, percent
Cr^{+++} (as chromium phosphate)	3.2	1–15
Phosphoric acid	16.9	10–40
Collodial silica	32.1	15–50
Water	47.8	Balance

In an illustrative method which may be used in practicing the invention, the chromium trioxide in flake form is dissolved in water to form an orange colored solution. Phosphoric acid is added to this solution. Formic acid is then slowly added to the solution with stirring, producing a vigorous reaction with the evolution of CO_2 gas from the solution. An aqueous solution of chromium phosphate providing Cr^{+++} ions (trivalent chromium) is thus produced in accordance with the following reaction:

$$2CrO_3+3HCOOH+2H_3PO_4 \rightarrow 2CrPO_4+6H_2O+3CO_2$$

As is evident the formic acid reduces the six-valent chromium in the chromium trioxide to produce the trivalent Cr^{+++} ion.

After the thus obtained solution is diluted with the required amount of water, colloidal silica in the proportion shown above is mixed with the solution.

The mixture thus produced is a green liquid having a specific gravity of 1.19 and a pH of about 1.6. The coating solution is applied to the strand annealed steel material in any suitable manner such as by rolling, dipping, spraying, brushing or other methods. Typically, the steel strip, which has been allowed to cool to room temperature, is passed over rollers for applying the coating and then baked in an oven at about 300° C. for about 1 minute.

The coating thus produced was smooth, hard and tightly adherent and did not craze appreciably on bending of the coated sheet material. It was characterized by excellent electrical insulation properties, had minimal effect on watt-loss and permeability properties. It was found by test, for example, that such a coating deposited in an amount of .05 oz./sq. ft. on the steel sheet provides a Franklin insulation value of about 0.0–0.1 ampere, it being known by those skilled in the art that any Franklin value below .20 ampere is satisfactory for transformer use, and that the lower this value the better the insulating quality.

The colloidal silica which may be used in the described mixture is in the form of an aqueous suspension containing SiO_2 in an extremely finely divided form made by an ion exchange technique. Colloidal silica is available commercially under the trade mark of Ludox, a product of E. I. du Pont de Nemours & Company, which is an aqueous colloidal sol containing approximately 30% SiO_2 with less than 0.5% Na_2O as a stabilizer. A more detailed description of this colloidal silica is found in Robinson Patent 2,809,137, which description is incorporated herein by reference.

As an alternative to the colloidal silica there may be used colloidal alumina, which is a dispersion in water of alumina particles which are sufficiently finely divided to provide a colloidal sol in water. A colloidal form of alumina available commercially which may be used is sold under the trademark Baymal, a product of E. I. du Pont de Nemours & Company. This is a white, free-flowing powder consisting of minute fibrils of boehmite (AlOOH) alumina and which disperses readily in water to yield a colloidal sol. Further detailed descriptions of this material and colloidal sols thereof and methods of making them

are set forth in the patent to Bugosh 2,915,475. In general, for the purposes of this invention a concentration of 5–50 grams per liter of water of the finely divided colloidal alumina has been found suitable, with a range of 30–40 grams/liter affording optimum results.

Finely divided refractory materials other than those described above may also be found useful.

Although the temperature used for drying the coating as described above is preferred, the drying stage temperature may vary in a range of about 200° C. for 3 minutes to about 400° C. for about ½ minute.

The composition of the finally produced coating, which is transparent and pale green in color, is not presently known and cannot be definitely ascertained, and it is accordingly referred to herein simply as the cured product of the mixture of ingredients as above described.

While formic acid was proved particularly satisfactory as a reducing agent for use in the above mixture, other reducing agents may be used provided that they do not include contaminating ions which are harmful to the insulating properties of the coating or the dielectric liquid of the transformer or other apparatus in which the coated steel is used. Examples of other suitable reducing agents which may be found useful are oxalic acid, phosphorous acid and hypophosphorous acid.

It should be understood that while the described insulating coating is particularly applicable for use on strand annealed silicon steel material, it is not limited to such use. It will be found of advantage, for example, for coating such steel or other metallic material where relatively low curing temperatures are or must be used.

There is thus provided in accordance with the invention an improved insulating coating composition which has excellent electrical insulating properties, may be deposited in thin and tightly adherent layers to the steel surface, which does not contribute to electrical losses or other unfavorable electrical properties in the coated steel material, and which is applied easily in a continuous operation. The very tenacious adherence of the insulating coating is especially noteworthy in view of the very smooth surfaces which characterize strand annealed steel, as distinguished from steel annealed in coiled or stacked form as in conventional processes, and which ordinarily make it difficult for conventional insulating coatings to firmly adhere thereto.

While the present invention has been described with reference to particular embodiments thereof, it will be understood that numerous modifications may be made by those skilled in the art without actually departing from the scope of the invention. Therefore, the appended claims are intended to cover all such equivalent variations as come within the true spirit and scope of the invention.

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

1. An insulating coating composition comprising an aqueous mixture of (1) the reaction product of chromium trioxide, a reducing agent therefor for reducing the six-valent chromium to trivalent chromium, and phosphoric acid, (2) phosphoric acid, and (3) a finely divided refractory material, said reducing agent being selected from the group consisting of formic acid, oxalic acid, phosphorous acid and hypophosphorous acid, and said refractory material being selected from the group consisting of colloidal silica and colloidal alumina, said mixture comprising in percent by weight 1–10% chromium trioxide, 1–10% reducing agent, 10–40% phosphoric acid, 15–50% refractory material and the balance water.

2. Magnetic ferrous metal sheet material having thereon a thin, tightly adherent coating composed of the cured product of the mixture defined in claim 1, said sheet material being constituted by strand annealed silicon steel.

3. The method of making coated magnetic ferrous metal sheet material which comprises subjecting magnetic silicon steel to heat treatment above about 900° C. in single strand form, providing on the surface thereof a mixture

as defined in claim 1, and heating the same at a temperature of between 200° C. and 400° C.

References Cited

UNITED STATES PATENTS

3,562,011	2/1971	Hirst et al.	148—6.16 X
3,421,949	1/1969	Halversen	117—135.1 X
3,094,441	6/1963	Curtin	148—6.16
3,331,713	6/1967	Miller	148—113
3,030,601	2/1936	McDonald	148—6.16
2,768,104	10/1956	Schuster et al.	148—6.16
3,207,636	9/1965	Wada et al.	148—6.16

OTHER REFERENCES

Japanese Patent Publication No. SH043-7849, Mar. 26, 1968.

RALPH S. KENDALL, Primary Examiner

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